shifted to lower frequencies; this is well illustrated by complexes of (ethylenedinitrilo)-tetraacetic acid, which show only a band at ~1650 cm.$^{-1}$ if all the carboxyl groups are coordinated to cobalt, and also have a band at ~1750 cm.$^{-1}$ if one or more carboxyl groups are not bound.[15] Propionic acid has a band at 1725–1730 cm.$^{-1}$ [16] and tris-(3-mercaptopropionato)-cobalt-(III) a band at 1710 cm.$^{-1}$; this indicates no coordination between the carboxyl group and the cobalt ion. The potassium salt, $K_3[Co(SCH_2CH_2COO]$, has a strong band at 1575 cm.$^{-1}$, in the same range as ionic carboxylate salts, *i.e.*, again there is no indication of coordination. The infrared spectrum of triscysteinatocobalt(III) is rather complex and no analysis of it was attempted.

[15] F. A. Cotton, in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., pp. 387–390.

[16] P. J. Corish and D. Chapman, *J. Chem. Soc.*, 1746 (1957).

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Transition Metal Complexes of Secondary Phosphines. III.[1] Four- and Five-Coordinate Complexes of Nickel(II) Halides with Diphenylphosphine

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The reactions of diphenylphosphine with nickel halides in nonionizing solvents have yielded *trans*-$[NiI_2(HP(C_6H_5)_2)_2]$ and the five-coordinate complexes $[NiI_2(HP(C_6H_5)_2)_3]$ (X = Cl, Br, I). The properties and structures of the complexes have been investigated and are discussed.

Introduction

It has previously been reported that diphenylphosphine reacts with ethanolic nickel bromide to give the yellow diamagnetic complex $[Ni(P(C_6H_5)_2)_2(HP(C_6H_5)_2)_2]$[2] according to eq. 1.

$$NiBr_2 + 4(C_6H_5)_2PH = [Ni(P(C_6H_5)_2)_2(HP(C_6H_5)_2)_2] + 2HBr \quad (1)$$

We have found from our investigation of the reactions of diphenylphosphine with palladium halides that the nature of the complex obtained is influenced both by the solvent and by the particular halide used.[3] In particular, polar solvents such as ethanol favored acid elimination and the formation of phosphido complexes as in (1), whereas reactions in benzene were found to give complexes of the type $[PdX_2(HP(C_6H_5)_2)_n]$ (n = 2, 3). It was therefore of interest to study the effect of solvent on the reactions of nickel halides with diphenylphosphine. It was also anticipated that a study of the properties of the complexes $[NiX_2(HP(C_6H_5)_2)_2]$ (if capable of existence) would yield further information about the factors which affect the structure of nickel(II) complexes.[4]

Experimental

Microanalyses, molecular weights, dipole moments, and conductivity measurements and the preparation of diphenylphosphine were carried out as described in parts I[3] and II[1] of this series. The absorption spectra were measured with a Cary Model 14 spectrophotometer, using the method developed by Shibata and described by Maki[5] for the solid state measurements.

The magnetic susceptibilities of the finely powdered solids were measured at room temperature by the Faraday method on a sensitive magnetobalance, which had been calibrated using a platinum standard of high purity.

Anhydrous nickel bromide and iodide were obtained from City Chemical Corporation, New York, N. Y. "Anhydrous" nickel chloride was prepared from the hexahydrate (J. T. Baker Chemical Company) by drying under vacuum at 100°; on the basis of hydrogen analysis the formula suggested for the light brown solid thus produced is $NiCl_2 \cdot H_2O$. *Anal.* Calcd. for $NiCl_2 \cdot H_2O$: H, 1.4. Found: H, 1.1.

Preparation of the Complexes.—All preparations were carried out under nitrogen. The anhydrous nickel halides dissolve slowly in refluxing benzene, toluene, or dichloromethane solutions of diphenylphosphine (two moles for $[NiI_2(HP(C_6H_5)_2)_2]$, four moles for the remaining complexes) to give intensely colored solutions. After removal of residual nickel halide by filtration, the complexes either crystallized on standing or on addition of ether or n-hexane. The reaction times, yields, solvent systems, and analytical data are given in Table I and the physical properties of the complexes in Table II. A typical reaction procedure is described below.

Anhydrous nickel bromide (0.505 g., 2.31 mmoles) and diphenylphosphine (1.72 g., 9.23 mmoles) were refluxed together in dichloromethane (50 ml.) for 2 hr. to give a dark brown solution. After filtration through a fine sintered glass disk, the solution was diluted with ether (75 ml.) and cooled to give dark brown needles of $[NiBr_2(HP(C_6H_5)_2)_3]$.

In the reaction of $NiCl_2$ with diphenylphosphine, pure $[NiCl_2(HP(C_6H_5)_2)_3]$ crystallized first and was filtered off. On longer standing, a further crop of the dark brown chloro complex was obtained along with large yellow crystals. Attempted separation by fractional crystallization from benzene resulted in the decomposition of $[NiCl_2(HP(C_6H_5)_2)_3]$ and the resulting orange-red solution deposited yellow rods (20% yield, m.p. 168–175°

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[1] Part II: R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, **2**, 306 (1963).

[2] K. Issleib and E. Wenschuh, *Z. anorg. allgem. Chem.*, **305**, 15 (1960).

[3] R. G. Hayter, *J. Am. Chem. Soc.*, **84**, 3046 (1962).

[4] (a) 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), and references therein; (b) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961), and references therein; (c) R. G. Hayter and F. S. Humiec, *ibid.*, **84**, 2004 (1962).

[5] G. Maki, *J. Chem. Phys.*, **29**, 162 (1958).

TABLE I

ANALYTICAL AND PREPARATION DATA FOR THE COMPLEXES $[NiX_2(HP(C_6H_5)_2)_n]$ ($n = 2, 3$)

Compound	Reaction time, hr.	Yield,[a] %	Solvent	% Carbon Calcd.	% Carbon Found	% Hydrogen Calcd.	% Hydrogen Found	% Halogen Calcd.	% Halogen Found	% Phosphorus Calcd.	% Phosphorus Found	% Nickel Calcd.	% Nickel Found
$[NiI_2(HP(C_6H_5)_2)_2]$	3	34	CH_2Cl_2[b]	42.1	42.2	3.2	3.25	37.1	36.8	9.0	9.0	8.6	8.7
$[NiI_2(HP(C_6H_5)_2)_3]$	2	71	C_6H_6[c]	49.6	49.8	3.8	3.8	29.1	29.5	10.7	10.8	6.7	7.2
$[NiBr_2(HP(C_6H_5)_2)_3]$	2	65	CH_2Cl_2[b]	55.6	55.3	4.3	4.7	20.6	20.1	12.0	11.4	7.55	7.4
$[NiBr_2(HP(C_6H_5)_2)_3]\cdot 0.5C_6H_6$[d]	6	74	C_6H_6	57.4	57.5	4.45	4.4	19.6	19.9	11.4	11.1	7.2	7.2
$[NiCl_2(HP(C_6H_5)_2)_3]\cdot 0.5C_6H_6$	19	35	C_6H_6	64.3	64.2	4.95	5.3	9.75	9.3	12.8	12.8	8.1	7.5

[a] Based on nickel halide. [b,c] Complex crystallized on the addition of (*b*) ether or (*c*) *n*-hexane. [d] After drying under vacuum at 80° for 8 hr., about half of the solvate benzene is lost. A similarly solvated complex was also obtained from toluene solution. *Anal.* Calcd. for $C_{36}H_{33}Br_2NiP_3\cdot 0.5$toluene: C, 57.6; H, 4.6; Br, 19.4; P, 11.3. Found: C, 57.7; H, 4.7; Br, 19.6; P, 11.6.

TABLE II

PROPERTIES OF $[NiX_2(HP(C_6H_5)_2)_n]$ ($n = 2, 3$)

Compound	M.p. (dec.)	Color	$10^6\chi_M$ (uncorr.)	Molecular weight Calcd.	Molecular weight Found	Molecular weight Solvent
$[NiI_2(HP(C_6H_5)_2)_2]$[a]	170[b]	Brown	−295	685	606[c]	CH_2Br_2
					671[d]	C_6H_6
$[NiI_2(HP(C_6H_5)_2)_3]$	115	Dark blue	+462[e]	871	525[d]	C_6H_6
$[NiBr_2(HP(C_6H_5)_2)_3]$	95	Dark brown	−389	777	395[c]	CH_2Br_2
					480[c]	C_6H_6
$[NiCl_2(HP(C_6H_5)_2)_3]\cdot 0.5C_6H_6$	98	Dark brown	−240		...	

[a] This compound has a dipole moment of 3.8 D. (see Table III). [b] Decomposed below m.p. [c] Isopiestic measurement. [d] Ebullioscopic measurement, value obtained by extrapolation to zero concentration. [e] $10^6\chi_M$ (corr.) = +900, μ_{eff} = 1.48 B.M. (the diamagnetic correction was calculated using Pascal's constants obtained from P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., 1956, p. 91).

TABLE III

DIPOLE MOMENT OF $[NiI_2(HP(C_6H_5)_2)_2]$ IN BENZENE SOLUTION[a]

$\epsilon_{12} = 2.267 + 2.577\omega_2$ $P_T = 440.2$ cc.
$n_{12} = 1.4976 + 0.1052\omega_2$ ω_2 0–60 × 10^{-4} $R_D = 146.8$ cc.
$V_{12} = 1.1461 - 0.6203\omega_2$ $P_O = 293.4$ cc.
$\mu = 3.8$ D.

[a] For notation and details of measurement see ref. 1.

dec.), which were identical with $[Ni(P(C_6H_5)_2)_2(HP(C_6H_5)_2)_2]$ as prepared by the method of Issleib and Wenschuh.[2]

Anal. Calcd. for $C_{48}H_{42}NiP_4$: C, 71.9; H, 5.3; P, 15.5. Found: C, 72.3; H, 5.4; P, 15.1.

Results

Initial experiments confirmed the formation of $[Ni(P(C_6H_5)_2)_2(HP(C_6H_5)_2)_2]$ in ethanol as reported previously by Issleib and Wenschuh.[2] This complex was also obtained from the reactions of nickel halides, thiocyanate, and nitrate with diphenylphosphine in ethanol, 1-butanol, or acetic acid. In most cases, a transient red coloration, rapidly fading to yellow, was initially observed. No evidence was found for any intermediate complex, analogous to the phosphorus-bridged dimers $[PdX(P(C_6H_5)_2)(HP(C_6H_5)_2)]_2$.[3]

In hydrocarbon solvents, such as benzene and toluene, or in methylene chloride, however, anhydrous nickel halides react with diphenylphosphine even at room temperature to give intensely colored solutions of the halide complexes $[NiX_2(HP(C_6H_5)_2)_n]$ ($n = 2, 3$; see Table I). Partial elimination of acid occurred only in the case of $NiCl_2$ and then more extensively in methylene chloride than in benzene, a mixture of $[NiCl_2(HP(C_6H_5)_2)_3]$ and $[Ni(P(C_6H_5)_2)_2(HP(C_6H_5)_2)_2]$ being obtained in each case. Nickel bromide and iodide also gave complexes of the type $[NiX_2(HP(C_6H_5)_2)_3]$, but only the iodide gave in addition a four-coordinate complex, $[NiI_2(HP(C_6H_5)_2)_2]$. In the absence of excess phosphine, benzene solutions of the bromo and chloro complexes rapidly deposit nickel halide and show no evidence for the existence of stable four-coordinate complexes.

Structure of the Complexes.—$[NiI_2(HP(C_6H_5)_2)_2]$ is diamagnetic in the solid state, a nonelectrolyte in nitrobenzene solution, monomeric in benzene, and has a dipole moment of 3.8 D. Since a *trans* compound would have a zero dipole moment and a *cis* compound one in the range 8–11 D.,[6] $[NiI_2(HP(C_6H_5)_2)_2]$ apparently is present in benzene solution in both isomeric forms, with the *trans* form predominating. The absorption spectrum of $[NiI_2(HP(C_6H_5)_2)_2]$ in benzene solution and in the solid state (Table IV and Fig. 1) is consistent with a square-planar structure. In particular, $[NiI_2(HP(C_6H_5)_2)_2]$ shows no absorption band near 900 mμ (ϵ_{max} 300–400) similar to that present in tetrahedral iodides of the type $[NiI_2(PR(C_6H_5)_2)_2]$ (R = alkyl, C_6H_5).[4a]

The properties of the complexes $[NiX_2(HP(C_6H_5)_2)_3]$ (X = Cl, Br, I) are consistent with the analytical evidence, which suggests the presence of five-coordinate nickel(II) at least in the crystal. The solid bromo and chloro complexes are essentially diamagnetic, as are the complexes $[NiX_2(triarsine)]$[7] and $[NiX(diarsine)_2][ClO_4]$,[8] which are known to contain five-coordinate nickel(II). In contrast, $[NiI_2(HP(C_6H_5)_2)_3]$ has an unexpectedly large paramagnetic susceptibility, corresponding to μ_{eff} = 1.48 B.M. Since the susceptibility showed no dependence on field strength it

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(6) R. G. Wilkins and M. J. G. Williams, in J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., p. 174.

(7) G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 4433 (1961); G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1960).

(8) C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960).

TABLE IV

ABSORPTION SPECTRA OF $[NiX_2(HP(C_6H_5)_2)_n]$ AND $[NiX_2(triarsine)]$

Compound	Conditions	λ_{max}, mμ (extinction coefficients for solutions)
$[NiI_2(HP(C_6H_5)_2)_2]$	Benzene soln.	800 (37, sh), 550 (490, sh), 460 (2340), 380 (4840)
$[NiI_2(HP(C_6H_5)_2)_2]$	Solid	650–550 (sh), 465, 350–410 (sh), 337, 321
$[NiI_2(HP(C_6H_5)_2)_3]$	Benzene soln.	812 (315), 595 (907), 462 (1790), 375 (4700)
$[NiI_2(HP(C_6H_5)_2)_3]$	1.0×10^{-3} *M* soln. in benzene containing 6×10^{-4} *M* $(C_6H_5)_2PH$	807 (855), 603 (1780), 500 (1220), 380 (4150, sh)
$[NiI_2(HP(C_6H_5)_2)_3]$	Solid	800, 650–550 (sh), 503, 460–350 (sh)
$[NiBr_2(HP(C_6H_5)_2)_3]$	0.885×10^{-3} *M* soln. in benzene containing 0.1 *M* $(C_6H_5)_2PH$	785 (526), 556 (607), 400 (5320)
$[NiBr_2(HP(C_6H_5)_2)_3]$	Solid	700–800 (sh), 465, 300–50 (sh)
$[NiI_2(triarsine)]$[a]	Solution	780 (900), 620 (1300), 500 (1000), 400 (2200)
$[NiBr_2(triarsine)]$[a]	Solution	700–800 (500), 560 (800), 480 (950), 400 (1400)

[a] Data taken from ref. 4.

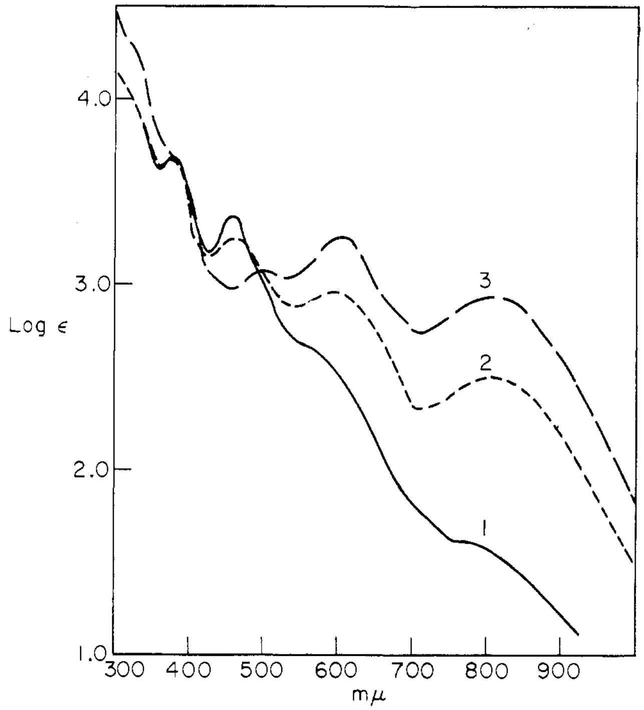

Fig. 1.—Absorption spectra of $[NiI_2(HP(C_6H_5)_2)_n]$ ($n = 2, 3$) in benzene: 1, $[NiI_2(HP(C_6H_5)_2)_2]$; 2, $[NiI_2(HP(C_6H_5)_2)_3]$; 3, $[NiI_2(HP(C_6H_5)_2)_3]$ (10^{-3} *M* solution containing 6×10^{-4} *M* $(C_6H_5)_2PH$).

cannot be attributed to a ferromagnetic impurity such as nickel metal, and its origin is, at present, unknown. Molecular weight measurements indicate that the bromo and iodo complexes are extensively dissociated in solution, while solutions of $[NiCl_2(HP(C_6H_5)_2)_3]$ decompose too rapidly to be studied. All three complexes give nonconducting solutions in nitrobenzene and decompose rapidly in nitromethane.

The absorption spectra of the complexes in the region 300–1000 mμ were measured under a variety of conditions and the data are summarized and compared with the spectra of $[NiX_2(triarsine)]$ (X = Br, I)[7] in Table IV. The spectrum of $[NiI_2(HP(C_6H_5)_2)_3]$ was measured both in pure benzene solution and in the presence of about a 0.6-mole excess of diphenylphosphine (Fig. 1). No further change in spectrum was observed up to a 30-mole excess of phosphine, showing that 0.6 mole is sufficient to completely repress dissociation and that there is no apparent tendency under these conditions take up a fourth phosphine ligand. The solid state spectrum of $[NiI_2(HP(C_6H_5)_2)_3]$ is very similar to that found in the presence of excess ligand, showing that the solid complex and that present in the phosphine-containing solutions are identical.

These spectra also indicate that $[NiI_2(HP(C_6H_5)_2)_3]$ dissociates in solution and are thus consistent with the molecular weight data.

The lowest energy band resolved in $[NiI_2(HP(C_6H_5)_2)_2]$ at 460 mμ coincides with a band in the spectrum of $[NiI_2(HP(C_6H_5)_2)_3]$ in pure benzene. The latter band disappears on addition of excess phosphine and is replaced by a weaker band at 500 mμ. The 460 mμ band thus probably is due to $[NiI_2(HP(C_6H_5)_2)_2]$ arising from dissociation (eq. 2) while the new band closely

$$[NiI_2(HP(C_6H_5)_2)_3] \rightleftharpoons [NiI_2(HP(C_6H_5)_2)_2] + (C_6H_5)_2PH \qquad (2)$$

corresponds to the 503 mμ band in the spectrum of solid $[NiI_2(HP(C_6H_5)_2)_3]$ and is probably characteristic of the tris-phosphine complex. In contrast, the bands at 812 and 595 mμ in the spectrum of $[NiI_2(HP(C_6H_5)_2)_3]$ both increase in extinction coefficient in the presence of excess phosphine and do not shift position appreciably. This behavior is expected on the basis of the proposed dissociation, since the absorption due to $[NiI_2(HP(C_6H_5)_2)_2]$ is relatively weak in the range 550–1000 mμ.

The solution spectrum of $[NiBr_2(HP(C_6H_5)_2)_3]$ shows similar changes in the presence of excess ligand, but a much larger excess of diphenylphosphine (*ca.* 100 moles) is needed in this case to repress dissociation. The spectra of undissociated $[NiX_2(HP(C_6H_5)_2)_3]$ (X = Br, I) are, respectively, very similar to those of $[NiX_2(triarsine)]$ (X = Br, I),[7] and both series of complexes probably have similar structures based on square-pyramidal nickel(II).

Discussion

Four-Coordinate Complexes.—The nickel iodide complexes of diphenylalkyl phosphines are usually tetrahedral in structure and certainly all the known member complexes of this type can be isolated in a tetrahedral form.[4] It is thus surprising that the closely related complex, $[NiI_2(HP(C_6H_5)_2)_2]$, is square-planar and no evidence was found for a tetrahedral form even in solution. A comparison of the solution spectrum of $[NiI_2(HP(C_6H_5)_2)_2]$ with that of the square-planar complex $[NiI_2(P((n\text{-}C_4H_9)_2(C_6H_5))_2]$[4a] shows that they are very similar but that the lowest energy absorption band (probably a ligand field band) occurs at slightly higher energy in the diphenylphosphine complex. The ligand field strength of diphenylphosphine is therefore slightly greater than that of $(C_6H_5)(n\text{-}C_4H_9)_2P$ and certainly greater than that of $(C_6H_5)_2(n\text{-}C_4H_9)P$ and $(C_6H_5)_3P$.[4a] The square-planar structure of the four-coordinated diphenylphosphine complex can thus be rationalized, since strong field ligands tend to form spin-paired complexes.

Five-Coordinate Complexes.—Before the present work, only two examples of five-coordinate nickel(II) complexes with monodentate ligands were known, $[Ni(CN)_5]^{3-}$,[9] which is found only in solution and is the subject of some uncertainty,[10,10a] and $[Ni(C{\equiv}CC_6H_5)_2(P(C_2H_5)_2(C_6H_5))_3]$.[11] These compounds and the three of this type reported in this paper are all dissociated in solution, usually into four-coordinate species. If polydentate ligands are used, the five-coordinate nickel complexes are more stable with respect to dissociation and similar complexes can be obtained, in some cases, with palladium and platinum also.[12,13]

The conditions which favor the formation of five-coordinate d^8 complexes have been summarized by Nyholm,[12] and the known five-coordinate monodentate-ligand complexes fit into his scheme. They all contain ligands of relatively low electronegativity; the stability of the diphenylphosphine complexes decreases, I > Br > Cl, with increase in the electronegativity of the anionic ligands, and the corresponding complexes of palladium and platinum are unknown or have a different structure.[3] In view of these findings, it is perhaps surprising that so few five-coordinate complexes of nickel(II) derived from substituted phosphines have previously been reported, although this may be due both to the use of unsuitable experimental conditions and to the probable extensive dissociation of such complexes. Undoubtedly the use of polydentate phosphines will yield complexes of this type, as the polydentate arsines have already.

We attempted to prepare five-coordinate complexes by reaction between diphenylmethylphosphine and anhydrous nickel halides in benzene or methylene chloride. $(C_6H_5)_2(CH_3)P$ is expected to be less electronegative than $(C_6H_5)_2PH$ and hence should favor five-coordination, although this tendency may be overcome by its greater steric requirements. Also, we have observed previously that $(C_6H_5)_2PH$ and $(C_6H_5)_2(CH_3)P$ behave similarly toward palladium bromide, both giving tris-phosphine complexes of the type $[PdBr(PR(C_6H_5)_2)_3]Br$ (R = H, CH_3).[3] However, with nickel halides, $(C_6H_5)_2(CH_3)P$ gave only $[NiX_2(P(CH_3)(C_6H_5)_2)_2]$ even in the presence of a large excess of ligand. It thus appears that quite small changes in the steric or electronic properties of the ligand are sufficient to favor markedly one structure over another. Molecular models, for instance, show that $[NiCl_2(PR(C_6H_5)_2)_2]$ (R = CH_3, C_6H_5) cannot attach a third phosphine at one of the octahedral sites, although when R = H this can easily be achieved. Diphenylphosphine thus may be a particularly suitable ligand for the preparation of five-coordinate nickel(II) complexes, owing to a favorable combination of steric and electronic factors. It has also been used to prepare a five-coordinate cobalt(II) complex.[2]

Acknowledgments.—The author is indebted to Dr. L. Vaska for the measurement of the magnetic moments and to Mr. F. S. Kumiec for the measurement of absorption spectra and other assistance.

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[9] B. S. Morris and R. S. Nyholm, quoted in *Chem. Rev.*, **53**, 263 (1953); R. L. McCullough, L. H. Jones, and R. A. Penneman, *J. Inorg. Nucl. Chem.*, **13**, 286 (1960).

[10] W. P. Griffith, *Quart. Rev.* (London), **16**, 188 (1962).

[10a] NOTE ADDED IN PROOF.—A recent paper has presented additional evidence in favor of $[Ni(CN)_5]^-$, although, in aqueous solution, the complex may exist as $[Ni(CN)_5H_2O]^-$ (R. A. Penneman, R. Bain, G. Gilbert, L. H. Jones, R. S. Nyholm, and G. K. N. Reddy, *J. Chem. Soc.*, 2266 (1963)).

[11] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

[12] R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961).

[13] G. A. Mair, H. M. Powell, and L. M. Venanzi, *ibid.*, 170 (1961); C. A. Savage and L. M. Venanzi, *J. Chem. Soc.*, 1548 (1962).