Frederick Smith Co. All solvents used were reagent grade and were commercially available. Analyses were performed under the supervision of Mr. J. Nemeth of the University of Illinois Microanalytical Laboratory and also by Galbraith Laboratories.

Preparation of the Complexes.—In the following syntheses and throughout the text the substituted phenanthroline ligands shall be abbreviated as follows: 1,10-phenanthroline, phen; 4,7-dimethyl-1,10-phenanthroline, 4,7-dmp; 3,4,7,8-tetramethyl-1,10-phenanthroline, 3,4,7,8-tmp, etc.

All the tris complexes mentioned herein were prepared from the hydrated metal chlorides and appropriate ligands in a tetrahydrofuran (THF)-methanol solvent as was previously described in the preparation of some analogous 2,2'-bipyridine complexes.[3] $Ni(2,9\text{-}dmp)_2(NO_3)_2 \cdot H_2O$ was made by the method of Hall, *et al.*,[5] who prepared the analogous complex with 4,4',6,6'-tetramethylbipyridine. Analyses for these complexes are presented in Table I.

Compd	% calcd			% found		
	C	H	N	C	H	N
$Ni(phen)_3Cl_2 \cdot 3H_2O$	59.52	4.16	11.57	59.03	4.14	10.88
$Ni(4,7\text{-}dmp)_3Cl_2 \cdot 3H_2O$	62.41	5.24	10.40	62.78	5.20	10.28
$Ni(5,6\text{-}dmp)_3Cl_2 \cdot H_2O$	65.32	4.96	10.88	64.77	5.27	10.86
$Ni(3,4,7,8\text{-}tmp)_3Cl_2 \cdot 5H_2O$	62.08	6.30		61.87	6.04	
$Ni(2,9\text{-}dmp)_2(NO_3)_2 \cdot H_2O$	54.48	4.25		54.22	4.17	

Spectral Measurements.—The nmr spectra were obtained at approximately 28° with Varian DP-60 and T-60 spectrometers. All shifts in D_2O were measured relative to the high-field multiplet of THF which was used as an internal reference.

Results and Discussion

The isotropic shifts of the 1,10-phenanthroline complexes prepared here are listed in Table II. For Ni-$(phen)_3{}^{2+}$ in D_2O, the 2,9 and 3,8 proton resonances were unambiguously assigned on the basis of their half-widths. Of these the 2,9 proton resonance was extremely broad and could be located at best on the oscilloscope. The 4,7 and 5,6 proton resonances have approximately the same half-widths, and therefore the 4,7- and 5,6-dimethyl-substituted complexes were synthesized in order to identify these two resonances unequivocally. The contact shifts for Ni$(phen)_3{}^{2+}$ are remarkably similar to those of Ni$(bipy)_3{}^{2+}$ [2] and further illustrate the similarity of these two ligands.

TABLE II
CONTACT SHIFTS OF THE PHENANTHROLINE COMPLEXES

Compd[a]	Solvent	$\Delta\nu_{2,9}$	$\Delta\nu_{3,8}$	$\Delta\nu_{4,7}$	$\Delta\nu_{5,6}$
$Ni(phen)_3Cl_2 \cdot 3H_2O$	D_2O	−8800[b]	−2496	−537	−998
$Ni(2,9\text{-}dmp)_2(NO_3)_2 \cdot H_2O$[c]	CD_3NO_2	(+949)	−2813	−582	−891
$Ni(4,7\text{-}dmp)_3Cl_2 \cdot 3H_2O$	D_2O		−2253	(+705)	−1102
$Ni(5,6\text{-}dmp)_3Cl_2 \cdot H_2O$	D_2O		−2426	−498	(−57)
$Ni(3,4,7,8\text{-}tmp)_3Cl_2 \cdot 5H_2O$	D_2O		(−405)	(+733)	−1060

[a] The contact shifts are reported in hertz at 60 MHz. The diamagnetic references are the respective tris iron(II) complexes except for $Ni(2,9\text{-}dmp)_2(NO_3)_2$ where the free ligand is used. Methyl proton resonances are enclosed in parentheses. [b] This resonance was measured on the oscilloscope and is accurate to only ±1000 Hz. [c] Only one set of resonances was found for this complex and this would imply that a rapid racemization process is occurring in solution.

Since octahedrally coordinated nickel(II) should be orbitally nondegenerate in D_3 symmetry, the observed isotropic shifts of the tris complexes are entirely due to a contact interaction.[6] Any pseudocontact contribution to the isotropic shifts is expected to be negligible. On this basis the isotropic shifts should provide direct

(5) J. R. Hall, M. R. Litzow, and R. A. Plowman, *Aust. J. Chem.*, **19**, 201 (1966).

(6) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

evidence of the mechanism of spin delocalization in Ni$(phen)_3{}^{2+}$. Also for the complex Ni$(2,9\text{-}dmp)_2$-$(NO_3)_2$, which has coordinated nitrate and is most likely octahedrally coordinated,[7] no sizable pseudocontact shifts are expected.

As shown previously the contact shifts of Ni$(phen)_3{}^{2+}$ and its methyl-substituted analogs[2,4] reflect the dominance of a σ-delocalization mechanism presumably caused by delocalization of positive spin density in the highest filled ligand σ MO, along with some participation from π delocalization which need not necessarily be related to metal–ligand π bonding.[8] The problem is now to relate this π delocalization to a specific ligand π MO and to propose a reasonable π spin delocalization mechanism; however, using the Hückel π spin densities recently reported for 1,10-phenanthroline,[9] we can find no simple π-delocalization mechanism which will properly explain the observed methyl proton contact shifts in these substituted phen complexes. As an example spin delocalization into either the highest filled π MO or lowest empty π^* MO of the methyl-substituted phenanthroline ligands predicts[4] positive contact shifts for the 2,9-CH_3, 4,7-CH_3, and 5,6-CH_3 protons whereas it is observed that $\Delta\nu_{5,6}$ in Ni$(5,6\text{-}dmp)_3{}^{2+}$ is negative. At the present time, it is then not yet possible to relate this π spin delocalization in Ni$(phen)_3{}^{2+}$ to any particular ligand π MO or simple combination of π MO's. The exact mechanism by which positive methyl proton contact shifts are observed in these complexes is still unknown and might, as suggested by La Mar and Van Hecke,[4] be due to some indirect spin polarization mechanism rather than to spin delocalization *via* metal–ligand π bonding.

(7) This complex is anlogous to $Ni(4,4',6,6'\text{-}tmb)_2(NO_3)_2 \cdot H_2O$ (tmb = tetramethylbipyridine) which was characterized by Hall, *et al.*,[5] and has identical properties.

(8) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

(9) G. N. La Mar and G. R. Van Hecke, *J. Amer. Chem. Soc.*, **91**, 3442 (1969).

Contact Shifts in Octahedral Nickel(II) and Cobalt(II) Complexes of 4-Methylpyridine N-Oxide

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In recent years,[1–4] we have been interested in the use of isotropic shifts of paramagnetic transition metal ion complexes to obtain information on bonding and structure. If the complexes are magnetically isotropic, as in

(1) M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **91**, 1361 (1969).

(2) M. F. Rettig and R. S. Drago, *ibid.*, **91**, 3432 (1969).

(3) R. E. Cramer and R. S. Drago, *ibid.*, **92**, 66 (1970).

(4) R. E. DeSimone and R. S. Drago, *ibid.*, **92**, 2343 (1970).

TABLE I
ELECTRONIC SPECTRAL DATA FOR $[Co(4-CH_3C_5H_4NO)_6](ClO_4)_2$

Solvent	Concn, M	λ_{max}, mμ	ν_{max}, cm^{-1}	ϵ_{max}
Nujol mull	. . .	514	19,455	. . .
		566	17,688	. . .
		1210	8,264	. . .
Nitromethane^a	0.0252	~510 sh	~19,600	. . .
		548	18,248	46.9
		1275	7,843	7.5

^{a} 0.1637 M 4-methylpyridine N-oxide in nitromethane.

the case of octahedral Ni(II), the isotropic shift is simply the contact shift and is given by[5]

$$\Delta\nu_c = \frac{-A_i g_{av}^2 \beta_e^2 S(S+1)\nu_0}{g_N \beta_N (3kT)} \quad (1)$$

where ν_0 is the probe frequency, A_i the nuclear spin-electron spin coupling constant (in gauss), $A_i = +(8\pi/6_S)g_N\beta_N|\psi_0|^2$, g_{av} the average G value of the electron, β_e the Bohr magneton, g_N the nuclear g value, β_N the nuclear magneton, S is the total electron spin of the system, k the Boltzmann constant, and T the absolute temperature.

ics Spectrograde nitomethane was stored over Linde 4-A sieves prior to use.

Syntheses.—$[M(4-CH_3pyO)_6](ClO_4)_2$ [M = Co(II), Ni(II)] were both prepared by the method previously reported[10] for the Ni(II) complex. *Anal.* Calcd for $[Co(C_6H_7NO)_6](ClO_4)_2$: C, 47.40; H, 4.60; N, 9.21. Found: C, 47.23; H, 4.82; N, 9.29. Calcd for $[Ni(C_6H_7NO)_6](ClO_4)_2$: C, 47.40; H, 4.61; N, 9.21. Found: C, 47.60; H, 4.62; N, 9.16.

The methods used to determine the solid-state and solution electronic spectra and the nmr spectra were described earlier.[10]

Calculations.—SCC extended-Hückel type of molecular orbital calculations were used to evaluate the eigenvectors.[3] The method used to calculate the electron–proton coupling constants from the eigenvectors has previously been described.[11]

Results

The electronic spectral results for the Co(II) complex are presented in Table I. Examination of these data indicates that we have the same complex in solution as in the solid state. This result was previously shown for the Ni(II) complex.[10] In all cases, the solution spectra were obtained in the presence of excess ligand to prevent dissociation of the complex. Recently,[12] the compound $[Co(pyO)_6]X_2$ was prepared and characterized.

TABLE II
NUCLEAR MAGNETIC RESONANCE DATA FOR $M(4-CH_3C_5H_4NO)_6^{2+}$ COMPLEXES

Position	$\nu_0{}^a$	$\nu_1{}^a$	$\Delta\nu_c{}^b$	Ratio^c	$A_{obsd}{}^e$
			M = Ni(II)		
2-H	$+222 \pm 25$	-470 ± 5^d	$+692 \pm 25$	-1.28 ± 0.07	-0.0499
3-H	-977 ± 10	-435 ± 5^d	-542 ± 10	. . .	$+0.0389$
4-CH$_3$	-1123 ± 10	-142 ± 2^d	-1117 ± 10	2.07 ± 0.06	$+0.0802$
			M = Co(II)		
2-H	$+334 \pm 25$	-470 ± 5	$+804 \pm 25$	-1.23 ± 0.06	. . .
3-H	-1090 ± 10	-435 ± 5	-655 ± 10	. . .	. . .
4-CH$_3$	-1507 ± 10	-142 ± 2	-1365 ± 10	2.08 ± 0.05	. . .

^{a} All chemical shifts are measured relative to TMS in hertz. ^{b} Positive shifts are those upfield from the position in the free ligand; negative shifts are downfield. ^{c} These values refer to the ratios of the contact shifts of the 2-H and 4-CH$_3$ protons relative to that of the 3-H proton. ^{d} R. W. Kluiber and W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, **87**, 5350 (1965), have obtained (using a similar procedure) the diamagnetic resonances for the ligand at a concentration 0.7 M in deuteriochloroform. Their values are -484, -424, and -141 Hz for the 2-H, 3-H, and 4-CH$_3$ protons, respectively. ^{e} Coupling constants in gauss; g_{av} for Ni(II) complex is 2.16.

In this article, we investigate the contact shift pattern in hexakis(4-methylpyridine N-oxide)nickel(II) perchlorate and hexakis(4-methylpyridine N-oxide)cobalt-(II) perchlorate. The shifts for these complexes are compared with each other and with results from an SCC molecular orbital calculation. The delocalization pattern observed enables us to conclude that the metal–oxygen–nitrogen bond is not linear. X-Ray studies[6–9] indicate nonlinearity in complexes of phosphine oxides and N-oxides in the solid state. The proton nmr contact shifts are dominated, even in the case of nickel(II), by a direct π-delocalization mechanism, but one cannot conclude anything about the relative amounts of σ vs. π spin delocalization in the ligand. The reason for this is made clear only by examining the results from an MO calculation.

Experimental Section

Reagents.—4-Methylpyridine N-oxide (reagent grade) was obtained from City Chemical Co. and recrystallized from C_2H_5-OH–$(C_2H_5)_2O$ just before use. The hexaaquometal(II) perchlorates (G. F. Smith) were used as obtained. Eastman Organ-

Nuclear magnetic resonance spectral data are given in Table II. Since the solutions contained excess ligand, it was necessary to determine the isotropic shifts by means of the mole fraction equation after determining that the systems were in the fast-exchange region.[13] The contact shifts for the Ni(II) complex were then converted to electron–proton hyperfine coupling constants by using eq 1. g_{av} was determined from μ_{eff} by using the relationship $\mu_{eff} = g_{av}\sqrt{S(S+1)}$.

Discussion

As has been previously discussed,[14] the geometric factors in a tetragonally distorted transition metal ion complex with six equivalent ligands are such that all pseudocontact contributions to the shift vanish when the ligands are rapidly exchanging. Furthermore, any distortions would be expected to be dynamic and rapid on the nmr time scale. Consequently, the data obtained on this system are for all practical purposes free from pseudocontact contributions. The data in Table II show that α spin (spin aligned with the field) is localized on the meta and 4-methyl protons and β spin is

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(9) C. I. Bränden and I. Lindqvist, *Acta Chem. Scand.*, **15**, 167 (1961).

(10) D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, **5**, 2009 (1966).

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(14) M. L. Wicholas and R. S. Drago, *ibid.*, **91**, 5963 (1969).

localized on the α proton. The methyl protons of 4-methylpyridine N-oxide contribute directly to the π-bonding and π-antibonding molecular orbitals and the negative contact shift of these protons coupled with β spin on the para proton of pyridine N-oxide indicates that α spin is delocalized into the π system.

In octahedral nickel(II), the two unpaired electrons are in the σ-bonding e_g orbitals and thus one might expect the delocalization mechanism to be dominated by σ-type molecular orbitals, particularly if the metal–oxygen–nitrogen bond were linear so that the π orbitals of the 4-methylpyridine N-oxide were orthogonal to the e_g set. In $Ni(C_5H_5N)_6{}^{2+}$, the contact shifts are dominated by a σ-delocalization mechanism[3] and what little spin there is in the π system gets there through exchange polarization and is β spin. Exchange polarization would also have introduced β spin in the π system of 4-methylpyridine N-oxide so this cannot account for the observed shifts. In the octahedral nickel(II) complexes of benzylamine[15] and aniline,[16] the contact shifts observed for the phenyl protons are typical of those expected for a π-delocalization mechanism with α spin in the π ring system. In these ligands the lone pair is not orthogonal to the "π orbitals" of the ring and σ bonding to Ni(II) places α spin directly into these "π ring orbitals."

In 4-methylpyridine N-oxide, the oxygen has three lone pairs of electrons that are involved in molecular orbital formation but are largely localized on oxygen. On oxygen, only the p_z orbital (z perpendicular to the ring) is not orthogonal to the ring π system. In one possible geometrical arrangement of the ligands, all of the ring p_z orbitals can be parallel or perpendicular to the x, y, and z axes of the complex coordinate system (*i.e.*, all oxygens on x, y, and z axes). For such an orientation, the ligand p_y or p_x orbitals could mix with the metal e_g set (local symmetry about Ni(II) is octahedral) but the p_z orbitals could not. Therefore, in nickel(II) complexes α spin could not be put in the π system *via* oxygen p_z because with local octahedral symmetry all of the unpaired spin on nickel(II) is in e_g orbitals. Coordination involving a bent Ni–O–N bond, but one in which the ligand orientation is otherwise that described above, can be eliminated. The overall symmetry of the nickel in a complex with this geometry would permit mixing of the $d_{x^2-y^2}$ and d_{z^2} metal–ring carbon and nitrogen "π" orbitals, but overlap would be small, because the distance is large and this effect is discounted. Upon coordination, the 4-methylpyridine N-oxide must be twisted in such a way that the π molecular orbital which is largely oxygen p_z mixes with the σ-bonding e_g set of the nickel(II). In this symmetry, the σ and π designation is meaningless and the free-ligand symmetry is used here for convenience. In the solid state, a single-crystal X-ray investigation[7] of bis-(pyridine N-oxide)bis(2,4-pentanedionato)nickel(II) indicates this twisted mode of coordination by the pyridine N-oxide to the nickel.

In the molecular orbital calculation, the σ-donor orbital which is mainly oxygen p_x or p_y is highest in energy but the π donor orbital which is mainly oxygen p_z is next to the highest and only 0.2 eV lower in energy. We

have attempted to fit spin densities in the nickel(II) complexes with an SCC MO calculation as was previously done with a series of substituted pyridine complexes.[3] The one-electron coupling constants are reported in Table III. Since the proton contact shifts

	π*(18)	σ(19)	π(20)	σ(21)
2-H	−5.069	+0.0063	−3.0210	+17.426
3-H	−0.8398	+0.7935	...	+9.820
4-CH₃	+6.744	+0.0005	+3.053	+6.594

are being determined by a π-delocalization mechanism and since there is a node at the 3 position in the filled π(20) molecular orbital, only two protons remain to fit spin densities. With a node at the 3 position, the π contribution to the proton shift is dominated by spin polarization so restricted MO calculations cannot be applied at this position. Since the weighting constants for the one-electron coupling constants for σ and π orbitals require two unknowns, there are no protons left over as checks on the procedure. However, even though a fit of the spin densities is not meaningful, the molecular orbital calculations provide considerable insight into the interpretation of the mechanism of spin delocalization in the 4-methylpyridine N-oxide complexes.

The general pattern of the observed proton contact shifts has the gross features of a π-delocalization mechanism. In the absence of information about the ligand molecular orbitals, it was incorrectly concluded[17] that the proton contact shifts "clearly support a π mechanism for spin delocalization." We can see from Table III that if in the complex even an order of magnitude more spin were delocalized in the highest energy filled σ orbital, σ(19), than in the π orbital, it would not be reflected in the proton contact shifts because the proton contributions to the σ molecular orbital are so slight. Consequently, the contact shifts of atoms other than the protons must be determined before one can determine the relative importance of spin density delocalized in the σ and π molecular orbitals of this ligand. Conceivably, a good procedure for treating the π contribution at the 3-H would shed some light on the problem. Data pertaining to the ^{14}N or ^{13}C contact shifts would be most enlightening. We can conclude that even though the observed proton shifts are dominated by a π-delocalization mechanism, we do not know the relative importance of σ- and π-spin delocalization in the complex because the small proton coefficients in the σ molecular orbital cause the proton contact shifts to be insensitive to what really is happening there. Such a conclusion could not have been reached without our MO results and this example serves further to justify our claims about the necessity of having decent ligand wave functions before even qualitative interpretations of spin delocalization mechanisms in complexes can be made from proton contact shifts.

There are additional problems complicating the interpretation. The molecular orbital σ(21) is 3.4 eV below σ(19) in energy and consequently mixes to a lesser extent with the metal and is less important in the spin delo-

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(17) R. W. Kluiber and W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, **88**, 1399 (1966).

calization. Since the proton coefficients in this MO are so large, it could have a significant effect on the observed contact shift pattern. Unfortunately, the contact shifts of two protons do not provide enough information to answer this question or to distinguish between the relative importance of π and π^* orbitals. The only conclusion that can be drawn is that the ligand is so arranged in the complex that orbitals with π symmetry can overlap the e_g set.

Examination of Table II shows that the ratios of the shifts in Ni(II) and Co(II) complexes are identical and one might incorrectly infer that these data indicate the spin delocalization mechanisms are essentially the same. The similarity is at first glance surprising, since one does not in general expect the mechanisms of delocalization to be the same in six-coordinate[18] cobalt-(II) and nickel(II) and one expects pseudocontact contributions for the six-coordinate Co(II) complex. In a previous report[14] from this laboratory, it was demonstrated that, for systems with rapidly exchanging ligands, the pseudocontact shift would be greatly reduced or become zero. The similarity of our cobalt(II) shifts with those obtained in more dilute solution indicates ion pairing is not extensive and rapid exchange with the excess ligand present eliminates contributions to the isotropic shift from pseudocontact effects. Since we are observing contact shifts for cobalt(II), we can ask the question why are the ratios of the proton shifts identical for Co(II) and Ni(II) when Co(II) has unpaired electrons in both e_g and t_{2g} sets (*i.e.*, σ- and π-type orbitals) and nickel(II) only has them in the e_g set. Here we have the interesting case that the nickel-ligand geometry allows the e_g orbitals on the nickel to mix with both σ- and π-type ligand orbitals. Furthermore, since the proton coefficients are so small in the σ MO, the π-delocalization pattern (Table III) dominates the proton shifts in both the cobalt(II) and nickel(II) complexes contrary to what is to be expected generally. If the ligand σ and π molecular orbitals mixed only with the e_g or t_{2g} set, respectively, different proton shifts would have been expected in cobalt(II) and nickel(II). If the e_g orbitals of the metal ion distributed spin differently between the π and σ MO's of the ligand than the t_{2g} set does, we would also have expected different delocalization patterns in nickel(II) and cobalt(II). Again, the small proton coefficients in the σ MO preclude our gaining information about this and ^{13}C shifts would be enlightening.

It is interesting to point out that as a consequence of the small proton coefficients in the σ MO and the ligand geometry we can say after the fact that the ratio method[16] would have worked on this system if it were needed for the cobalt(II) complex. However, the ratios of the 2-H and 4-CH$_3$ shifts to the 3-H shift in bis(2,4-pentanedionato)bis(4-methylpyridine N-oxide)-nickel(II), 1.85 and 2.35, and bis(4-methylpyridine N-oxide)bis(dipivaloylmethido)nickel(II), 1.88 and 2.47, are significantly different from these same ratios in the hexakis(4-methylpyridine N-oxide)nickel(II) perchlorate, 1.28 and 2.07. The shifts for the former two compounds were reported assuming that the systems were in the fast-exchange region.[19] If the reported shifts are correct, then this demonstrates that even

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(19) R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **87**, 5350 (1965).

though the ligand is coordinated to the same metal ion, the proton delocalization pattern is similar, but not identical in the series of nickel(II) complexes even though the proton pattern is the same in this and in the six-coordinate nickel(II) and cobalt(II) complexes. As has been previously claimed,[20] it is practically impossible to determine *a priori* when the delocalization mechanisms will be the same in different complexes. Very slight differences in coordination geometries can lead to varying participation by different molecular orbitals in the delocalization mechanism. This shortcoming makes the ratio method for factoring out the pseudocontact shift extremely unreliable contrary to a recent claim made for its judicious utility.[21]

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Preparation of a New Ternary Lithium Silicon Nitride, LiSi$_2$N$_3$, and the High-Pressure Synthesis of Magnesium Silicon Nitride, MgSiN$_2$

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Prior to this study the only known ternary compound of lithium, silicon, and nitrogen was Li$_5$SiN$_3$, first prepared by Juza, *et al.*,[2] who also synthesized the compounds Li$_5$TiN$_3$ and Li$_5$GeN$_3$. These materials were prepared by reaction of the binary nitrides at temperatures of 850–1300° and were reported to be light in color, easily hydrolyzable, and saltlike in their properties.

David and Lang[3] have reported the ambient-pressure synthesis of magnesium silicon nitride, MgSiN$_2$, by the direct reaction of the binary nitrides. Earlier work led to the synthesis of CaSiN$_2$ by Wöhler and Bock[4] and to the preparation of BeSiN$_2$ by Eckerlin, *et al.*[5]

The purpose of this communication is to report the ambient-pressure, high-temperature synthesis of lithium silicon nitride, LiSi$_2$N$_3$, and the high-pressure, high-temperature synthesis of magnesium silicon nitride, MgSiN$_2$. Powder X-ray diffraction data for these ternary compounds are also reported.

Experimental Section

A. Lithium Silicon Nitride.—LiSi$_2$N$_3$ was prepared directly

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