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Nickel(II)–2,2′-Bipyridylamine System. I. Synthesis and Stereochemistry of the Complexes

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The reaction of 2,2′-bipyridylamine (abbreviated BPAH) with divalent nickel salts results in the formation of several products, the type of which depends on the metal:ligand ratio and the coordinating ability of the associated anion. Thus, tetrahedral [Ni(BPAH)Cl$_2$] and octahedral [Ni(BPAH)$_3$](ClO$_4$)$_2$ and [Ni(BPAH)$_2$Cl$_2$] have been isolated and characterized. In these complexes, dipyridylamine coordinates in a bidentate manner through the two pyridine nitrogens. Deprotonation of the amine at ambient temperature in butanol results in the conversion of the paramagnetic [Ni(BPAH)$_2$Cl$_2$] species into a six-coordinate polymeric material of the general formula Ni(BPA)$_2$ where the deprotonated bipyridylamine moiety (abbreviated BPA) is coordinating in a tridentate manner with the amine nitrogen acting as a bridge. This polymer is cleaved quite readily by the action of water, pyridine, and, presumably, other complexing solvents. Deprotonation of [Ni(BPAH)-Cl$_2$] at high temperatures in naphthalene or reaction of the deprotonated polymer with nickel(II) chloride, also at high temperatures, yields a red crystalline trinuclear complex of the molecular formula [Ni$_3$(BPA)$_4$Cl$_2$]. Deprotonation of bis(2,2′-bipyridylamine)copper(II) chloride and bis(2,2′-bipyridylamine)palladium(II) perchlorate give the expected four-coordinate square-planar product. The deprotonated complexes of palladium, copper, and nickel are compared and correlations are made between their ease of formation and the geometry and electronic arrangement of the central metal ion.

Introduction

A ligand which, under the proper conditions, would give complexes containing divalent nickel in its various stereochemistries should permit an evaluation of the factors that influence the formation and relative stability of these different geometries. The 2,2′-bipyridylamine (abbreviated BPAH) complexes of divalent cobalt and copper have been reported.[1-3] Spectral studies[1] show that for divalent cobalt, both tetrahedral [Co(BPAH)Cl$_2$] and octahedral [Co(BPAH)$_2$-(NCS)$_2$] and [Co(BPAH)$_3$](ClO$_4$)$_2$ are formed. In addition, Lyons and Geldard[4] have treated the palladium complex [Pd(BPAH)$_2$](ClO$_4$)$_2$ with base to obtain the square-planar neutral complex [Pd(BPA)$_2$] where BPA is the deprotonated bipyridylamine ion. Extrapolation of these results to the nickel(II) system indicates that 2,2′-bipyridylamine might be an acceptable ligand with which to isolate complexes of the three different stereochemistries; further, deprotonation of bipyridylamine could provide a route to the square-planar nickel species paralleling that of the palladium derivative.

The experimentation reported herein describes the preparation and characterization of the divalent nickel 2,2′-bipyridylamine complexes of various geometries. In addition, the deprotonated complexes of nickel, palladium, and copper are compared and correlations are made between their relative formations and stabilities.

Experimental Section

Materials.—2,2′-Bipyridylamine was obtained from Reilly Tar and Chemical Co. and purified by recrystallization from a benzene–heptane mixture. Butyl alcohol was distilled over calcium sulfate. Sodium butoxide was prepared from sodium

metal in dry butanol and used immediately. All other materials were reagent grade chemicals and employed without further purification.

Synthesis of the Compounds. Dichloro-2,2′-bipyridylaminenickel(II).—Nickel chloride hexahydrate (4.7 g, 0.02 mole) was dissolved in butanol and heated to 100°. A hot butanol solution of 2,2′-bipyridylamine (3.4 g, 0.02 mole) was added and the reaction mixture was brought to reflux. An olive precipitate formed which was filtered while still hot, washed with benzene, and dried under vacuum; yield 5.4 g. The analytical data for all compounds are given in Table I.

Dibromo-2,2′-bipyridylaminenickel(II) and diiodo-2,2′-bipyridylaminenickel(II) were isolated as olive and brown solids, respectively, by a manner analogous to that previously described.

Dichlorobis(2,2′-bipyridylamine)nickel(II).—Nickel chloride hexahydrate (4.7 g, 0.02 mole) was dissolved in a butanol–methanol mixture (90:10) and heated to boiling. This solution was rapidly added to a hot butanol solution of 2,2′-bipyridylamine (6.8 g, 0.04 mole). The mixture was heated to reflux to facilitate the removal of the methanol and water. A pale blue product precipitated which was filtered while hot, washed with benzene and petroleum ether, and dried under vacuum; yield 7.4 g.

Dibromobis(2,2′-bipyridylamine)nickel(II) and diiodobis(2,2′-bipyridylamine)nickel(II) were isolated as pale blue and green solids, respectively, by the same method as described for the chloro derivative.

Tris(2,2′-bipyridylamine)nickel(II) Perchlorate.—A boiling methanol solution of nickel perchlorate hexahydrate (3.66 g, 0.01 mole) was slowly added to a hot methanol solution of 2,2′-bipyridylamine (5.1 g, 0.03 mole). On cooling, the complex crystallized out as pale violet needles; yield 3.5 g.

Tris(2,2′-bipyridylamine)nickel(II) Iodide Hydrate.—Employment of a methanol solution of nickel iodide hexahydrate and 2,2′-bipyridylamine in a 3:1 ratio resulted in the formation of the tris complex by a procedure comparable to that described for the perchlorate analog. The complex was obtained as purple crystals out of methanol.

Bis(2,2′-bipyridylamido)nickel(II).—A solution of sodium butoxide (2.9 g, 0.03 mole) in 50 ml of butanol was added dropwise to a rapidly stirred slurry of dichlorobis(2,2′-bipyridylamine)nickel(II) (7.1 g, 0.015 mole) in 500 ml of dry butanol. The fine suspension of sodium chloride that formed was removed by centrifuging. The resulting solution was heated to reflux and a green-brown solid precipitated out; yield 5.4 g. Alternatively,

(1) J. Goodgame, *J. Chem. Soc., Sect. A*, 63 (1966).
(2) W. R. McWhinnie, *J. Chem. Soc.*, 5165 (1964).
(3) S. Kirschner, *Inorg. Syn.*, **5**, 14 (1957).
(4) J. F. Geldard and F. Lyons, *J. Am. Chem. Soc.*, **84**, 2262 (1962).

TABLE I
DATA FOR THE COMPLEXES

Complex	Color	Calcd C	H	N	M^a	X^b	Found C	H	N	M	X	$10^6 \chi_m$	Moment, BM
[Ni(C₁₀H₉N₃)Cl₂]	Olive	39.9	3.0	14.0	19.6	23.6	39.7	3.3	13.8	18.4	23.7	5418	3.5
[Ni(C₁₀H₉N₃)Br₂]	Olive	30.8	2.3	10.8	15.1	41.0	30.4	2.4	11.1	...	42.2	5497	3.6
[Ni(C₁₀H₉N₃)I₂]	Brown	24.8	1.9	8.7	12.2	52.5	24.9	2.0	9.0	...	...	5330	3.6
[Ni(C₁₀H₉N₃)₂Cl₂]	Blue	50.9	3.8	17.8	12.5	15.0	51.0	3.8	17.8	12.2	15.7	4264	3.2
[Ni(C₁₀H₉N₃)₂Br₂]	Blue	42.8	3.2	15.0	10.5	28.5	43.6	3.2	15.2	...	..	4631	3.3
[Ni(C₁₀H₉N₃)₂I₂]	Green	36.7	2.8	12.8	9 0	38.8	37.0	2.8	13.0	...	37.6	4779	3.3
[Ni(C₁₀H₉N₃)₃](ClO₄)₂	Violet	43.1	3.5	16.3	7.7	9.2	46.8	3.8	16.5	7.5	...	4238	3.2
[Ni(C₁₀H₉N₃)₃]I₂·H₂O	Violet	42.7	3.4	14.9	7.0	30.2	42.8	3.6	14.6	...	30.8	4648	3.3
[Ni(C₁₀H₈N₃)₂]ₓ	Olive	60.1	4.0	21.1	14.7	...	59.8	4.3	21.1	13.3	...	3694	3.0
[Ni₃(C₁₀H₈N₃)₄Cl₂]	Purple	51.9	3.5	18.1	19.0	7.7	51.9	3.5	18.1	19.2	7.7	5720	3.7^d
[Pd(C₁₀H₈N₃)₂]	Gold	53.8	3.6	18.8	24.2	...	53.6	3.7	18.4	...	...	...	...
[Cu(C₁₀H₈N₃)₂]	Blue	59.5	4.0	20.8	15.8	...	58.6	4.0	20.6	...	...	...	...

a M is the respective metal atom. *b* X is the respective halogen atom. *c* Diamagnetic corrections are given by P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1956, pp 78–93. *d* Based on the assumption of only one paramagnetic nickel ion.

the same product can be obtained by the vacuum evaporation of the butanol. Also, treatment of tris(2,2'-bipyridylamine)nickel-(II) perchlorate with sodium butoxide leads to the same product.

Dichlorobis[bis(2,2'-bipyridylamido)nickel(II)]nickel(II).—A slurry of dichlorobis(2,2'-bipyridylamine)nickel(II) (4.7 g, 0.01 mole) in 150 g of naphthalene was heated to 185°. Sodium butoxide (0.01 mole) in butanol was slowly added and a deep purple solution resulted. The naphthalene was removed under vacuum and the product extracted with benzene. Subsequent recrystallization from acetone (or benzene) gave purple needles; yield 1.6 g.

Bis(2,2'-bipyridylamido)copper(II).—A solution of sodium butoxide (1.9 g, 0.02 mole) was slowly added to a slurry of bis(2,2'-bipyridylamine)copper(II) chloride[3] in butanol. The solution was stirred at a rapid rate during and after addition. An intense blue-green solution resulted. The sodium chloride, which precipitated, was removed by centrifuging; the butanol was evaporated under vacuum, and the solid which was isolated was recrystallized as deep blue prisms from chloroform; yield 3.0 g.

Bis(2,2'-bipyridylamido)palladium(II).[4]—Treatment of bis-(2,2'-bipyridylamine)palladium(II) perchlorate (3.2 g, 0.005 mole) with potassium hydroxide in methanol (0.56 g, 0.01 mole) results in the formation of the deprotonated species. The solution was evaporated to dryness under vacuum, and the resulting solid was recrystallized from benzene; yield 2.0 g.

Molecular Weight Determinations.—The molecular weights referred to in the text were obtained cryoscopically in benzene and, alternately, in chloroform and benzene by osmometry. The cryoscopic measurements were made using a No. 8163B platinum resistance thermometer and a Mueller temperature bridge, Leeds and Northrup Model No. 8069, to measurement the temperature differences. The osmometric measurements were taken in a Mechrolab osmometer, Model 301.

Magnetic Susceptibility Measurements.—The magnetic susceptibilities were obtained by the Gouy method using nickel(II) chloride hexahydrate and ferrous ammonium sulfate hexahydrate as standards. Diamagnetic corrections were made for the ligands and anions so that the reported values (Table I) are attributed solely to the metal atoms.

Conductivity Measurements.—Resistivity values for the complexes were obtained by the use of an Industrial Instruments, Inc., Model RC-16B conductivity bridge and a cell with a constant of 0.500 cm⁻¹. The measurements were made at 25° and a bridge frequency of 1000 cps. The molar conductance values are mentioned in the text.

Spectra.—Spectra in the visible and ultraviolet region were measured on a Cary Model 14 recording spectrophotometer. Solution spectra were obtained in matched fused-quartz cells; solid spectra by employment of thick Nujol mulls between quartz plates. An attenuator was used in the reference beam when necessary. The spectral bands are listed in Table II.

The infrared spectra were obtained on a Perkin-Elmer Model 137 recording spectrophotometer equipped with sodium chloride optics. Nujol and/or Fluorolube was employed as the medium. Pertinent absorption bands are listed in Table III.

Discussion

The nickel(II)–2,2'-bipyridylamine system permits three of the stereochemical geometries of divalent nickel to be studied. With the use of proper conditions, mononuclear complexes of tetrahedral and octahedral symmetries and a polynuclear complex containing nickel atoms surrounded by both tetrahedral and square-planar arrays have been isolated. The type of complex formed is dependent upon the ligand-to-metal ratio, the coordinating ability of the anion, and reaction conditions such as solvent and temperature.

The reaction in boiling butanol between 2,2'-bipyridylamine and nickel(II) chloride hexahydrate in a 1:1 ratio results in the formation of an olive complex of the empirical formula [Ni(BPAH)Cl₂] where BPAH is the abbreviation for 2,2'-bipyridylamine. Attempts to prepare this complex in methanol, ethanol, or unheated butanol resulted in a product of indefinite analysis. Apparently the high temperature of boiling butanol (117°) is necessary to remove all of the coordinated water on the nickel.

Despite the fact that the difference in ligand strength of the pyridine nitrogen and that of the halogen is sufficient to permit the C_{2v} component to manifest itself appreciably in both the spectrum and room temperature magnetic moment value, this complex may be approximately described on the basis of theoretical predictions for T_d symmetry. The magnetic moment of 3.5 BM, though low for pure tetrahedral complexes, is consistent for what would be expected for compounds containing ligands of vastly different coordinating abilities. The perturbation arising from the dissimilarity between the chloride and dipyridylamine groups is sufficient to remove the orbital degeneracy of the ground state; since it is this degeneracy that is responsible for the large orbital contribution to the mag-

TABLE II

POSITIONS OF ELECTRONIC TRANSITION ABSORPTIONS

Band positions, cm^{-1}	ϵ	Band positions, cm^{-1}	ϵ
[Ni(BPAH)Cl₂] in Nujol		**[Ni(BPAH)₂Cl₂] in Nujol**	
8,600 sh[a]	...	10,000 sh	...
11,000	...	12,350 sh	...
12,000	...	16,400	...
15,900	...	25,000	...
18,200	...	41,700	...
22,500	...		
[Ni(BPAH)Br₂] in Nujol		**[Ni(BPAH)₂Br₂][b] in Nujol**	
8,100 sh	...	9,900	...
10,900 sh	...	12,200 sh	...
11,500	...	16,400	...
15,400	...		
16,900	...		
20,000	...		
[Ni(BPAH)Br₂] in Cyclohexanone		**[Ni(BPAH)₂I₂][b] in Nujol**	
7,900 sh	20	9,700	...
10,400	86	11,400 sh	...
11,600	76	16,250	...
15,600	30		
17,900	100		
20,000	230		
[Ni(BPAH)I₂] in Nujol		**[Ni(BPAH)₃](ClO₄)₂ in Methanol**	
7,900 sh	...	10,900	7
10,900	...	12,600	2
14,900 sh	...	17,700	5
16,700 sh	...	31,750	43,000
19,200	...	38,900	49,500
[Ni(BPAH)I₂] in Cyclohexanone		**[Ni(BPA)₂]ₓ in Nujol**	
7,900 sh	57	11,000	...
10,100	108	12,900 sh	...
10,900	128	17,200 sh	...
14,700 sh	90	24,400	...
16,950 sh	600	31,250	...
18,500	700		
21,300	1,550		
		Ni₃(BPA)₄Cl₂ in Dichloromethane	
		6,800	18
		12,500 sh	7
		19,200	1,500
		29,000	25,500
		31,800	27,000

[a] sh = shoulder. [b] Spectrum not obtained in its entirety.

netic moment observed in regular tetrahedral complexes, a lowering of the magnetic moment results.

The effect of the C$_{2v}$ component is even more striking in the electronic spectrum of the complex. However, although the symmetry is C$_{2v}$, the observed spectrum of the chloride complex, as well as that of the analogous bromide and iodide derivatives, is in fair agreement with the theoretical predictions for T$_d$ symmetry. In a C$_{2v}$ crystal field, the orbital triplet levels are split as follows: A₂ → A₂, T₁ → A₂ + B₁ + B₂, T₂ → A₁ + B₁ + B₂. Therefore, the ν_1 ($^3T_1(F)$ → $^3T_2$) and ν_3 ($^3T_1(F)$ → $^3T_1(P)$) bands should be split into three components,

whereas the ν_2 band ($^3T_1(F)$ → $^3A_2$) should be unaffected. It is seen in Table II that, for the three halogen complexes, the ν_3 band is unambiguously divided into three components; the splittings range between 4300 and 6500 cm^{-1} and separations increase in the order Cl > Br > I. This suggests that the distortion is greatest with the chloride analog and is probably related to the steric requirements of the halogens. Further, the peaks at 11,970, 11,490, and 10,870 cm^{-1} in the spectra of the chloride, bromide, and iodide, respectively, are assigned to the ν_2 absorption. However, these complexes each have two additional absorptions falling in the 7800–8600- and 10,100–11,000-cm^{-1} regions. While the low-energy bands are almost certainly components of the ν_1 transitions, assignments of the absorptions in the 10,100–11,000-cm^{-1} region are complicated by the possible transitions arising from the ^{1}D free-ion term. However, the large values for the extinction coefficients suggest that the absorptions at 11,000 (chloride), 10,400 (bromide), and 10,100 cm^{-1} (iodide) are probably the highest energy components of the ν_1 transition.

When the reaction between 2,2'-bipyridylamine and nickel(II) chloride, in boiling butanol, is carried out with a 2:1 stoichiometric ratio of reactants, a pale blue complex of the empirical composition [Ni(BPAH)₂Cl₂] is formed. As with the synthesis of the tetrahedral analog, it was necessary to employ a high-boiling solvent in order to isolate the anhydrous complex. In methanol or ethanol, a highly soluble species was formed which is probably [Ni(BPA)₂(H₂O)₂]Cl₂. If the reaction is run in butanol at ambient temperature, this soluble species is formed; as the solution is heated to boiling, the anhydrous product precipitates. The magnetic moment (3.2 BM) and electronic spectrum are in agreement with the assignment of essentially octahedral symmetry to this molecule, although a tetragonal component is quite apparent. The electronic spectrum of the complex [Ni(BPAH)₂Cl₂] shows five spectral bands with maxima at 10,000, 12,350, 16,400, 25,000, and 41,700 cm^{-1}, respectively. Analysis of the spectrum leads to the assignment of the bands at 10,000 and 16,400 cm^{-1} to spin-allowed d–d transitions; that at 12,350 cm^{-1} is assigned to a spin-forbidden $^3A_{2g}(F)$ → $^1E_g(D)$ transition that has gained strength through intensity sharing; finally, the absorption at 25,000 cm^{-1} is assigned to a Laporte-allowed charge-transfer band. Assignment of the band at 10,000 cm^{-1} to $^3A_{2g}$ → $^3T_{2g}(F)$ and that at 16,400 cm^{-1} to $^3A_{2g}$ → $^3T_{1g}(F)$ leads to a crystal field splitting parameter value (10Dq) of 10,200 cm^{-1}. On this basis, the third transition ^3Ag → $^3T_{1g}(P)$ should be found at about 26,900 cm^{-1}. This area, however, is obscured by the much more intense Laporte-allowed transition. It will be noted that the lowest energy d–d transition is not Gaussian but has been broadened almost to the point of splitting. This splitting is caused by a tetragonal distortion of the octahedron which lowers the symmetry from pure O$_h$.

The reaction, in hot methanol, of 2,2'-bipyridyl-amine and nickel(II) perchlorate hexahydrate in a 3:1

TABLE III

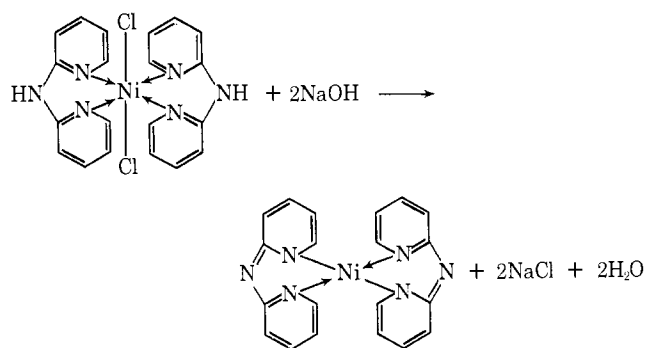SPECTRAL BAND ASSIGNMENTS IN THE 1400–3500-CM⁻¹ REGION[a]

Compound	NH str	ua	Py I	ua	Py II	ua	Py III	Py IV
						1480 s		
LH	3300 m	1660 w	1600 s	1575 w	1540 s	1470 m	1445 vs	1420 sh
						1480 } vs, x		
LD	2350 m	...	1595 s	1560 m	1535 m	1470 }	1440 vs	1410 sh
							1470 vs	1430 sh
[NiHCl₂]	3290 m	...	1630 s	...	1550 s	1500 w	1460 vs	1420 sh
[Ni(LH)₂Cl₂]	3290 m	...	1630 s	...	1580 s	1520 m	1480 vs	1430 m
[Ni(LH)₃](ClO₄)₂	3300 m	...	1620 s	...	1580 m	1520 m	1480 vs	1400 m
			1600 m		1555 w		1480 vs	
[NiL₂]ₓ	...	1650 w	1590 m	...	1545 w	...	1470 vs	1430 vs
			1610 s					
Ni₃L₄Cl₂	...	1650 w	1600 s	...	1555 m	...	1470 vs	1430 vs
							1470 sh	1430 w
[PdLHCl₂]	3290 m	...	1630 s	...	1580 s	1520 m	1460 vs	1410 w
							1480 sh	1430 m
[Pd(LH)₂](ClO₄)₂	3290 m	...	1630 s	...	1580 s	1520 m	1460 vs	1410 sh
					1550 sh		1450 sh	
[PdL₂]	...	1630 w	1600 s	...	1540 m	...	1430 vs	...
							1480 } vs, x	1420 sh
[Cu(LH)₂]Cl₂	3290 w	...	1630 s	...	1580 s	1520 s	1455 }	1405 m
							1465 } vs, x	
[CuL₂]	...	...	1605 s	...	1540	...	1445 }	...

[a] Abbreviations are as follows: LH, 2,2-bipyridylamine; LD, the deuterated amine analog; L, 2,2-dipyridylamido analog; str, bond stretching vibration; ua, unassigned; w, weak; m, medium; s, strong; vs, very strong; x, broad absorption; sh, shoulder; py, pyridine ring vibration.

molar ratio results in a product with the composition [Ni(BPAH)₃](ClO₄)₂, which, on the basis of its magnetic moment, molar conductivity (182 ohm⁻¹ cm², 10⁻³ M in methanol), and electronic spectrum is found to have pure octahedral symmetry with the three 2,2'-bipyridylamine ligands coordinating in a bidentate manner. The magnetic moment of the complex, 3.2 BM, is in the expected range of divalent nickel in an octahedral field. The electronic spectrum taken in methanol showed five bands. Of these, only two can be assigned to spin-allowed d–d transitions, the one at 10,900 cm⁻¹ to the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and the one at 17,700 cm⁻¹ to the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transitions, respectively; the band at 12,600 cm⁻¹ is assigned to the spin-forbidden $^3A_{2g}(F) \rightarrow {}^1E_g(D)$ transition. The other two absorptions at 31,750 and 38,800 cm⁻¹ are very intense and are of the Laporte-allowed charge-transfer type. A $10Dq$ value of 11,100 cm⁻¹ is consistent with these assignments, and, on this basis, the third d–d transition should appear at 28,950 cm⁻¹, an area obscured by strong charge-transfer bands.

It is interesting to note that a calculation of the crystal field splitting parameter based on the method of the average ligand field environment[5] for the compound [Ni(BPAH)₂Cl₂] gives a value within 5% of the experimentally determined figure.

The presence of an amine proton on the 2,2'-bipyridylamine appeared to offer an opportunity to transform octahedral dichlorobis(2,2'-bipyridylamine)-nickel(II) into its square-planar counterpart by deprotonation with base according to the reaction

(5) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 887 (1956).

[Reaction scheme: dichlorobis(2,2'-bipyridylamine)nickel(II) + 2NaOH ⟶ bis(2,2'-bipyridylamido)nickel + 2NaCl + 2H₂O]

With bis(2,2'-bipyridylamine)palladium(II) perchlorate, deprotonation with NaOH or KOH in alcohol gave high yields of the yellow, benzene-soluble, deprotonated complex. Application of the same procedure to bis(2,2'-bipyridylamine)copper(II) chloride resulted in low yields of the deprotonated species. The predominant product appeared to be a hydroxide complex. This phenomenon of competitive hydroxide formation was more severe with dichlorobis(2,2'-bipyridylamine)nickel(II), where deprotonation with KOH in alcohol gave only nickel hydroxide and complicated polymeric hydroxide–bipyridylamine complexes. This problem of hydroxide formation was solved by employment of sodium butoxide as the deprotonating agent and carefully drying solvents so that water was totally excluded. By the use of this procedure, the deprotonated nickel complex was isolated in high yields as a yellow-green insoluble powder. Elemental analysis indicated that the complex had the expected empirical formula, Ni(BPA)₂, where BPA is the deprotonated 2,2'-bipyridylamine moiety. The infrared spectrum showed the complete absence of ab-

sorptions due to the N–H stretching frequency. The similarities of this spectrum with that of the deprotonated copper(II) and palladium(II) species verified that deprotonation had taken place. However, the other characteristics exhibited by the deprotonated nickel complex indicated that the symmetry of that particular species was something other than square-planar. The insolubility of the complex in nonpolar solvents is in marked contrast to the high solubility that neutral square-planar complexes usually exhibit; the magnetic moment of 3.0 BM and, finally, the electronic spectrum establish that the array surrounding the central nickel ion is a distorted octahedron. The spectrum of the complex has a very broad band centered at 11,000 cm^{-1} which was assigned to the $^3A_{2g}(F)$ → $^3T_{2g}(F)$ transition; the weaker shoulder at 12,900 cm^{-1} is the spin-forbidden $^3A_{2g}$ → $^1E_g(D)$; the band at 17,200 cm^{-1} was due to the $^3A_{2g}(F)$ → $^3T_{1g}(F)$ transition. A value for $10Dq$ of 10,850 cm^{-1} is consistent with these assignments. The $^3A_{2g}(F)$ → $^3T_{1g}(P)$ transition would be expected to occur at 31,200 cm^{-1} but is not observed owing to the presence of strong charge-transfer absorption at 24,400 cm^{-1}. The broadening and lack of Gaussian character exhibited by the $^3A_{2g}$ → $^3T_{2g}$ absorption is indicative of a tetragonal distortion from regular octahedral symmetry. On the basis of these data, the structure of the deprotonated complex is postulated as a six-coordinate three-dimensional polymer resulting from bridging of the amine nitrogen of the ligands to the apical positions of neighboring molecules as in
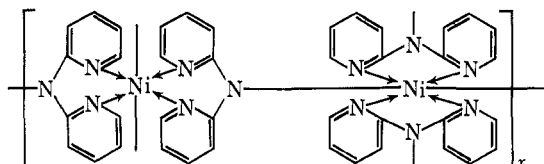

This structure is consistent with the observed tetragonal distortion since each nickel atom would be bonded to four pyridine nitrogens in the plane and two amine nitrogens in the axial positions reducing the compound to D$_{4h}$ symmetry. Also, some strain is expected owing to the rigidity of the bridge which should make the polymer highly susceptible to cleavage by donor solvents or other monodentate ligands. This expectation is realized since the polymer is easily cleaved by water and pyridine, presumably to give the monomeric six-coordinate analogs in which the solvent molecules are coordinating at the apices of the octahedron.

This six-coordinate polymeric structure appears to be the only species that is formed on deprotonation at moderate temperatures irrespective of the reaction conditions. Thus, deprotonations with *n*-butyllithium in benzene, conditions which are ideally suited for the formation of the square-planar species, still result in the formation of the polymer.
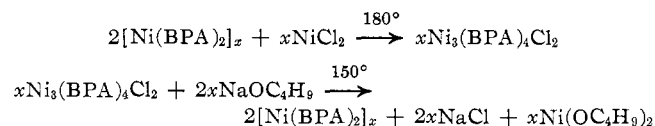
The existence of temperature-dependent polymer–monomer equilibria has been reported in divalent nickel systems with ligands, such as acetylacetone.[6] Here, a stable six-coordinate trimer is formed at ambient temperatures through oxygen bridging while at higher temperatures, in noncoordinating solvents, formation of the monomeric square-planar species is favored. Although this type of temperature-dependent polymer–monomer interconversion had not previously been observed for nickel complexes involving only nitrogen donors, the possibility of its existence could not be overlooked in the system under discussion.

Deprotonation of dichlorobis(2,2'-bipyridylamine)-nickel(II) in naphthalene at 185° with a 1:1 stoichiometric ratio of base to complex results in the formation of a soluble purple-red complex which can readily be recrystallized from benzene or acetone. Alternatively, this complex can be prepared by the reaction of nickel-(II) chloride hexahydrate and the deprotonated polymer in boiling *o*-dichlorobenzene. Elemental analyses (Table I), molecular weight determinations (theory, 928; found, 890), the magnetic susceptibility value (Table I), and infrared and visible spectroscopy suggest the molecular formula [Ni$_3$(BPA)$_4$Cl$_2$]. The structure of this complex (shown below) is postulated as containing two nickel atoms surrounded by a square-planar array of bipyridylamido moieties bonded to a central tetrahedral nickel atom. A more complete discussion of the structure and properties of this complex and its analogs will be given in the next article of this series which will be forthcoming shortly.
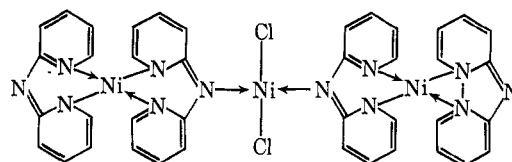

The trinuclear complex and the bis(2,2'-bipyridyl-amido)nickel(II) species can be easily interconverted at high temperatures by the reaction methods

$$2[Ni(BPA)_2]_x + xNiCl_2 \xrightarrow{180°} xNi_3(BPA)_4Cl_2$$

$$xNi_3(BPA)_4Cl_2 + 2xNaOC_4H_9 \xrightarrow{150°} 2[Ni(BPA)_2]_x + 2xNaCl + xNi(OC_4H_9)_2$$

The infrared spectra of the complexes show some very interesting trends. Of particular interest is the variation in the positions of the pyridine ring vibrations of the free ligand as compared to those of the complexes. In the deprotonated species, there are only slight alterations in the positions of these vibrational bands as compared to the free ligand (no more than 10-cm^{-1} shift). In contrast are the appreciable shifts (30–40 cm^{-1}) that are observed in the spectra of the protonated complexes. This pattern can be explained on the basis of metal–ligand back bonding. This bonding tends to increase the electron density in the π system of the ring resulting in the shifting of the vibrational bands to higher energies. This is what is observed with the protonated complexes. In the deprotonated species, resonance forms, such as the one depicted below, permit further delocalization of the

(6) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1966, p 888.

π system, and, consequently, tend to reduce the charge accumulation within the pyridine ring. The over-all effect is that there is very little alteration in the band positions.
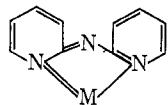
The N–H stretching vibration, verified by deuteration experiments, is not affected by complex formation. This is further evidence that, in the protonated complexes, only the two ring nitrogens are involved in bonding to the metal ion. Of course, the N–H band is completely absent in the spectra of the deprotonated complexes.

A comparison of the ease of formation of the deprotonated palladium, copper, and nickel bipyridylamine complexes, and their relative chemical stabilities once formed, can be correlated to the electronic structures of the respective central metal ions. There are no regular octahedral complexes of palladium(II).[6] The most common and most stable geometry of divalent palladium is the square plane. The factors that account for the stability of this configuration in palladium are, first, the large degree of out-of-plane π bonding between the appropriate ligand orbitals and the very much available $4d_{xz}$, $4d_{yz}$, and $5p_z$ orbitals of the metal; second, an increase in the in-plane π bonding and strength of σ bonding in square-planar as compared to octahedral complexes. In the deprotonated palladium complex the ligand has the ability to partake in extensive π bonding through the resonance structures shown earlier for the nickel analog. The bis(2,2'-bipyridyl-amido)palladium(II) complex would, therefore, be expected to be an easily formed, stable product with little propensity to interact through the axial positions with other ligands. The experimental results have confirmed the prediction. While there is also a small increase in the σ-bond strength and in-plane π bonding for the divalent copper and divalent nickel square-planar complexes, the increase in out-of-plane π bonding

is much smaller than with palladium. This is due to the poorer overlap of the 3d orbitals of the first transition series as compared to the overlap of the 4d orbitals of the second-row transition series; thus, the square-planar complexes of copper and especially nickel are not nearly as stable as those of palladium. Copper(II) complexes differ from those of nickel(II) because of the complication of a large Jahn–Teller distortion in the former. This effect is responsible for the fact that divalent copper has no complexes of regular octahedral symmetry. All six-coordinate copper(II) complexes have large tetragonal distortions, and, in the extreme case, reach the point of square-planar symmetry. This weakness in the bonding at the axial positions of copper should enhance the conversion of the tetragonal dichlorobis(2,2'-bipyridylamine)copper(II) to the square-planar deprotonated species. One finds little tendency for formation of a bridged six-coordinate polymer as observed in the nickel system. Apparently, the increase in stability due to bonding in a square-planar system in conjunction with the decrease in the strength of the axial bonds due to the Jahn–Teller distortion is enough to stabilize the planar configurations with divalent copper. Finally, in the divalent nickel system, the octahedral geometry is a very stable arrangement and not subject to any Jahn–Teller distortion. Consequently, even though there is some increase in the strength of the individual bonds in square-planar symmetry as compared to the octahedral arrangement, the over-all bond energy still favors octahedral formation when possible. With the bipyridylamine moiety the amine nitrogen enables divalent nickel to retain its desired stereochemical configuration, through bridging, and results in the formation of the observed six-coordinate polymer rather than the predicted square-planar monomer.