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**Nickel(II) Complexes of Some Quadridentate Schiff Base Ligands. I<sup>1</sup>**

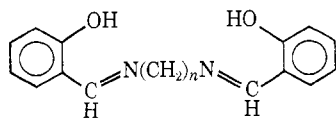
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A series of nickel(II) complexes, NiL, of the Schiff bases formed by condensation of 5-chloro-2-hydroxybenzophenone with a series of alkanediamines,  $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$  ( $n = 2-12$ ), have been synthesized and their physicochemical properties investigated. Unlike their salicylaldehyde analogs, the NiL complexes derived from long-chain alkanediamines are highly soluble in nondonor solvents. In nondonor solvents these complexes are low-spin planar monomers with the Schiff bases acting as quadridentate ligands, although there is a small degree of molecular association in some cases. In the solid state, some of the complexes ( $n = 5-12$ ) contain both octahedral and square-planar Ni(II) usually in the ratio 1:2, and a trimeric structure has been proposed to account for this behavior. For  $n = 3-12$ , the complexes reversibly form bis-pyridine adducts:  $\text{NiL} + 2\text{C}_5\text{H}_5\text{N} \rightleftharpoons \text{NiL} \cdot 2\text{C}_5\text{H}_5\text{N}$ . The solid pyridine adducts were isolated from pyridine solution as paramagnetic solids and these complexes are assigned a trans-octahedral structure. A square-pyramidal complex,  $\text{NiL} \cdot \text{H}_2\text{O}$ , has been isolated for  $n = 4$ .

**Introduction**

Salicylaldehyde can be condensed with a series of alkanediamines to give a series of Schiff bases, **1**. The

1, Sal ( $n = 2-12$ )

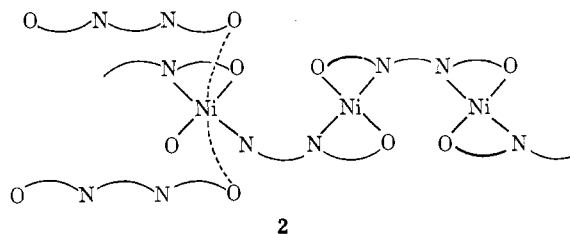
deprotonated salicylaldimines, **1**, form potential quadridentate ligands bonding *via* the two N and the two O atoms.<sup>2</sup>

When  $n = 2$ , molecular models show that the ligands can wrap comfortably around divalent first-row transition metals to form square-planar complexes. This stereochemistry is adopted by the Co(II) complex<sup>3</sup> and is approximately adopted by the Cu(II) complex with some out-of-plane distortion due to weak intermolecular Cu-O bonds.<sup>4</sup> An approximately planar but similarly dimeric structure is expected for the Ni(II) complex.<sup>5</sup> Increasing length of the bridging  $\text{N}(\text{CH}_2)_n\text{N}$  chain ( $n = 2-4$ ) is expected initially to increase steric strain in the ligand ring, resulting in distortion from planarity. Spectral and magnetic data support this prediction in cobalt(II)<sup>6</sup> and zinc(II),<sup>7</sup> as well as copper(II),<sup>8</sup> for which there is also some crystallographic evidence.<sup>9</sup> For nickel(II), increasing  $n$  ( $n = 2-4$ ) causes a red shift in the absorption band near  $18,000 \text{ cm}^{-1}$ , interpreted in terms of effective weakening of ligand field strength.<sup>10</sup> This shift is likely associated

with similar distortions from planarity of the complexes.<sup>2</sup>

For very long  $\text{N}(\text{CH}_2)_n\text{N}$  bridges ( $n > 6$ ), increasing  $n$  should impose decreasing steric constraints on complexes due to the increasing flexibility of the long alkyl chain. In this case, the environment about the metal atom tends toward the preferred stereochemistry for the particular metal, and for Ni(II) (as well as Cu(II)), this would be square planar, given a monomeric structure.

Hoyt and Everett,<sup>11</sup> in the hope of inducing sufficient distortion from planar toward tetrahedral to reach the point of spin-multiplicity change (planar,  $S = 0$ ; tetrahedral,  $S = 1$ ), synthesized the series of NiSal complexes with  $n = 5-12$ . The magnetic moments of these complexes were found to range widely in the intermediate range between the values expected for low spin ( $S = 0$ ) and high spin ( $S = 1$ ), but no tetrahedral species were evident from the spectra. The results could be explained in terms of the polymeric structure **2** in which the observed partial paramag-



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netism of the complexes could arise from a combination of the diamagnetism of some planar Ni(II) atoms in **2** and the paramagnetism of other Ni(II) atoms made octahedral and therefore high spin by bonding to oxygen atoms of neighboring chains. Structure **2** is reasonable, but, in view of the steric arguments, it does not represent the only way of explaining the results. The insolubility of the compounds in common solvents prevented molecular weight determination or other solution measurements.

We have now prepared a series of nickel complexes with the Schiff bases **3** obtained from the condensation of diaminoalkanes and 5-chloro-2-hydroxybenzophenone. This series of complexes, NiL, should have many properties in common with NiSal, but it is a

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(1) Presented in part at the 3rd Coordination Chemistry Conference of the Royal Australian Chemical Institute, Canberra, Aug 1970.

(2) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966).

(3) W. P. Schaefer and R. E. Marsh, *Acta Crystallogr., Sect. B*, **25**, 1675 (1970).

(4) D. Hall and T. N. Waters, *J. Chem. Soc. A*, 2644 (1960).

(5) H. Montgomery and B. Morosin, *Acta Crystallogr.*, **12**, 551 (1961); L. M. Shkol'nikova, E. A. Shugam, and L. G. Makarevich, *Zh. Strukt. Khim.*, **4**, 927 (1963).

(6) H. Weigold and B. O. West, *J. Chem. Soc. A*, 1310 (1967); M. Hariharan and F. L. Urbach, *Inorg. Chem.*, **8**, 556 (1969).

(7) G. E. Batley and D. P. Graddon, *Aust. J. Chem.*, **20**, 885 (1967).

(8) E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, **4**, 391 (1969); S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Nucl. Chem. Lett.*, **4**, 107 (1968); *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968).

(9) T. P. Cheeseman, D. Hall, and T. N. Waters, *Proc. Chem. Soc., London*, 379 (1963).

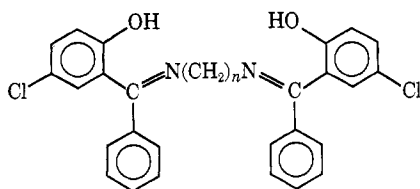
(10) R. H. Holm, *J. Amer. Chem. Soc.*, **82**, 5632 (1960).

(11) W. C. Hoyt and G. W. Everett, Jr., *Inorg. Chem.*, **8**, 2013 (1969).

TABLE I  
 ANALYTICAL DATA ON LIGANDS AND COMPLEXES<sup>a</sup>

	Ligand <sup>b</sup> (LH <sub>2</sub> )			Mp, °C	Ni complex (NiL)					py adduct (NiL·2C <sub>5</sub> H <sub>5</sub> N)				
	C	H	N		C	H	N	Ni	Color <sup>c</sup>	C	H	N	Ni	Color <sup>c</sup>
C <sub>28</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	68.72	4.53	5.72	186-188	61.57	3.69	5.13	10.8	B					
(1,2; eth)	68.33	4.59	5.11		61.27	3.87	4.66	10.7						
C <sub>29</sub> H <sub>24</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	69.19	4.66	5.56	158-159	62.18	3.96	5.00	10.5	B					
(1,2; prop)	69.69	4.76	5.84		62.20	3.86	4.81	10.5						
C <sub>32</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	70.74	5.19	5.15	212-213	64.05	4.37	4.67	9.8	R					
(1,2; cyclohex)	70.08	5.49	4.77		63.80	4.45	4.58	9.8						
C <sub>29</sub> H <sub>24</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	69.11	4.80	5.56	157-159	62.18	3.96	5.00	10.5	B	65.21	4.49	7.79	8.1	B
(1,3; prop)	68.11	4.94	4.68		62.11	3.87	4.32	10.4		65.43	4.77	8.12	8.0	
C <sub>30</sub> H <sub>26</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> <sup>d</sup>	69.63	5.06	5.41	203-204	60.99	4.43	4.74	9.9	Y	61.07	5.10	7.12	7.5	Y
(1,4; but)	68.98	5.16	4.94		60.99	4.28	4.30	9.4		61.00	5.20	7.01	7.6	
C <sub>31</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	70.05	5.31	5.27	125-127	63.32	4.46	4.76	10.0	M	65.97	4.86	7.60	7.9	G
(1,5; pent)	69.32	5.19	5.28		62.75	4.49	4.20	10.0		65.75	4.61	7.22	7.9	
C <sub>32</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	70.46	5.54	5.13	170-172	63.85	4.69	4.65	9.8	M	66.34	5.03	7.26	7.7	G
(1,6; hex)	70.13	5.67	4.83		63.53	5.11	4.66	9.5		66.40	5.00	7.14	7.5	
C <sub>33</sub> H <sub>32</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	70.84	5.76	5.01	97-98	64.33	4.91	4.55	9.5	M	66.69	5.20	7.23	7.6	G
(1,7; hept)	70.33	5.73	5.00		64.85	5.18	4.35	9.6		66.85	5.24	7.12	7.5	G
C <sub>34</sub> H <sub>34</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	71.19	5.97	4.88	113-116	64.80	5.12	4.45	9.3	M	67.03	5.37	7.10	7.4	G
(1,8; oct)	70.87	6.74	3.83		64.87	5.22	4.01	9.2		67.66	5.64	6.91	7.4	
C <sub>35</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	71.54	6.17	4.76	98-100	65.25	5.32	4.35	9.1	M	67.35	5.52	6.98	7.3	G
(1,9; non)	72.21	6.15	4.00		65.28	5.39	4.22	9.1		67.73	5.58	6.60	7.3	
C <sub>38</sub> H <sub>38</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	71.86	6.36	4.65	104-106	65.68	5.51	4.25	8.9	M	67.67	5.68	6.86	7.2	G
(1,10; dec)	72.05	6.74	3.98		65.45	5.61	3.97	8.9		67.66	6.04	6.56	7.3	
C <sub>38</sub> H <sub>42</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> <sup>e</sup>	72.49	6.72	4.45	85-88	66.49	5.87	4.08	8.6	M	68.82	6.24	6.42	6.9	G
(1,12; dodec)	71.82	6.83	4.53		66.30	6.42	4.29	8.7		69.09	6.26	6.29	6.8	

<sup>a</sup> Per cent calculated data are in the first row and per cent found are in the second row for each compound. <sup>b</sup> Parent amine of the Schiff base, 1,*n*-diaminoalkane, is given in parentheses, abbreviated as 1,*n*; alk. <sup>c</sup> B = brown, R = red, Y = yellow, M = mustard yellow, G = yellow-green. <sup>d</sup> Ni complex—monohydrate; py adduct—trihydrate. <sup>e</sup> py adduct—4-methylpyridine (C<sub>5</sub>H<sub>7</sub>N) adduct.



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much better series for study because of the greater solubility of complexes in nondonor solvents. The greater solubility gives access to a wider range of physical measurements and hence to more definite structural information. It has already been noted that the solubility of the Co(II) and Ni(II) derivatives of *o*-hydroxybenzophenones in nondonor solvents is considerably greater than that of the corresponding salicylaldehyde compounds.<sup>12-14</sup>

### Experimental Section

**Preparation and Analysis. Ligands.**—To 2 mol of 5-chloro-2-hydroxybenzophenone dissolved in methanol was added 1.1 mol of the appropriate diamine (Aldrich Chemical Co.). The resulting solution was refluxed until the Schiff base precipitated either as yellow crystals or as a yellow oil. The crude product was recrystallized from 1-butanol.

**Nickel Complexes, NiL, *N,N'*-R-bis(5-chloro-2-hydroxybenzophenimine)nickel(II).** (i) **R = Ethylene, 1,2-Propylene, 1,2-Cyclohexyl.**—To 0.1 mol of nickel acetate dissolved in boiling methanol was added 0.1 mol of ligand dissolved in 1-butanol. The complex which precipitated immediately was washed with boiling methanol and petroleum ether (bp 40-60°) and dried *in vacuo* (drying pistol) at 100°.

(ii) **R = -(CH<sub>2</sub>)<sub>3</sub>-.**—The crude product was prepared as in (i). This was recrystallized from pyridine and the resulting pyridine adduct was depyridinated by heating *in vacuo* at 140° for 4 hr.

(iii) **R = -(CH<sub>2</sub>)<sub>4</sub>-.**—To 0.1 mol of nickel acetate dissolved in

boiling methanol was added 0.1 mol of ligand dissolved in 1-butanol. On the addition of 1 ml of piperidine a yellow-brown powder precipitated. This was filtered and water was added to the green mother liquor. A yellow-green powder precipitated which was filtered, washed with methanol, and dried in the air. The complex formed was of the form NiL·H<sub>2</sub>O·*n*CH<sub>3</sub>OH. This complex was heated *in vacuo* at 120° and the yellow complex NiL·H<sub>2</sub>O was obtained. Further heating at higher temperatures partially decomposed the complex.

(iv) **R = -(CH<sub>2</sub>)<sub>*n*</sub>-**, *n* = 5-12.—To 0.1 mol of nickel acetate dissolved in boiling methanol was added 0.1 mol of ligand dissolved in 1-butanol. On the addition of 1 ml of piperidine, the complex precipitated and was filtered, washed with boiling methanol, and dried *in vacuo* at 100°. Repeated attempts to recrystallize these complexes were almost all unsuccessful. The complexes were extremely soluble in such solvents as benzene and chloroform. The complexes would not crystallize from solvents such as these and could only be recovered as powders by evaporating to dryness or by addition of a solvent in which the complexes were insoluble (*e.g.*, cyclohexane). The only exceptions were the *n* = 5, 7 complexes which could be recrystallized from benzene-methyl acetate mixtures.

**Pyridine Adducts, NiL·2py.**—The anhydrous complexes were dissolved in pyridine and the solutions were allowed to evaporate to dryness. The resulting solids were washed with methanol and dried in a desiccator.

Table I lists the analytical data on the compounds. Carbon, hydrogen, and nitrogen analyses were carried out by Dr. E. Challen and Mr. J. Susman of the School of Chemistry, University of New South Wales. Nickel was determined gravimetrically as the dimethylglyoxime after the complexes had been decomposed in a mixture of concentrated nitric (4 ml), sulfuric (2 ml), and perchloric (2 ml) acids.

**Visible-near-infrared spectra** were obtained using a Zeiss PMQ II spectrophotometer with an RA3 reflectance attachment.

**Molecular weights** were determined cryoscopically in freezing benzene and are listed in Table II.

**Temperature dependence of magnetic susceptibility** was determined using a cryostat-controlled Gouy balance. Measurements were made at two magnetic field strengths and no dependence on field strength was observed within experimental error. The data were fitted to a Curie-Weiss law,  $\mu = \sqrt{(T + \theta)}$ , by a least-squares fitting procedure. Correlation coefficients *R* were calculated to determine the goodness of fit. The calculations were performed by a computer program CURIW using an IBM 1130 computer.

(12) D. P. Graddon and G. M. Mockler, *Aust. J. Chem.*, **20**, 21 (1967).

(13) D. P. Graddon and G. M. Mockler, *ibid.*, **21**, 907 (1968).

(14) D. P. Graddon and G. M. Mockler, *ibid.*, **21**, 1487 (1968).

TABLE II  
MOLECULAR WEIGHT DATA ON NiL AND NiL·2C<sub>5</sub>H<sub>5</sub>N  
COMPLEXES IN FREEZING BENZENE

L <sup>a</sup>	NiL			NiL·2C <sub>5</sub> H <sub>5</sub> N		
	Concn <sup>b</sup>	Mol wt	Complexity	Concn	Mol wt	Complexity
5	4.80	814	1.39	3.46	283	0.38
	9.91	830	1.42	7.19	288	0.39
	14.6	844	1.44			
	5.1	543	0.90	3.94	288	0.38
6	10.2	582	0.97	7.68	299	0.39
				11.0	309	0.41
	4.93	910	1.48	3.66	281	0.36
7	10.7	986	1.60	4.29	304	0.39
	15.1	1065	1.73	7.70	300	0.39
	4.71	605	0.96	4.62	300	0.38
8	9.24	665	1.06	8.86	296	0.38
				13.0	292	0.37
	5.19	948	1.47	4.67	320	0.40
9	10.8	995	1.55	8.76	318	0.40
	15.7	931	1.45	12.4	316	0.39
	5.54	638	0.97	4.25	296	0.36
10	10.8	682	1.04	8.79	290	0.36
	15.8	707	1.08	12.8	286	0.35
	4.53	567	0.84	5.13	332	0.38 <sup>c</sup>
12	9.41	685	1.00	10.3	334	0.39
	13.9	769	1.12			

<sup>a</sup> The ligands L are designated by the length *n* of the alkyl chain -(CH<sub>2</sub>)<sub>*n*</sub>- between the N atoms. <sup>b</sup> Concentrations in units of 10<sup>-3</sup> M. <sup>c</sup> 4-Methylpyridine adduct.

### Results and Discussion

*n* = 2.—Complexes of the type NiL were prepared with the following diamines: 1,2-diaminoethane, 1,2-diaminopropane, and 1,2-diaminocyclohexane. These complexes are all diamagnetic (Table III) and their

TABLE III  
ROOM-TEMPERATURE MAGNETIC MOMENTS  $\mu_{\text{eff}}$   
(BM) OF NiL AND NiL·2C<sub>5</sub>H<sub>5</sub>N

Ligand <sup>a</sup>	Initial prepn	NiL	
		(prepn from C <sub>5</sub> H <sub>5</sub> N adduct)	NiL·2C <sub>5</sub> H <sub>5</sub> N
1,2; eth	Diamagnetic	...	...
1,2; prop	Diamagnetic	...	...
1,2; cyclohex	Diamagnetic	...	...
1,3; prop	1.66, 2.31, 2.40	Diamagnetic	3.19
1,4; but	3.20 <sup>b</sup>	...	3.28 <sup>c</sup>
1,5; pent	2.10, 1.89, 2.09 <sup>e</sup>	1.86	3.25
1,6; hex	1.89, 1.86, 2.12	2.10	3.15
1,7; hept	2.30, 1.75, 1.99 <sup>e</sup>	2.14	3.12
1,8; oct	2.06, 1.96, 1.96	1.79	3.00
1,9; non	1.90, 1.75, 1.92	1.95	3.12
1,10; dec	2.16, 2.07, 1.80	2.06	3.14
1,12; dodec	2.18, 1.90, 2.01	2.08	3.44 <sup>d</sup>

<sup>a</sup> See Table I for abbreviations. <sup>b</sup> Monohydrate. <sup>c</sup> Trihydrate. <sup>d</sup> 4-Methylpyridine adduct. <sup>e</sup> Diamagnetic form also isolated.

visible-near-infrared spectra (Table IV) all display one spectral band at  $\sim 18,000$  cm<sup>-1</sup> (Figure 1) in the solid state, in chloroform, and in pyridine. The complexes are insufficiently soluble in benzene to permit molecular weight determinations, but the spectra indicate that the metal environment is the same in solution as in the solid.

These results suggest that, like their salicylaldehyde counterparts, the complexes are all monomers containing low-spin square-planar Ni(II), and this configuration is retained even in donor solvents such as pyridine. Here the Schiff bases act as quadridentate ligands.

*n* = 3.—The complex NiL, initially prepared, displays a spectrum (Table II) consistent with a low-spin square-planar structure but gives magnetic moments in

TABLE IV  
ELECTRONIC SPECTRA OF NiL COMPLEXES<sup>a</sup>

Ligand <sup>b</sup>	Solid	Soln		
		Benzene	Chloroform	Pyridine
1,2; eth	18.0	Insol	18.3 sh (168)	18.3 sh (202)
1,2; prop	18.0 sh	Insol	18.2 sh (172)	18.0 sh (168)
1,2; cyclohex	18.5 sh	Insol	18.5 (408)	18.5 (388)
1,3; prop	17.0 sh	Insol	Insol	11.0 (20)
1,4; but <sup>c</sup>	15.7	Insol	16.4 (80)	16.4 sh (30)
	10.6		10.5 (16)	10.4 (21)
	7.6		7.5 (22)	
1,5; pent	17.5	17.6 (138)	17.9 (137)	17.0 sh (30)
	8.8	...	...	10.2 (18)
1,6; hex	17.5 sh	17.4 (147)	17.8 (121)	17.0 (14)
	8.8	...	...	9.8 (11)
1,7; hept	17.5 sh	17.5 (197)	17.6 (142)	17.0 (16)
	8.8	...	...	10.1 (15)
1,8; oct	17.5 sh	17.6 (134)	17.7 (157)	16.9 (17)
	9.0	...	...	10.0 (15)
1,9; non	17.5 sh	17.5 (182)	17.7 (172)	16.7 (19)
	8.8	...	...	10.0 (17)
1,10; dec	17.0 sh	17.1 (164)	17.3 (146)	16.5 (15)
	9.2	...	...	9.8 (13)
1,12; dodec	17.0 sh	17.6 (146)	17.7 (155)	16.4 (13)
	9.1	...	...	10.0 (19)

<sup>a</sup>  $\lambda$  in 10<sup>3</sup> cm<sup>-1</sup>;  $\epsilon$  values in parentheses; sh = shoulder. <sup>b</sup> See Table I for abbreviations. <sup>c</sup> Monohydrate.

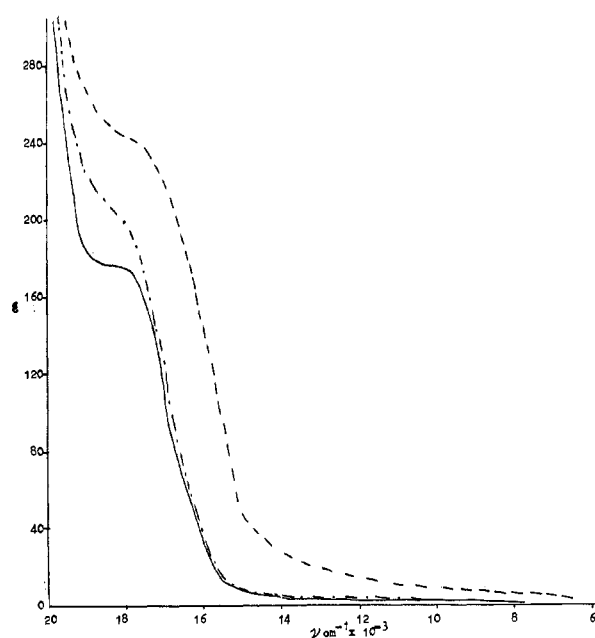


Figure 1.—Electronic spectra of the NiL complexes with *n* = 2: —, chloroform solution (0.01 M); - - - - -, pyridine solution (0.01 M); - · - · - ·, solid state (arbitrary scale).

the range 1.6–2.4 BM which vary from one preparation to the next. When the complex is recrystallized from pyridine and the two coordinated pyridine molecules are removed by heating, the diamagnetic square-planar complex, with a spectrum identical with that of the initial complex, is obtained.

This complex resembles the *n* = 2 complex and is apparently a square-planar monomer. However, when dissolved in pyridine solution, it has a new spectral band at 11,000 cm<sup>-1</sup> ( $\epsilon$  20), indicating the formation of an octahedral bis-pyridine adduct, NiL·2py



This paramagnetic (Table V) octahedral adduct with a solid-state spectrum (Table VI) identical with the pyridine solution spectrum can be isolated from the pyridine solution. In chloroform solution, spectral

TABLE V  
ROOM-TEMPERATURE MAGNETIC MOMENTS  $\mu_{\text{eff}}$   
(BM) OF NiL AND NiL·2C<sub>3</sub>H<sub>5</sub>N IN SOLUTION  
(CONCENTRATION UNITS 10<sup>-1</sup> M)

L <sup>a</sup>	NiL				NiL(C <sub>3</sub> H <sub>5</sub> N) <sub>2</sub> in benzene	
	Benzene		Pyridine		Concn	$\mu_{\text{eff}}$
3	Insoluble		4.24	2.91	...	...
5	4.64	1.18	Insoluble		3.63	1.19
6	4.64	0	3.38	2.80	3.67	0.52
7	4.43	0.63	2.64	2.81	2.60	0
8	3.42	0	3.97	2.84	3.19	0.79
9	3.77	0.77	4.12	2.81	3.60	1.15
10	3.44	0.39	3.39	2.83	2.58	0.39
12	2.64	1.15	3.95	2.86	1.77	0.61 <sup>b</sup>

<sup>a</sup> See Table II, footnote a. <sup>b</sup> 4-Methylpyridine adduct.

TABLE VI  
ELECTRONIC SPECTRA OF NiL·2C<sub>3</sub>H<sub>5</sub>N COMPLEXES<sup>a</sup>

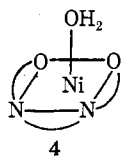
L <sup>b</sup>	Solid state	Benzene soln
3	..., 11.0	17.0 (86) <sup>c</sup>
4 <sup>d</sup>	17.8 sh, 10.4	16.6 (70), 10.5 (25), 7.6 (25)
5	17.0, 9.8	17.6 (189)
6	17.0, 9.6	17.5 (135)
7	17.0 sh, 9.8	17.5 (180)
8	16.6, 9.8	17.5 (130)
9	16.7, 9.5	17.5 (132)
10	16.6, 9.6	17.3 (150)
12 <sup>e</sup>	17.0, 10.3	17.5 (170)

<sup>a</sup>  $\lambda$  in 10<sup>3</sup> cm<sup>-1</sup>;  $\epsilon$  values in parentheses; sh = shoulder. <sup>b</sup> See Table II, footnote a. <sup>c</sup> In chloroform. <sup>d</sup> Trihydrate. <sup>e</sup> 4-Methylpyridine adduct.

measurements (Table VI) indicate that the reaction 1 is reversed.

The red shift of about 1000 cm<sup>-1</sup> in going from  $n = 2$  to  $n = 3$  parallels that observed in the salicylaldimine analogs<sup>9</sup> and may reasonably be attributed to increasing distortion from strict planarity.

$n = 4$ .—The green complex initially formed is of the type NiL·H<sub>2</sub>O· $n$ CH<sub>3</sub>OH. On heating this complex to 120° the yellow complex NiL·H<sub>2</sub>O is formed. Further heating leads to partial decomposition of the complex. The monohydrate is paramagnetic (Table III) and gives spectral bands<sup>15</sup> (Table IV, Figure 2) consistent with the complex having a square-pyramidal structure, 4,



like that observed in the single-crystal X-ray study<sup>16</sup> of the monopyridine adduct of *N,N'*-ethylenebis(salicylaldimine)cobalt(II). The spectral bands are tentatively assigned in the following manner: <sup>3</sup>B<sub>1</sub> → <sup>3</sup>E (F) (7600 cm<sup>-1</sup>), <sup>3</sup>B<sub>1</sub> → <sup>3</sup>A<sub>2</sub> (F) (10,600 cm<sup>-1</sup>), <sup>3</sup>B<sub>1</sub> → <sup>3</sup>B<sub>2</sub> (F), <sup>3</sup>B<sub>1</sub> → <sup>3</sup>E<sub>2</sub> (F) (components of the band at ~15,700 cm<sup>-1</sup>). This assignment must remain tentative because the differences in spectra among a square-pyramidal, a distorted square-pyramidal, and a trigonal-bipyramidal structure are not always clear. Molecular models suggest that a square-pyramidal or slightly distorted square-pyramidal structure would be preferred. We have ruled out the possibility of the two bands at 7600 and 10,600 cm<sup>-1</sup> representing a split

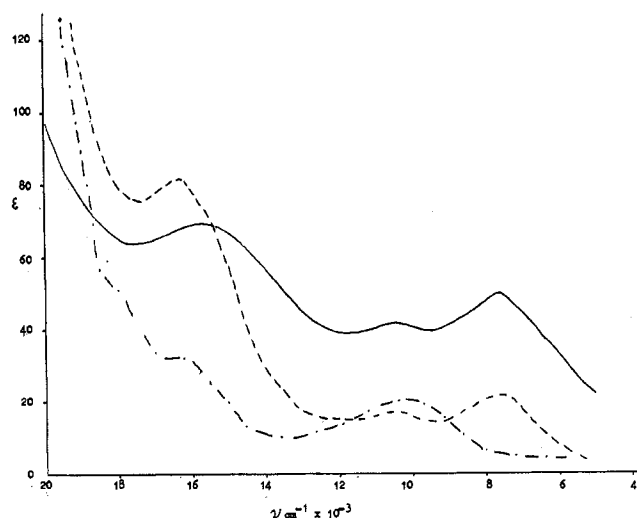


Figure 2.—Spectra of NiL·H<sub>2</sub>O with  $n = 4$ : ----, chloroform solution (0.01 M); - · - · -, pyridine solution (0.01 M); —, solid state (arbitrary scale).

“octahedral” <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub> band due to distortion from O<sub>h</sub> symmetry, because the spectra of all the remaining octahedral pyridine adducts, including the pyridine adduct of this complex, have one unsplit band at ~10,000 cm<sup>-1</sup>. When the complex is dissolved in chloroform, the spectrum is little changed (Table IV) indicating that the stereochemistry of the complex remains essentially the same in a nondonor solvent. The green complex NiL·H<sub>2</sub>O· $n$ CH<sub>3</sub>OH displays a spectrum similar to that of the monohydrate suggesting that the methanol molecules are trapped in the crystal lattice rather than coordinated to the Ni(II) atom.

When the monohydrate is dissolved in pyridine, a typical octahedral Ni(II) spectrum (Table VI, Figure 2) is obtained, the spectral band of the five-coordinate compound at 7500 cm<sup>-1</sup> disappearing, and the spectrum of the paramagnetic (Table V) pyridine adduct NiL·2py·3H<sub>2</sub>O resembles that of the pyridine solution. The adduct is likely to be a trans-octahedral monomer with the water molecules trapped in the crystal lattice, although it is possible that one of the water molecules remains coordinated to the nickel atom. In benzene solution, the adduct dissociates to form the five-coordinate monohydrate as shown by the change in spectrum (Table VI): NiL·2py·3H<sub>2</sub>O ⇌ NiL·H<sub>2</sub>O + 2py + 2H<sub>2</sub>O.

$n = 5-12$ . (i) **Solid-State Behavior.**—There is an abrupt change in the properties of the complexes when  $n = 5$  in the ligand L and this observation is paralleled by similar behavior of the salicylaldimines 1 with increasing  $n$ . In contrast with the wide range of magnetic moments observed for the salicylaldimines, the NiL complexes have room-temperature moments in the narrow range 1.9 ± 0.3 BM. This suggests some similarity between all the NiL complexes, independent of  $n$ , but moments of 1.9 BM must be regarded as anomalous for Ni(II).

In low-spin states ( $S = 0$ ), which may arise in square-planar, in five-coordinated, and in very distorted octahedral and tetrahedral nickel(II), the magnetic moment is expected to be zero or nearly so. In high-spin states ( $S = 1$ ), which may arise in tetrahedral, five-coordinated, and octahedral nickel(II) complexes, moments ranging from 2.9 to 4.2 BM are predicted by theoretical

(15) L. Sacconi, *Transition Metal Chem.*, **4**, 222 (1968).

(16) M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc. A*, 2411 (1970).

considerations. Thus spin-state crossover situations, where high- and low-spin states are simultaneously thermally populated, can arise in (a) configurations intermediate between tetrahedral and planar, (b) strongly distorted octahedral complexes, and (c) five-coordinated complexes. Case (a) was sought by Hoyt and Everett,<sup>11</sup> (b) was sought by Ballhausen and Liehr and Maki,<sup>17</sup> and (c) was mentioned by Ciampolini.<sup>18</sup> In any such crossover, the magnetic moment is given by a Boltzmann distribution and is therefore expected to be strongly temperature dependent; in fact, in crossover situations so far examined in complexes of various metals, the moments have shown a stronger temperature dependence than predicted by the simple Boltzmann equation.<sup>19</sup>

The observed magnetic moments do not show much temperature dependence (Table VII). The data were

TABLE VII  
TEMPERATURE DEPENDENCE OF MAGNETIC MOMENTS OF NiL

L <sup>a</sup>	Temp range, °K	$\mu_{av}^b$	$\sigma^b$	$\theta$	R <sup>c</sup>
2	85-328	<i>e</i>			
2 <sup>d</sup>	85-340	<i>e</i>			
3	108-292	2.246	0.048	23.0	0.998
4	89-330	<i>f</i>			
4 <sup>e</sup>	112-333	3.382	0.117	30.1	0.997
5	88-353	1.639	0.038	7.9	0.992
6	89-328	2.021	0.038	7.8	0.994
7	87-327	1.813	0.028	8.8	0.994
8	89-330	1.882	0.022	9.6	0.998
9	93-327	1.919	0.044	-3.5	0.993
10	89-325	1.626	0.042	16.1	0.986
12	85-330	1.867	0.100	60.3	0.994

<sup>a</sup> See Table II, footnote a. <sup>b</sup> Standard deviations,  $\sigma$ , calculated from  $\sigma = \sqrt{\sum(\mu_{av} - \mu_i)/(n-1)}$ . <sup>c</sup> Correlation coefficients, R, calculated from

$$R = \frac{n \sum T_i x_i - \sum T_i \sum x_i}{\sqrt{[n \sum x_i^2 - (\sum x_i)^2][n \sum T_i^2 - (\sum T_i)^2]}}$$

where  $x_i = 1/\chi_i$ . All summations,  $i = 1-n$ , for molar susceptibilities  $\chi_i$ . <sup>d</sup> Ni(1,2; prop). <sup>e</sup> Molar susceptibility is constant within experimental error, suggesting a TIP contribution of  $4 \times 10^{-4}$  cgs emu. <sup>f</sup> TIP  $\approx 6 \times 10^{-4}$  cgs emu. <sup>g</sup> Ni(1,4; but)  $\cdot H_2O \cdot 4CH_3OH$ . <sup>h</sup> Detailed magnetic data over an absolute temperature range will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1308. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

found to give reasonable fits to a Curie-Weiss law (as indicated by values of the correlation coefficient near 1.0), and no other general curve could be found to give a good representation of the temperature dependence. The main limitation in accuracy arises from the low-volume susceptibilities (due to low density and high molecular weight) of most of the complexes.

The magnetic properties of the various members of the series are thus quite similar, within experimental error, and the temperature dependence, as indicated by the Weiss constant  $\theta$ , is not large. The existence of a spin-state crossover can therefore be ruled out,

(17) C. J. Ballhausen and A. D. Liehr, *J. Amer. Chem. Soc.*, **81**, 538 (1959); G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

(18) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).

(19) R. L. Martin and A. H. White, *Transition Metal Chem.*, **4**, 114 (1968); A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, **8**, 1837 (1969); C. M. Harris and E. Sinn, *Inorg. Chim. Acta*, **2**, 296 (1968).

as can the existence of strong exchange interactions<sup>20</sup> within small clusters of paramagnetic molecules, which could similarly explain the room-temperature moments but which would require a much greater temperature dependence than is observed. Weak lattice, wide exchange interactions are not ruled out by the observed temperature dependence but could not rationalize the absolute magnitudes of the moments. The only remaining possibility is the coexistence of high- and low-spin species in a ratio that is constant over the experimental temperature range.

One exception to the general trend of magnetic properties is the  $n = 12$  complex, for which a good fit was obtained to the Curie-Weiss law, but with the largest value of  $\theta$  for the series. Thus the temperature dependence of the magnetic moment of this complex is considerably greater than for the rest of the series. Otherwise (Tables II-VI) it conforms well with the remainder of the series and is therefore unlikely to have a markedly different structure. If the reduction of the moment of the  $n = 12$  complex below the "normal" value (*ca.* 3.2 BM) were due entirely to a high spin-low spin crossover or to exchange interaction, we would expect a considerably greater temperature dependence of the magnetic moment than is observed. It is therefore much more likely that this complex has its moment reduced by the same factors as the remainder of the series, but in this particular compound some intermolecular antiferromagnetic interaction is also present.

The visible-near-infrared spectra of the complexes (Table IV, Figure 3) consists of two maxima, one at

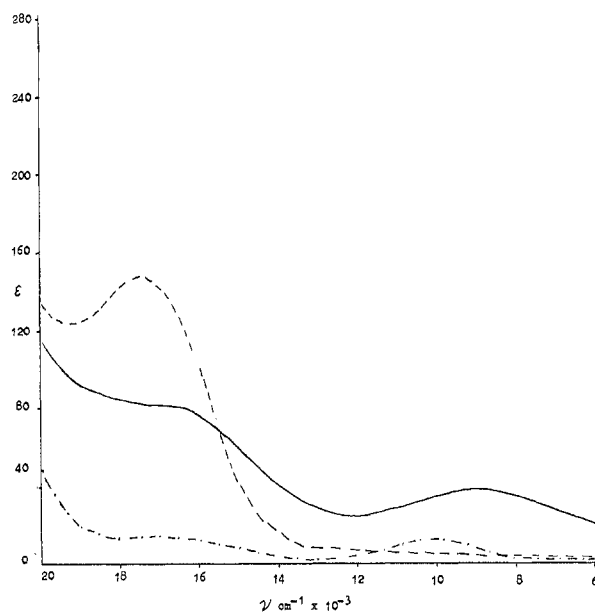


Figure 3.—Spectra of the complex NiL with  $n = 6$ : ----, benzene solution (0.01  $M$ ); - · - · -, pyridine solution (0.01  $M$ ); —, solid state (arbitrary scale). Similar spectra are obtained for all the complexes with  $n = 5-12$ .

$\sim 17,000 \text{ cm}^{-1}$  and one at  $\sim 9,000 \text{ cm}^{-1}$ . The band at  $\sim 9,000 \text{ cm}^{-1}$  is characteristic of high-spin octahedral Ni(II) ( ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ) while the band at  $\sim 17,000 \text{ cm}^{-1}$  appears to be the resultant of the low-spin square-planar band ( ${}^1A_1(F) \rightarrow {}^1B_1(G)$ ) as in the  $n = 2, 3$

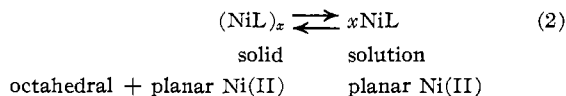
(20) E. Sinn, *Coord. Chem. Rev.*, **5**, 313 (1970).

complexes) and the less intense octahedral band ( ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (F)) expected in the same region (as in pyridine adducts of the  $n = 3, 4$  complexes). These results are consistent with the simultaneous presence of octahedral and square-planar nickel environments. In octahedral environments, we expect room-temperature moments similar to those of the dipyridine adducts ( $3.2 \pm 0.2$  BM) while the moments should be much smaller in planar environments. Allowing for experimental error of up to 0.1 BM in complexes with moments  $\mu_{\text{obsd}}$  falling in the range 1.75–2.1 BM, a 1:2 ratio of octahedral to planar is indicated (here  $\mu_{\text{obsd}} = \mu_{\text{oct}}/\sqrt{3}$ ; assuming a reasonable value of 0.5 BM for the planar nickel(II),  $\mu_{\text{obsd}}$  would be raised slightly by 0.04 BM). (Only one compound, one of the four preparations of the  $n = 7$  complex, falls significantly outside this range.) Complexes with  $\mu_{\text{obsd}} > 2$  BM may have a higher proportion of octahedral nickel atoms, but it seems unlikely from the data that the octahedral:planar ratio can exceed 1:1. Possibly a rather high residual moment in the planar species might explain  $\mu_{\text{obsd}} > 2$ . (A moment of 0.5 BM for the planar form adds 0.03 BM to  $\mu_{\text{obsd}}$  if the ratio is 1:1.) X-Ray powder diffraction patterns of these complexes indicate that they are amorphous in the solid state. This fact rules out the very desirable X-ray structural investigations.

In addition to the normal partially paramagnetic forms, diamagnetic forms of some of these complexes could also be formed by allowing them to crystallize slowly from benzene–methyl acetate solution. The diamagnetic forms of the  $n = 5$  and 7 complexes were formed in this way. X-Ray powder diffraction patterns indicate that these complexes are crystalline, but we have not yet succeeded in obtaining crystals suitable for X-ray structural determination. We have so far been unable to discover conditions under which the other complexes could be obtained in crystalline forms.

(ii) **Solution Behavior.**—In contrast to the salicylaldehyde-based complexes, these complexes are extremely soluble in nondonor solvents such as benzene and chloroform, so much so that these solvents cannot be used satisfactorily to recrystallize them.

Solution magnetic moments in benzene (Table VI) are reduced to almost zero where  $n$  is an even number and to 0.6–1.2 BM where  $n$  is odd. This suggests that when dissolved in a nondonor solvent, the octahedral Ni(II) present in the solid state largely disappears due to break-up of molecular association



In agreement with this, the octahedral band at  $\sim 9000$   $\text{cm}^{-1}$ , present in the solid state, disappears (Table IV, Figure 3) in solution leaving the single planar band at  $\sim 17,500$   $\text{cm}^{-1}$  ( $\epsilon$  150–200) which also occurs in the planar  $n = 2, 3$  complexes.

Molecular weight determinations (Table II) in freezing benzene show that these low-spin square-planar species are monomeric, indicating that in these examples the ligands L function as quadridentates in solution. Where  $n$  is an odd number, the molecular weight results are greater than those of monomers indicating the presence of the monomer–polymer equilibria shown

in eq 2. In all cases, the monomer is the dominant species in benzene solution.

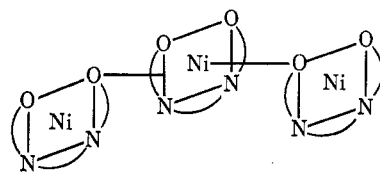
**NiL·2py. Solid State.**—When the complexes NiL are dissolved in pyridine, solution magnetic moments in the range 2.8–2.9 BM are obtained (Table V) suggesting the presence of the high-spin octahedral adducts NiL·2py. This is supported by spectral data (Table VI) which show the presence of two octahedral bands (Figure 3), one at  $\sim 17,000$   $\text{cm}^{-1}$  ( $\epsilon \sim 20$ ) and the other at  $\sim 10,000$   $\text{cm}^{-1}$  ( $\epsilon \sim 20$ ), in pyridine solution. These adducts can be isolated from pyridine solution. The magnetic moments in the range 3.0–3.5 BM and solid-state spectral bands at  $\sim 17,000$  and  $\sim 10,000$   $\text{cm}^{-1}$  are in good accord with a trans-octahedral structure.

**Solution Behavior.**—When dissolved in a nondonor solvent, such as benzene, the octahedral spectral bands disappear and are replaced by the square-planar NiL band at  $\sim 17,500$   $\text{cm}^{-1}$  (Table IV). The solution magnetic moments drop to 0–1.2 BM (Table V) and the molecular weight measurements drop to one-third of the values for monomers, indicating the equilibrium in eq 1 is set up, with the equilibrium position largely to the right.

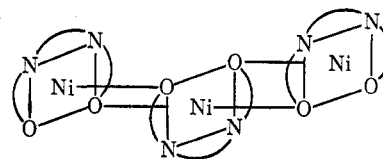
### Conclusion

In nondonor solvents, the anhydrous complexes NiL are low-spin square-planar monomers with the Schiff bases acting as quadridentate ligands. Where  $n = 2, 3$ , this stereochemistry is maintained in the solid state. Where  $n = 5$ –12, the complexes contain low-spin square-planar Ni(II) and high-spin octahedral Ni(II) in the approximate ratio 2:1. While the possibility that each compound contains a mixture of high-spin and low-spin complexes cannot be definitely excluded, the available evidence suggests that the high-spin and low-spin Ni(II) atoms occur in the one complex.

Molecular models suggest that the trimeric structure 5



5



6

would fit the physical data obtained in this investigation. The possibility of further polymerization from this trimer with alternate octahedral and square-planar units cannot be disregarded for some of the complexes with magnetic moments greater than  $\sim 2.1$  BM.

Structure 6 would be consistent with the magnetic data only if the two five-coordinated Ni(II) atoms were low spin, which is unlikely since five-coordinated Ni(II) in the closely related salicylaldehydes is high spin.<sup>15</sup> Moreover, low-spin five-coordinated Ni(II) complexes with As and P ligands exhibited a broad,

intense band at 14,000–20,000  $\text{cm}^{-1}$ .<sup>21</sup> Thus if low-spin five-coordinated Ni(II) existed in **6**, similar bands at lower frequencies are expected, due to the lower ligand field by the O and N ligands. Such bands are not apparent in the spectra, and structure **5** seems more probable.

The amorphous nature of the solid complexes, as indicated by their X-ray diffraction patterns, implies that structure **5** may only be the statistical preference. Either **5** does not arise sufficiently often to give rise to a regular arrangement in a crystalline state or perhaps the shape of **5** differs from one molecule to the next (*e.g.*, due to the flexible alkyl chain), thereby leading to disorder.

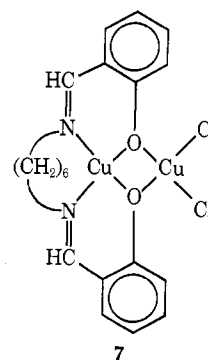
The properties of the adducts  $\text{NiL} \cdot 2\text{py}$  suggest that they have a trans-octahedral monomeric structure while, for  $n = 4$ , the complex  $\text{NiL} \cdot \text{H}_2\text{O}$  appears to have a square-pyramidal structure with the water molecule in the apical position.

In all cases the ligands L act as quadridentates about individual nickel atoms, with intermolecular associations *via* Ni–O bonds a possibility for  $n = 5$ –12 complexes. This fact suggests that similar quadridentate liganding may also occur in the analogous salicylaldimine complexes, in preference to the bridged bidentate structure **2**, postulated for the NiSal complexes with  $n = 5$ –12<sup>11</sup> and previously for the analogous zinc complexes.<sup>22</sup> We could then explain the apparently anomalous behavior of CuSal with  $n = 6$ , which would previously have been considered an infinite polymer,

(21) G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, **3**, 1544 (1964).

(22) B. Kirson and H. Sechter, *Bull. Soc. Chim. Fr.*, 2743 (1965).

but which forms a crystalline derivative with copper chloride,<sup>23</sup> **7**. This derivative closely resembles a series



of binuclear complexes containing tetradentate Sal ligands but does not fit into a series of copper chloride derivatives of bidentate salicylaldimine complexes.<sup>24</sup> Similarly, mass spectral data on the cobalt(II) complexes with salicylaldimines **7** ( $n = 3$ –6) suggested that these complexes, though insoluble in common solvents, were monomeric with the Schiff bases acting as quadridentates.<sup>25</sup>

**Acknowledgments.**—We wish to thank Professor S. E. Livingstone, University of New South Wales, for the use of a Zeiss PMQ II spectrophotometer and solution magnetic moment apparatus. We are also grateful for apparatus provided by a USAF research grant.

(23) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968).

(24) C. M. Harris and E. Sinn, *ibid.*, **30**, 2723 (1968).

(25) M. Harihan and F. L. Urbach, *Inorg. Chem.*, **8**, 556 (1969); J. Manassen, *ibid.*, **9**, 996 (1970).

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## Four- and Five-Coordinate Complexes of Nickel(II) with Diethylphosphine

By P. RIGO\* AND M. BRESSAN

Received August 3, 1971

Diethylphosphine forms four-coordinate diamagnetic  $[\text{Ni}(\text{HP}(\text{C}_2\text{H}_5)_2)_3\text{X}]^+$  complexes ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$ ), as well as the diamagnetic five-coordinate  $\text{Ni}(\text{HP}(\text{C}_2\text{H}_5)_2)_3\text{X}_2$  ( $\text{X} = \text{Br}, \text{I}$ ) and  $[\text{Ni}(\text{HP}(\text{C}_2\text{H}_5)_2)_4\text{X}]^+$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$ ) complexes. The compounds have been characterized by conductivity, magnetic measurements, and electronic spectra. The stability of the five-coordinate complexes in solution has been found to depend markedly on the type of solvent and on the presence of free ligands. Moreover, spectral data show that the previously reported six-coordinate  $\text{Ni}(\text{HP}(\text{C}_2\text{H}_5)_2)_4\text{X}_2$  can better be formulated in the solid state as the five-coordinate ionic compounds  $[\text{Ni}(\text{HP}(\text{C}_2\text{H}_5)_2)_3\text{X}]\text{X}$ .

### Introduction

Numerous investigations carried out on the reaction of nickel(II) salts with tertiary phosphines have shown that the stereochemistry of the complexes is strongly dependent upon the type of the anionic ligand, as well as on the nature of the organic substituents at the phosphorus atom of the phosphine. Four- and five-coordinate complexes have been obtained, which contain one, two, three, and four molecules of phosphine.<sup>1–5</sup>

(1) G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964), and references therein.

(2) P. Rigo, C. Pecile, and A. Turco, *Inorg. Chem.*, **6**, 1636 (1967).

(3) P. Rigo, G. Guastalla, and A. Turco, *ibid.*, **8**, 375 (1969).

(4) K. A. Jensen and O. Dahl, *Acta Chem. Scand.*, **22**, 1044 (1968).

(5) D. W. Allen, F. G. Mann, and I. T. Millar, *J. Chem. Soc. A*, 1101 (1969).

By contrast, relatively few complexes of nickel(II) with secondary phosphine have been characterized. Dicyclohexylphosphine forms the four-coordinate complexes  $\text{Ni}(\text{HP}(\text{C}_6\text{H}_{11})_2)_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ).<sup>6</sup> The reaction of diphenylphosphine with nickel(II) halides in nonionizing solvents yields *trans*- $[\text{Ni}(\text{HP}(\text{C}_6\text{H}_5)_2)_2\text{I}_2]$  and five-coordinate  $\text{Ni}(\text{HP}(\text{C}_6\text{H}_5)_2)_3\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ).<sup>7</sup> With diethylphosphine only the six-coordinate complexes  $\text{Ni}[\text{HP}(\text{C}_2\text{H}_5)_2)_4\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) have been reported.<sup>6</sup>

As part of a study of the properties, spectra, and stereochemistry of complexes of nickel(II) with sec-

(6) K. Issleib and G. Doell, *Z. Anorg. Allg. Chem.*, **305**, 1 (1960).

(7) R. G. Hayter, *Inorg. Chem.*, **2**, 932 (1963).