generally accepted assignment of the ground state to a nondegenerate $\Gamma_1$ wave function.[2] The $\Gamma_i$ designations pertain to the representations of the total wave function containing both the spin and the orbital parts ($\Gamma_1 = a_{1g}$). In the two-hole formalism for the $d^8$ configuration the major component of the ground state is $^1(b_{1g}{}^*)^2 = {}^1A_{1g}$. (The $x$ and $y$ axes have been chosen to pass through the ligands.) On the basis of low-temperature polarized spectra of single crystals the peak at 30,300 $cm^{-1}$ in solution was attributed to transitions to degenerate $\Gamma_5$ states ($\Gamma_5 = e_g$) whose principal components were $^1(b_{1g}{}^*e_g)^1E_g$ states. The MCD, which indicates a Zeeman splitting of excited states, therefore strongly supports this assignment since transitions to nondegenerate states would be incapable of such Zeeman splitting. The value of $\delta_m$ of 0.45 corresponds to an effective magnetic moment of 0.8 BM. For the $(b_{1g}{}^*e_g)^1E_g$ state the magnetic moment is just the magnitude of the off-diagonal angular momentum matrix element $\langle\psi_a L \psi_b\rangle$ (where $\psi_a$, $\psi_b$ are the degenerate wave functions[6]) which is 1 BM. The MCD corresponds, therefore, in order of magnitude with the expected splitting of the degenerate $^1E_g$ states.

Although weaker $\Gamma_5$ transitions are predicted to lie at lower energies, calculated at 21,100 and 18,700 $cm^{-1}$ for the crystalline $K_2PtCl_4$ together with several close lying transitions to nondegenerate states, it has not been possible to observe an appreciable MCD in these regions with the present equipment as has been indicated in Figure 1.

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[6] R. F. Fenske, D. S. Martin, Jr., and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962).

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# Chloroform Solvates of Tetrapyridinenickel(II) Perchlorate and Tetrafluoroborate

BY MICHAEL R. ROSENTHAL[1] AND RUSSELL S. DRAGO

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In a previous study of pyridine complexes of nickel(II), the complexes $Ni(C_5H_5N)_4(ClO_4)_2$ and $Ni(C_5H_5N)_4(BF_4)_2$ were prepared and characterized as six-coordinate spin-free tetragonal complexes.[2] In this article we report a novel chemical reaction that these materials undergo. When these complexes are suspended in acidic solvents, solvent molecules are taken up by the solid and a stereochemical change occurs to produce a four-coordinate, spin-paired nickel(II) cation. This reaction occurs apparently without dissolution of the complex.

### Experimental Section

The blue tetragonal complexes were prepared by previously reported syntheses.[2] Chloroform was shaken with calcium chloride, allowed to stand overnight, and distilled. Dichloromethane was used after being stored for 2 weeks over molecular sieves. Infrared Spectra were obtained with a Perkin-Elmer Model 521 recording spectrometer, equipped with a $N_2$ purge to exclude moisture. X-Ray diffraction powder patterns were obtained using a copper $K\alpha_1$ target ($\lambda$ 1.54050 A) and a powder camera with a rotating sample holder. Samples for analysis were weighed in closed "pigs," which were loaded in a dry atmosphere box to exclude moisture. The magnetic susceptibility was measured by the Gouy method.

*Anal.* Calcd for $Ni(C_5H_5N)_4(ClO_4)_2 \cdot CHCl_3$: C, 36.4; H, 3.03. Found: C, 35.0; H, 3.03. Calcd for $Ni(C_5H_5N)_4(BF_4)_2 \cdot CHCl_3$: C, 37.1; H, 3.12. Found: C, 37.3; H, 3.49.

These analyses can be compared to those obtained after the chloroform has been removed in a dry atmosphere. *Anal.* Calcd for $Ni(C_5H_5N)_4(ClO_4)_2$: C, 41.8; H, 3.48. Found: C, 41.8; H, 3.59. Calcd for $Ni(C_5H_5N)_4(BF_4)_2$: C, 43.7; H, 3.74. Found: C, 42.4; H, 3.94.

### Results and Discussion

The complexes $Ni(C_5H_5N)_4(ClO_4)_2$ and $Ni(C_5H_5N)_4(BF_4)_2$ have been reported and characterized[2] as having six-coordinate, tetragonal structures containing monodentate coordinated anions. The perchlorate complex is soluble in dichloromethane, and the solution has an electronic spectrum identical with that of the Nujol mull. However, when either of those complexes is suspended in chloroform or the tetrafluoroborate complex is suspended in dichloromethane, the complexes do not dissolve, but change in color from pale blue to yellow. This color change is rapid for the tetrafluoroborate complex in chloroform.[3] These yellow compounds are extremely hygroscopic, changing to blue almost immediately upon contact with moist air. When these yellow compounds are removed from their "solution" by filtration in a dry atmosphere box, they may be stored in a moisture-free environment several months before changing back to a pale blue color, but when placed under vacuum, away from moist air, they return to a blue color much more rapidly. This color change may be accomplished in the case of the methylene chloride solvate on a vacuum filter apparatus in the dry atmosphere box. For $Ni(C_5H_5N)_4(ClO_4)_2 \cdot CHCl_3$ 12 hr pumping in a vacuum desiccator is required, while 24 hr pumping in a vacuum desiccator is needed for $Ni(C_5H_5N)_4(BF_4) \cdot CHCl_3$. Once the yellow compounds have been converted back to the blue color in the absence of moisture, they are reactive to the solvent, whereas the blue compound formed in moist air is impervious to attack by the solvents.

Infrared spectra and X-ray powder patterns (Table I) indicate that the original compounds and the blue materials obtained from desolvation of yellow compounds under anhydrous conditions are identical. The yellow compounds show structured infrared bands indicating $C_{3v}$ coordinated anions. On the other hand, the blue compounds obtained from the yellow compounds through exposure to moist air analyze well for

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[1] Abstracted in part from the Ph.D. Thesis of M. R. Rosenthal, University of Illinois, Urbana, 1965.

[2] M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **4**, 840 (1965).

[3] Similar behavior is noted for a methylene chloride solvate of $Ni(C_5H_5N)_4(BF_4)_2$.

TABLE I

X-RAY DATA FOR $Ni(C_5H_5N)_4(ClO_4)_2$[a]

| $Ni(C_5H_5N)_4(ClO_4)_2$ $d_{hkl}$ | | Blue compound recovered from $Ni(C_5H_5N)_4(ClO_4)_2 \cdot CHCl_3$ $d_{hkl}$ | |
|---|---|---|---|
| 8.28 | | 8.33 | |
| 7.41 | doublet very intense | 7.47 | doublet very intense |
| 7.11 | | 7.04 | |
| 5.81 | | 5.74 | |
| 5.39 | | 5.32 | |
| 4.56 | | 4.52 | |
| 4.32 | | 4.36 | |
| 4.12 | very intense | 4.10 | very intense |
| 3.69 | | 3.71 | |
| 3.19 | | 3.18 | |
| 2.91 | | 2.92 | |

[a] Cu $K\alpha_1$ radiation ($\lambda$ 1.54050 A); 2.5-hr exposure time.

$Ni(C_5H_5N)_4(anion)_2 \cdot 2H_2O$ and their infrared spectra indicate coordinated water and Td anions. A broad absorption from 1040 to 1140 $cm^{-1}$ is observed in the case of the perchlorate, and a broad absorption from 960 to 1160 $cm^{-1}$ is found in the case of the tetrafluoroborate. Analyses of the compounds indicate the presence of one chloroform molecule, and infrared spectra of the compounds indicate that water is not present, that chloroform (or dichloromethane in the case of this solvate) is present, and that the anions are not coordinated.

It is postulated that the acidic solvent interacts forming a weak hydrogen bond with an oxygen of $ClO_4^-$ or fluorine of $BF_4^-$, removing the anion from the coordination sphere of the nickel(II) ion. This phenomenon occurs, it should be noted, without actual dissolution of the complex in the solvent. The yellow form obtained is the square-planar complex containing solvent and ionic anions.

Square-planar complexes of Ni(II) with several substituted pyridines have been reported and they are yellow in color.[4] The square-planar yellow complex, $Ni(C_5H_5N)_4{}^{2+}$, is highly susceptible to attack from water molecules, producing $Ni(C_5H_5N)_4(H_2O)_2{}^{2+}$.

A magnetic moment determined for $Ni(C_5H_5N)_4(BF_4)_2 \cdot CHCl_3$ indicates a marked reduction in its magnetic moment ($\mu_{eff} \sim 1$), relative to the fully paramagnetic blue compound ($\mu_{eff}$ 3.04). The low observed magnetism may be due to incomplete conversion of the solid to the diamagnetic form.

This appears to be the first reported case of a compound which undergoes stereochemical change due to "solvent" interaction in the solid state, resulting in a decrease in coordination number. The ability of these compounds to undergo such behavior is undoubtedly due to their highly tetragonal nature.[2]

**Acknowledgment.**—The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for its generous support of this research through Contract No. AT (11-1) 758.

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(4) L. E. Moore, R. B. Gayhart, and W. E. Bull, *J. Inorg. Nucl. Chem.*, **26**, 896 (1964); S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 671 (1964).

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## Chemistry of Decaborane–Phosphorus Compounds. VI. Phosphino-*m*-carboranes[1,2]

BY ROY P. ALEXANDER AND HANSJUERGEN SCHROEDER

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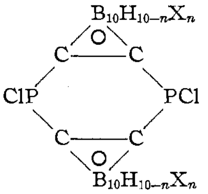
It was demonstrated in previous studies[1,3] that the dilithio salts of $o$-$B_{10}H_{10}C_2H_2$ and polyhalo-$o$-carboranes such as $o$-$B_{10}H_7Br_3C_2H_2$[1] and $o$-$B_{10}H_6Cl_4C_2H_2$[4] easily react with $PCl_3$ to form cyclic compounds containing a diphosphacyclohexane skeleton as illustrated below.

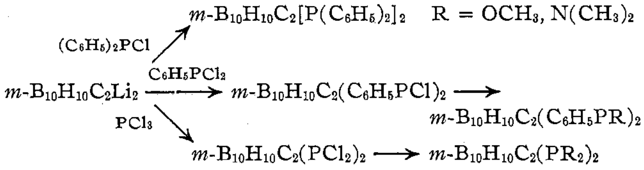


X = Br, Cl

$n$ = 0–4

The formation of noncyclic compounds such as $o$-$B_{10}H_{10}C_2(PCl_2)_2$, which was actually expected, could not be observed. In contrast to such behavior it was established in these laboratories that the reaction of $o$-$B_{10}H_{10}C_2Li_2$ with $SiCl_4$[5] and with substituted chlorophosphines[3] and chlorosilanes[5] affords exclusively noncyclic derivatives. The fact that these compounds could be converted into the respective six-membered diphospha- and disilacyclohexane ring compounds by reaction with $o$-$B_{10}H_{10}C_2Li_2$[1,5,6] is irrelevant to the unique type of reaction obtained with $PCl_3$.

In the $m$-carborane series, Papetti and Heying[7] recently showed that $m$-$B_{10}H_{10}C_2Li_2$ and $SiCl_4$ gave as expected noncyclic products. From the results in the $o$-carborane series mentioned above, the possibility that $m$-$B_{10}H_{10}C_2Li_2$ and $PCl_3$ could react to form a cyclic or macrocyclic ring arose. To explore this idea, some reactions between $m$-$B_{10}H_{10}C_2Li_2$ and chlorophosphines were conducted and the chemistry of the products obtained was further investigated. The details of this study are summarized in the reactions below.



No indication of a cyclic monomeric product was observed. However, in allowing two molar equivalents of $PCl_3$ and one molar equivalent of $m$-$B_{10}H_{10}C_2Li_2$ to react, $m$-$B_{10}H_{10}C_2(PCl_2)_2$ was obtained in 40% yield

(1) Preceding communication: H. D. Smith, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

(2) Nomenclature of the clovo boron–carbon hydrides is discussed by R. Adams, *ibid.*, **2**, 1087 (1963); the term $m$-carborane is used to designate 1,7-dicarbaclovododecaborane.

(3) R. P. Alexander and H. Schroeder, *ibid.*, **2**, 1107 (1963).

(4) H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963).

(5) S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963).

(6) S. Papetti, B. B. Schaeffer, H. J. Troscianiec, and T. L. Heying, *ibid.*, **3**, 1444 (1964).

(7) S. Papetti and T. L. Heying, *ibid.*, **3**, 1448 (1964).