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Square-Planar–Tetrahedral Isomerism of Nickel Halide Complexes of Diphenylalkylphosphines

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The nickel halide complexes of some diphenylalkylphosphines (alkyl = methyl, ethyl, *n*- and isopropyl, *n*-, iso-, *s*-, and *t*-butyl, and *n*-amyl) have been characterized. Eight examples of square-planar–tetrahedral isomerism have been identified as well as a novel type of isomerism shown by $[NiI_2(PR(C_6H_5)_2)_2]$ (R = isopropyl and *s*-butyl).

Introduction

In a preliminary communication, we have described the isolation and characterization of the crystalline square-planar and tetrahedral isomers of $[NiBr_2(P(C_2H_5)(C_6H_5)_2)_2]$.[2] Several other cases of this novel type of isomerism were also briefly noted for complexes of the type $[NiX_2(PR(C_6H_5)_2)_2]$ (X = Cl, Br, I; R = alkyl). The prior discovery of the same kind of isomerism with four closely related complexes (R = benzyl, X = Cl, Br, I; R = allyl, X = Br) was also reported about the same time.[3] In this paper, we describe in more detail our studies of the nickel halide complexes of some diphenylalkylphosphines during which eight pairs of square-planar–tetrahedral isomers were characterized. In addition, the complexes $[NiI_2(PR(C_6H_5)_2)_2]$ (R = isopropyl, *s*-butyl) were found to show a different type of isomerism, not yet fully understood.

Square-planar–tetrahedral isomerism has so far been observed only in certain series of nickel complexes, and only with the diphenylalkylphosphine ligands have both isomers been isolated in the pure state. A unique case of the coexistence of both isomers in the same unit cell has been demonstrated by an X-ray structural examination of the paramagnetic form of $[NiBr_2(P(CH_2C_6H_5)(C_6H_5)_2)_2]$.[4] Although no quantitative estimate has been made, it is evident from the study of complexes of this type that the energy difference between the two isomeric forms is small. For example, the structure of the isolated complex depends upon the nature of the alkyl group in the phosphine ligand and upon the technique used to crystallize the complex. Similar effects have been observed in other series of nickel complexes,[5] and equilibria between square-planar and tetrahedral forms have been demonstrated for a variety of N-substituted salicylaldimine complexes of nickel(II) either in solution[5a,b] or in the melt.[6]

Experimental

The microanalyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. The melting points, dipole moments, and absorption spectra were measured as previously described.[7] The magnetic moments were measured by the Faraday method and we are indebted to Dr. L. Vaska for these determinations.

The tertiary phosphines were obtained by reaction between sodium diphenylphosphide and the appropriate alkyl halide, except for diphenyl-*t*-butylphosphine, which was prepared by the Grignard method. The products were purified by distillation and characterized by analysis and proton nuclear magnetic resonance spectra, details of which will be reported later.

Preparation of the Complexes.—The complexes were prepared by addition of the phosphine (2 moles) to concentrated solutions of nickel halides in ethanol or, in a few cases, acetic acid. The solid complexes were rapidly precipitated in about 70–80% yield and were filtered, washed with ethanol, and air dried. In cases where both isomers have been isolated, this method of preparation yields the tetrahedral form, although in one case ($[NiBr_2P(n\text{-}C_3H_7)(C_6H_5)_2)_2]$) either form, or a mixture, can be obtained depending on the rate of crystallization. In cases where this method yields only the square-planar isomer, it has not yet proved possible to obtain the tetrahedral form either by crystallization or by precipitation from other solvent systems. Crystallizations were carried out under nitrogen from solutions containing 1–2% of the corresponding phosphine, which was added to repress dissociation. The solvent systems are summarized in Table II. Unless otherwise indicated, crystallization was completed by cooling the solutions to 0°. The solid complexes are all stable in air, and, of the isomeric complexes, those which were prepared by crystallization at low temperatures (*ca.* $-78°$) often isomerized at room temperature and were therefore stored at 0°. The characteristics of individual complexes are described in more detail below.

Results

Evidence for the Structure of the Complexes.—The structures of the solid complexes are deduced mainly from their absorption spectra in the range 350 to 1000 mμ and their room temperature magnetic moments. In some cases, comparison of the X-ray powder patterns of the nickel complexes with those of the corresponding tetrahedral zinc and cobalt and square-planar palladium compounds is helpful in establishing the isomorphism of certain pairs of complexes, which differ only in the central metal atom. On the basis of these observations, the complexes fall, on the whole, into two general categories: (i) Diamagnetic, dark red or brown compounds which show no absorption in the region 800–1000 mμ and whose powder patterns are often similar to

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(1) Shell Development Company, Emeryville, Calif.

(2) R. G. Hayter and F. S. Humiec, *J. Am. Chem. Soc.*, **84**, 2004 (1962).

(3) M. C. Browning, J. R. Mellor, D. J. Morgan, S. A. J. Pratt, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 693 (1962).

(4) B. T. Kilbourn, H. M. Powell, and J. A. C. Darbyshire, *Proc. Chem. Soc.*, 207 (1963).

(5) (a) L. Sacconi, M. Ciampolini, and N. Nardi, *J. Am. Chem. Soc.*, **86**, 819 (1964), and earlier references; (b) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1010 (1964), and earlier references; (c) D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 207 (1963).

(6) L. Sacconi, *ibid.*, 4608 (1963).

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

TABLE I

STRUCTURES OF $[NiX_2(PR(C_6H_5)_2)_2]$ IN THE CRYSTALLINE STATE[a]

X	Methyl	Ethyl	*n*-Propyl	Isopropyl	*n*-Butyl	Isobutyl	*s*-Butyl	*t*-Butyl	*n*-Amyl
Cl	P	P	P	P	T,[b] P	P	P	. . .	T,[b] P
Br	T	T,[b] P	T, P[c]	T,[b] P	T,[b] P	T,[b] P	T,[b] P	T	T
I	T	T	T	T, G[d]	T	T	T, G[d]	T	T

[a] P denotes square-planar, T tetrahedral, and G a dark green isomer of unknown structure. [b] The isomer obtained from ethanol. [c] Either (or both) isomers may be obtained from ethanol, depending on the conditions (see text). [d] The tetrahedral isomer precipitates first and, unless separated and dried rapidly, isomerizes to the dark green form.

those of the corresponding palladium complexes. These compounds are square-planar and probably *trans*, at least in the solid state. (ii) Paramagnetic (μ_{eff} 3.0–3.3 B.M.), intensely colored compounds (chlorides are blue-purple, bromides green, and iodides brown) which show an absorption band in the region 800–1000 mμ and whose powder patterns are usually similar to those of the corresponding zinc or cobalt complexes. These compounds probably have distorted tetrahedral structures, by analogy with $[NiX_2(P(C_6H_5)_3)_2]$ (X = Cl, I), whose structures have been determined by X-ray crystallography.[8]

The only nickel halide complexes of diphenylalkylphosphines which we have found not to fall into either of these two classes are the green isomers of $[NiI_2(PR(C_6H_5)_2)_2]$ (R = isopropyl, *s*-butyl).

The experimental results are summarized in terms of structures in Table I and given in full in Table II, while individual complexes are considered in more detail under the respective phosphine ligands.

Diphenylmethylphosphine.—No cases of isomerism were found with this ligand.

Diphenylethylphosphine.—The behavior of the dark green bromo complex in solution first drew attention to the possibility of a novel type of isomerism.[2] Solutions of the complex in polar solvents, such as chloroform or nitromethane, are green with a faint red reflection, while in benzene or carbon disulfide they are dark red, with little, if any, tinge of green. The square-planar isomer was isolated from concentrated solutions in carbon disulfide (obtained either from the tetrahedral isomer or by dissolving anhydrous nickel bromide in a solution of diphenylethylphosphine in carbon disulfide) on cooling to −78°. Dark red rhomb-like crystals formed during several hours and these were filtered and washed with cold carbon disulfide and hexane and dried in a nitrogen stream to give brown crystals. The change in color on drying indicates that the dark red crystals may be weakly solvated, and even after drying under vacuum at 25° for several hours a small amount of solvent is retained as shown by a weak infrared band at 1505 cm.$^{-1}$ (1522 cm.$^{-1}$ in pure CS_2) and by direct analysis for sulfur. The small amount of solvent (*ca.* 12.5 mole %) is probably occluded in the crystal, and although coordination by the solvent may play an important part in the isomerizatiion process, it is not essential for the formation of a stable solid isomer, since the planar isomer has also been obtained from methylene chloride–ether solution at −78°. The structures of the isomers were deduced from the solid-state spectra (Figure 1), magnetic moments, and X-ray powder patterns, as previously reported.[2]

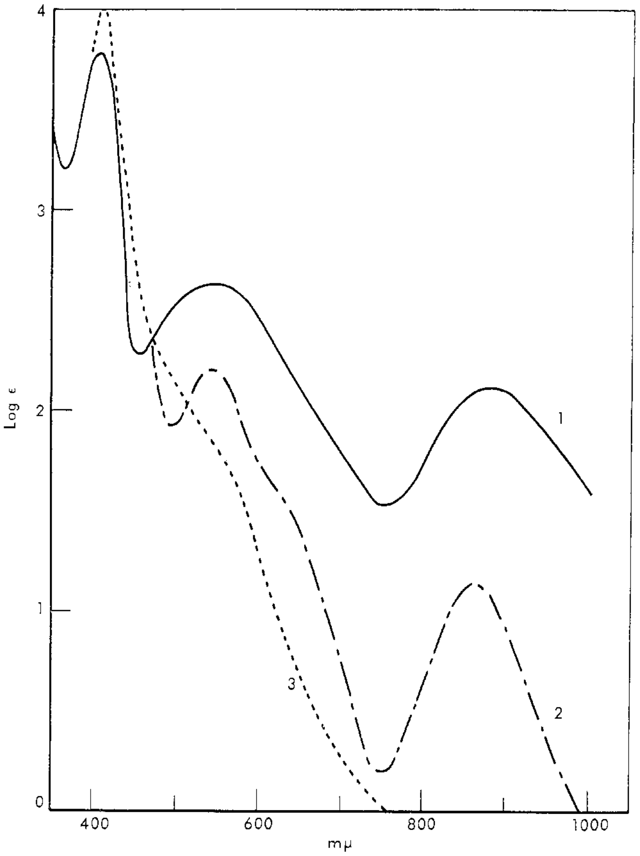

Figure 1.—Absorption spectra of $[NiBr_2(P(C_2H_5)(C_6H_5)_2)_2]$: 1, benzene solution of either isomer; 2, solid tetrahedral isomer; 3, solid square-planar isomer (the units of absorption for spectra 2 and 3 are arbitrary).

The square-planar form of $[NiBr_2(P(C_2H_5)(C_6H_5)_2)_2]$ can be stored essentially unchanged for several months in a refrigerator, but it slowly turns green during several days at 25°. This change is accelerated by increase in temperature, occurring mainly at 70–75° on a heated Kofler block. Melting subsequently takes place at 160–175° (the tetrahedral isomer melts at 165–175°). The magnetic behavior of the planar form of $[NiBr_2(P(C_2H_5)(C_6H_5)_2)_2]$ on heating (Table III) lends strong support to the supposition that this thermochroic behavior is due to isomerization to the tetrahedral isomer. The X-ray powder patterns and absorption spectra of the green solids obtained by heating the planar isomer in air (or nitrogen) at 80° for 1 hr. are identical with those of tetrahedral $[NiBr_2(P(C_2H_5)(C_6H_5)_2)_2]$.

The two isomers have virtually identical properties

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(8) G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963).

TABLE II

PREPARATION, ANALYSES, AND PROPERTIES OF THE SOLID COMPLEXES, $[NiX_2(PR(C_6H_5)_2)_2]$

R	X	Structure[a]	Cryst. solvent	Color	M.p., °C. (dec.)	μ_{eff}, B.M.	%, C		%, H		Absorption maxima, mμ
							Calcd.	Found	Calcd.	Found	
Methyl	Cl	P	CH_2Cl_2–ether	Red-violet	148–150	0	58.9	58.7	4.9	5.1	500–600 (sh), 460, 382
	Br	T	CH_2Cl_2–ether	Green-brown	159–164	3.37	50.45	50.7	4.2	4.4	845, 580–650 (sh), 532, 420
	I	T	CH_2Cl_2–ether	Brown-red	145–147	3.32	43.8	44.1	3.7	3.8	890, 600–730 (sh), 490–550 (sh), 448, 385
Ethyl	Cl	P	C_6H_6	Red	146–151	0	60.3	60.3	5.4	5.5	500–600 (sh), 462, 380
	Br	P	CS_2[b]	Brown	160–175	0	52.0	51.7	4.7	4.7[c]	555 (sh), 485 (sh), 411
	Br	T	CH_3NO_2	Green	149–170	3.20	52.0	51.8	4.7	4.7	862, 600–700 (sh), 542, 420 (sh), 387
	I	T	CH_2Cl_2–ether	Red-brown	127–138	3.10	45.4	44.7	4.1	3.9[d]	912, 650–750 (sh), 510–560 (sh), 452, 389
n-Propyl	Cl	P	CH_2Cl_2–ether	Red	152–157	0	61.5	61.5	5.85	6.2	500–600 (sh), 460, 380
	Br	P	CH_2Cl_2–ether	Red	130–147	0	53.4	53.2	5.1	4.9[e]	540 (sh), 490, 410
	Br	T	CH_3NO_2	Green	149–170	3.10	53.4	53.0	5.1	5.0[f]	865, 580–680 (sh), 542, 420, 390
	I	T	CH_2Cl_2–ether	Brown-red	120–129	3.06	46.85	47.6	4.5	4.35[g]	922, 650–740 (sh), 500–560 (sh), 448, 390
Isopropyl	Cl	P	CH_2Cl_2–ether	Red	160–165	0	61.5	61.5	5.85	6.1	500–600 (sh), 479, 390
	Br	P	C_6H_6–*n*-hexane	Brown	90–160	0[h]	56.5	56.8	5.3	5.5[i]	
	Br	T	CH_2Cl_2–ether	Green	171–177	3.05	53.4	53.1	5.1	5.2	852, 600–700 (sh), 570, 410
	I	T	Ethanol[j]	Brown	100–140	2.82	46.85	47.1	4.5	4.8	880–890, 520, 380
	I	G	Ethanol[k]	Green	105–140	0	46.85	47.2	4.5	4.2[l]	676, 500–540 (sh), 407
n-Butyl	Cl	P	Toluene–*n*-hexane[b]	Red	143–147[m]	...	...	...	...	...	...
	Br	P	Toluene–*n*-hexane[b]	Brown	90–160	0	54.7	54.6	5.45	5.4[n]	550 (sh), 490 (sh), 410
Isobutyl	Cl	P	CH_3NO_2	Red	113–124	...	62.6	62.5	6.2	6.4	480–590 (sh), 472, 380
	Br	P	CS_2–*n*-hexane[b]	Brown	70–74	...	54.7	54.5	5.45	5.6	552, 412, 320–350 (sh)
	Br	T	Ethanol[k]	Green	131–150	...	54.7	54.6	5.45	5.6	905, 570–700 (sh), 580, 417, 387
	I	T	Acetic acid[k]	Brown	118–133	...	48.2	48.4	4.8	4.9	950, 620–750 (sh), 520–580 (sh), 460
s-Butyl	Cl	P	CH_3NO_2	Red	138–152	...	62.6	62.4	6.2	6.3	490–600 (sh), 478, 389, 280–320 (sh)
	Br	P	Toluene–*n*-hexane[b]	Brown	85–90	...	54.7	54.7	5.45	5.6	...
	Br	T	CH_3NO_2	Green	158–169	...	54.7	55.4	5.45	5.7[o]	870, 570–700, 574, 425, 392
	I	T	Ethanol[j]	Brown	110–132	...	48.2	48.1	4.8	5.1	1055, 740–760 (sh), 670, 572, 530–480 (sh), 412
	I	G	Acetic acid[k]	Green	108–115	0	48.2	48.55	4.8	4.9	662, 450–540 (sh), 405
t-Butyl	Br	T	C_6H_6[k]	Green	193–203	...	54.7	55.05	5.45	5.45	892, 588, 450
	I	T	C_6H_6[k]	Brown	198–208	...	48.2	48.0	4.9	4.9	1057, 672, 540–580 (sh), 480–540 (sh), 422, 380
n-Amyl	Cl	P	Toluene–*n*-hexane[b]	Red	77–79	0	63.6	63.3	6.6	6.7[p]	480–600 (sh), 475, 380
	Cl	T	CH_3NO_2	Blue-purple	92–100	3.12	63.6	62.9	6.6	6.8	855–860, 550–650 (sh), 529, 380–420 (sh)
	Br	T	CH_3NO_2	Green-brown	113–128	...	55.85	56.0	5.8	5.8	855–860, 560–600 (sh), 540, 411, 400–380 (sh)
	I	T	CH_2Cl_2–ether	Brown-red	112–125	...	49.55	50.0	5.1	5.1	911, 600–700 (sh), 510, 442

[a] P = square-planar, T = tetrahedral, G = green isomer of unknown structure. [b] Crystallized by cooling to *ca.* −78.° [c] Calcd.: Br, 24.7; P, 9.6; Ni, 9.1. Found: Br, 24.85; P, 9.4; Ni, 9.9; S, 1.2 ± 0.5. [d] Calcd.: I, 34.25. Found: I, 34.2 [e] Calcd.: Br, 23.7; P, 9.2. Found: Br, 24.4; P, 9.1. [f] Calcd.: Br, 23.7; P, 9.2. Found: Br, 24.3; P, 9.3. [g] Calcd.: I, 33.0. Found: I, 32.9. [h] Shows weak paramagnetism, $10^6\chi_M$ (uncor.) = +111 c.g.s. units. [i] Crystallized with 0.75 mole of benzene. Calcd.: Br, 21.8; P, 8.4. Found: Br, 21.8; P, 8.55. [j] Obtained by rapid precipitation and separation from the reaction mixture. [k] Slow crystallization from reaction mixture gives pure complex. [l] Calcd.: I, 33.0. Found: I, 33.0. [m] Calcd.: Ni, 9.6. Found: Ni, 9.4, 9.2. [n] Calcd.: Br, 22.7; P, 8.8. Found: Br, 23.1; P, 8.8. [o] Calcd.: Br, 22.7. Found: Br, 22.3. [p] Calcd.: Cl, 11.0; P, 9.65. Found: Cl, 10.6; P, 9.8.

in solution, as shown by their similar dipole moments and solution spectra (Figure 1 and Table IV). The observed differences are probably due to partial dissociation, which invariably accompanies the solution of tertiary phosphine complexes of nickel halides and which renders the collection of reproducible solution

TABLE III

THE EFFECT OF HEAT ON THE MAGNETIC SUSCEPTIBILITY OF THE SQUARE-PLANAR ISOMER OF [$NiBr_2(P(C_2H_5)(C_6H_5)_2)_2$]

Treatment of the square-planar isomer	$10^6\chi_M$[a] (uncor.)	μ_{eff}, B.M.[a]
Stored at 0°	−315	0
10 days, 25°	+250	1.2
20 min., 20–40°	+2930	2.88
20 min., 40–62.5°	+2855	2.94
20 min., 62.5–80.2°	+2885	3.03
20 min., 80.2–92°	+3130	3.20
Tetrahedral isomer (25°)	+3870	3.20

[a] Measured at the higher end of the temperature ranges quoted.

data difficult. In agreement with other workers,[3] our observations indicate that equilibrium in solution is attained rapidly and no evidence for a time-dependent isomerization was found. This was confirmed with other isomeric pairs.

TABLE IV

PROPERTIES OF [$NiX_2(PR(C_6H_5)_2)_2$] IN SOLUTION

R	X	Structure of solid complex[a]	Dipole moment, D.	Molecular weight Calcd.	Molecular weight Found	Absorption spectrum in benzene: Absorption maxima, mμ (molar extinction coefficients)
Methyl	Cl	P	...	530	579[b]	830 (159), 475 (460), 375 (490)
	Br	T	6.35	619	601[b]	865 (87), 515 (336), 403 (584)
	I	T	7.65	713	857[b]	915 (432), 550 (sh), 455 (2810), 390 (3380)
Ethyl	Cl	P	3.2	558	550,[b] 535[c]	860 (73), 495 (401), 380 (1335)
	Br	P	5.9	647	698,[b] 625[c]	880 (102), 548 (433), 409 (. . .)
	Br	T	6.8	647	706[b]	880 (130), 548 (475), 408 (. . .)
	I	T	7.5	741	745,[b] 730[c]	932 (329), 650 (sh), 450 (sh), 398 (4140)
n-Propyl	Cl	P	...	586	581[b]	860 (65), 500 (488), 382 (7235)
	Br	P	6.6	675	748[b]	880 (134), 550 (390) ...
	Br	T	6.6	675	676[b]	880 (124), 550 (351) ...
	I	T	6.95	769	731[b]	935 (398), 600–700 (sh), 450 (3340), 397 (4060)
Isopropyl	Cl	P	3.3	586	536[b]	855 (53.5), 527 (514), 387 (5220)
	Br	P	5.9	734[d]	768[b]	...
	Br	T	6.2	675	871[b]	890 (67.5), 566 (605), 415 (5910), 350–300 (sh)
	I	T	...	...		925 (195), 628 (628), 470 (2625), 412 (sh), 354 (5370)
	I	G	...	769	814[b]	931 (206), 625 (656), 465 (2828), 412 (sh), 348 (5533)
n-Butyl	Br	P	...	...		875 (140), 547 (392)[e] ...
s-Butyl	I	G	...	...		942 (99), 629 (501), 470 (1447), 408 (sh), 355 (5490)

[a] P = square-planar, T = tetrahedral, G = green isomer of unknown structure. [b,c] Ebullioscopic measurement in benzene (*b*) or chloroform (*c*). Value found by extrapolation to zero concentration. [d] Solid contains benzene of solvation. [e] The tetrahedral isomer has absorption maxima at 880 (117) and 550 (476) mμ [C. R. C. Coussmaker, M. H. Hutchinson, J. R. Mellor, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 2705 (1961)].

Diphenyl-*n*-propylphosphine.—With this ligand also, only the bromo complex was obtained in both isomeric forms. Fast precipitation from concentrated ethanolic solution gives dark green tetrahedral [$NiBr_2(P(n\text{-}C_3H_7)(C_6H_5)_2)_2$] while, if the reaction mixture is sufficiently dilute to prevent immediate precipitation, the red square-planar isomer is formed by slow crystallization. Solutions of intermediate concentrations, which initially precipitate some of the tetrahedral isomer, also yield the square-planar form on longer standing or cooling. The planar isomer thus appears to be thermodynamically more stable than the tetrahedral isomer, although no isomerization was observed below the melting point of either form. Similar behavior was observed with nitromethane solutions, the tetrahedral isomer being obtained by rapid cooling (preferably with seeding) of the hot solution to about 0°, while the planar isomer crystallizes on allowing a solution of similar concentration to cool slowly to 0°. The planar isomer also crystallizes from methylene chloride–ether at 0°, from carbon disulfide at 0° (solvated with $0.25CS_2$), and from benzene–hexane at 0° (solvated with $0.5C_6H_6$).

From their X-ray powder patterns, the four planar complexes [$MX_2(P(n\text{-}C_3H_7)(C_6H_5)_2)_2$] (M = Ni, Pd; X = Cl, Br) are isomorphous. On the other hand, tetrahedral [$NiBr_2(P(n\text{-}C_3H_7)(C_6H_5)_2)_2$] is not isomorphous with the corresponding zinc compound.

Diphenylisopropylphosphine.—Square-planar [$NiBr_2(P(i\text{-}C_3H_7)(C_6H_5)_2)_2$] can be stored for long periods at 0°, but isomerization to the tetrahedral form occurs after about 1 day at 25°, the large brown crystals becoming coated with green solid. On heating, the complex melts over a wide range and, before melting is complete, green crystals (tetrahedral isomer?) form in the melt at about 120°. Partial isomerization probably accounts for the slight paramagnetism found in the solid planar isomer, which was isomorphous with [$PdBr_2(P(i\text{-}C_3H_7)(C_6H_5)_2)_2$] by X-ray powder pattern. Isomerization also occurs on contact with Nujol and the solid-state spectrum could therefore not be measured by the transmission method.[9]

The iodo complex, [$NiI_2(P(i\text{-}C_3H_7)(C_6H_5)_2)_2$], also crystallizes in two isomeric forms. The observed magnetic moment (2.82 B.M.) of the tetrahedral isomer is lower than usually found, probably due to contamination with the green diamagnetic isomer (or possibly to formation of an interallogon compound[4]). The solid-state spectrum is also consistent with a tetrahedral structure and shows absorption near 900 mμ (Figure 2).

The dark green form appears to be the more stable, since it is formed by slow crystallization from ethanol, acetic acid, nitromethane (as a monosolvate), and toluene–hexane. In the solid state, the complex is

(9) G. Maki, *J. Chem. Phys.*, **29**, 162 (1958).

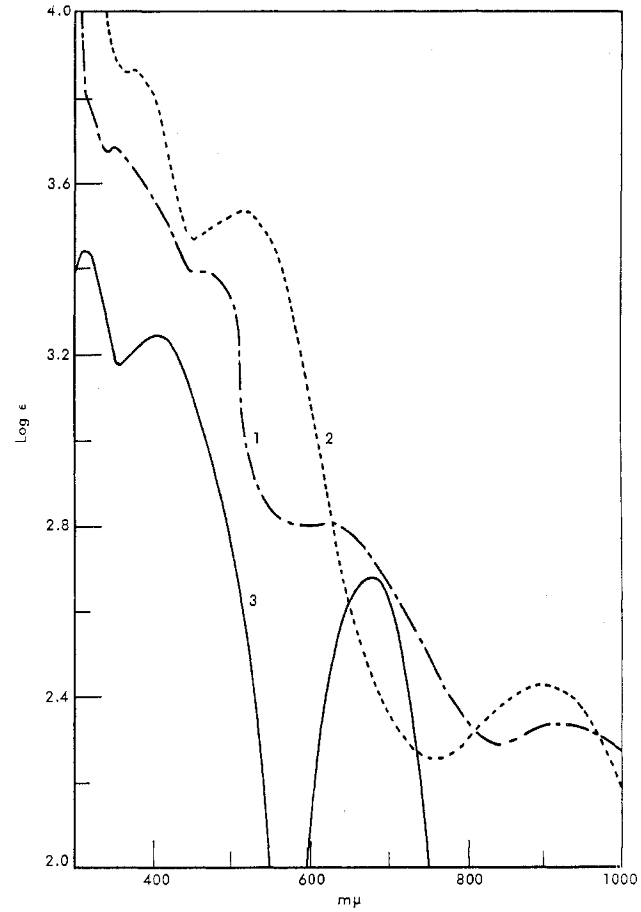

Figure 2.—Absorption spectra of $[NiI_2(P(i\text{-}C_3H_7)(C_6H_5)_2)_2]$: 1, benzene solution of either isomer; 2, solid tetrahedral isomer; 3, solid green isomer (the units of absorption for spectra 2 and 3 are arbitrary).

diamagnetic, but both its color and absorption spectrum differ from that expected for a *trans* square-planar complex, particularly in the presence of an absorption band at 676 mμ. Square-planar iodo complexes, for example, $[NiI_2(P(CH_2C_6H_5)(C_6H_5)_2)_2]$, are dark red or brown and do not absorb between 1000 and about 550 mμ.[3]

The two isomers have identical spectra in benzene solution and absorption bands due to both the tetrahedral isomer (925 mμ) and to the diamagnetic isomer (628 mμ) are visible (Figure 2). The extinction coefficient of the 925 mμ band (ϵ_{max} ~200) is smaller than the values usually found for iodo complexes (300–400). This is probably due to dilution of the tetrahedral isomer by the diamagnetic one, rather than to an intrinsically smaller extinction coefficient. Solutions of $[NiI_2(P(i\text{-}C_3H_7)(C_6H_5)_2)_2]$ are also unusual in showing marked thermochroism; toluene or methylene chloride solutions are dark brown when hot, take on a greenish cast at room temperature, and become intense green at −78°. The structure of the stable, dark green diamagnetic form of $[NiI_2(P(i\text{-}C_3H_7)(C_6H_5)_2)_2]$ is at present unknown, since both the more familiar types of tetrahedral and *trans* square-planar structures appear to be excluded. The molecular weight data and solubility characteristics of the complex indicate a monomeric, nonionic complex. Unfortunately, meaningful conductance measurements on this or any other nickel halide complex with a tertiary phosphine could not be obtained owing to extensive dissociation in dilute solutions in ionizing solvents to give free ligand and solvated nickel halide. A *cis* square-planar structure would be consistent with the data so far available, but a more positive structure determination may have to await an X-ray crystal structure investigation.

Diphenyl-*n*-butylphosphine.—The complexes of this ligand were first investigated by Coussmaker, *et al.*,[10] who isolated the three halide complexes in tetrahedral form by crystallization from nitromethane. We have confirmed their observations and also have obtained the square-planar forms of the chloro and bromo complexes by low-temperature crystallization from toluene–hexane. The red chloro complex is unstable, rapidly isomerizing to the blue-purple tetrahedral form in a few minutes at room temperature. The isomerization occurs more rapidly when the complex is slightly moist with solvent or Nujol. The complex was dried by pumping at 0° and could be stored at −78°, but, because of its thermal sensitivity, no measurements were made on the solid. Our assignment of structure is thus based on color, analysis for nickel, and isomerization to the known tetrahedral isomer, which was identified by its solid-state spectrum. The square-planar bromo isomer does not isomerize below its melting point.

Diphenyl-*t*-butylphosphine.—This ligand does not react with ethanolic nickel halides and, in this respect, resembles the triarylphosphines rather than the other diphenylalkylphosphines. Tetrahedral bromo and iodo complexes, however, were obtained by reaction between the ligand and anhydrous nickel halides in boiling benzene. Anhydrous nickel chloride does not react under these conditions, and no evidence for planar isomers of the bromo and iodo complexes was found.

Diphenyl-*n*-amylphosphine.—Both isomeric forms of $[NiCl_2(P(n\text{-}C_5H_{11})(C_6H_5)_2)_2]$ are stable at 25° and no isomerization was observed below the melting points.

Discussion

In a series of papers, Venanzi, Sutton, and their coworkers[11] have demonstrated that, in complexes of the type $[NiX_2L_2]$ (X = Cl, Br, I; L = tertiary phosphine), there is a change in structure from square-planar to tetrahedral as alkyl groups in the tertiary phosphine are successively replaced by phenyl. Thus, the trialkyl- and phenyldialkylphosphine complexes are planar, the triphenylphosphine complexes are tetrahedral, and the diphenylalkylphosphine complexes may be of either type. Our study shows that, in general, the change in structure occurs at $[NiBr_2(PR(C_6H_5)_2)_2]$. Thus, whereas the bromo complexes can often be obtained in both isomeric forms, the chloro complexes, on the one hand, are usually planar, and the iodo complexes, on the other hand, are tetrahedral. The behavior of the nickel halide complexes of diphenylallylphosphine is similar and only the bromo complex has

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[10] C. R. C. Coussmaker, M. H. Hutchinson, J. R. Mellor, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 2705 (1961).

[11] Reference 3 and earlier papers in the series.

been isolated in both forms.[3] Diphenylbenzylphosphine, however, is an exception among ligands of the type $(C_6H_5)_2PR$ in that all three pairs of isomeric halide complexes have been isolated and it is particularly suprising that the planar chloro complex isomerizes on heating, while the iodo complex is more stable in the planar form.[3] Among these complexes, where the factors which determine structural type are finely balanced, it is evident that small changes may favor one isomer over the other. However, taking the broad view over the large number of related complexes which have been studied, a number of consistent factors do emerge. These may be conveniently subdivided into ligand and solubility effects.

The Effect of Ligands on Isomer Formation.—It has previously been suggested that effects which weaken the ligand field around the metal atom will tend to favor the paramagnetic (tetrahedral) form relative to the diamagnetic (square-planar) form.[11] This suggestion is consistent with the behavior of both the neutral phosphine and the anionic halide ligands. Thus, the tetrahedral structure is *increasingly* favored in the orders $P(C_2H_5)_3 < P(C_2H_5)_2C_6H_5 < PC_2H_5(C_6H_5)_2 < P(C_6H_5)_3$ and SCN < Cl < Br < I, in each case as the crystal field strength of the ligand *decreases.* The effect of the halide ligands has been studied in solution[11] (by means of magnetic susceptibility measurements), and, in the present series, a similar trend is shown by the isolated solid complexes, presumably due to a similar cause. Undoubtedly, crystal packing and solubility effects are also important and may account for some apparent anomalies, for example, the unusually low stability of the planar $[NiCl_2(P(n\text{-}C_4H_9)(C_6H_5)_2)_2]$ isomer.

The effect of the alkyl group in the diphenylalkylphosphine is small compared with that of, say, the halide ligands. However, it may be significant that, as R increases in length from methyl to *n*-amyl, corresponding ligand field absorption bands, in particular the $^3T_{1g}(F) \rightarrow {}^3A_{2g}$ band due to the tetrahedral species in the 800–1000 mμ region, tend to move to longer wave length, suggesting a weakening ligand field. It is possible that the more frequent isolation of the tetrahedral isomer as R increases in length, particularly among the chloro complexes, is due to this effect, although the existence of trends based mainly on the isolation of solid complexes must be treated with caution.

The Effect of Solubility on Isomer Formation.—From an experimental point of view, it was found that the square-planar isomers were more readily obtained from nonpolar solvents and at low temperatures. The effect of temperature is particularly important and had not previously been used to isolate the less stable isomers. Indeed, a number of the planar isomers, although stable in the solid state at room temperature, could only be isolated by crystallization at −78°. This effect is probably mainly one of relative solubility, although it may also be that the amount of the planar isomer at equilibrium increases with decrease in temperature. The effect of solvent appears to be that the more polar solvents favor the more polar (tetrahedral) isomer and we have found that $[NiBr_2(P(C_2H_5)(C_6H_5)_2)_2]$ has a magnetic moment of 2.5–2.6 B.M. in chloroform solution ($7.4\text{–}31.5 \times 10^{-3}$ *M*) and 1.4 B.M. in benzene solution (1.4×10^{-3} *M*) in agreement with these views.

Isomerism of $[NiI_2(PR(C_6H_5)_2)_2]$ (R = Isopropyl, *s*-Butyl).—It is interesting to note that the unusual isomerism of the iodo complexes has been observed only when the alkyl group in the phosphine ligand is branched at the α carbon atom. It had been expected that diphenyl-*t*-butylphosphine would behave similarly, but only a tetrahedral iodo complex has been isolated. In addition, solutions of this complex do not show the marked thermochroic effect characteristic of the iodo complexes of the isopropyl and *s*-butyl ligands.

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Coordination of Thiocyanate and Selenocyanate in Some Diamine Complexes of Nickel(II) and Copper(II)

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Compounds of the type $Ni(AA)_2X_2$, $Ni(AA)_3X_2$, $Cu(AA)X_2$, and $Cu(AA)_2X_2$, where AA is 1,2-diaminoethane (ethylenediamine) or its C- or N-substituted derivatives and X is thiocyanate or selenocyanate, have been prepared and characterized. The infrared absorption bands due to the thiocyanate and selenocyanate groups are reported and discussed in terms of the structures of the complexes.

Two recent crystal structures of nickel(II)[2a] and copper(II)[2b] bis(ethylenediamine) thiocyanates have shown important differences between the two compounds. The nickel complex is essentially octahedral with *trans* isothiocyanato groups bound to the nickel by

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[2] (a) B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, **16**, 753 (1963); (b) B. W. Brown and E. C. Lingafelter, *ibid.*, **17**, 253 (1964).