surfaces as one would have been led to believe from discussions like that given in the Introduction.

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Registry No. $Fe_3(CO)_9(\mu_3\text{-}S)_2$, 22309-04-2; $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}CO)$, 74520-99-3; $Co_3Cp_3(\mu_3\text{-}S)_2$, 11105-79-6; $[Co_3Cp_3(\mu_3\text{-}S)_2]^+$, 81316-25-8; $Co_3Cp_3(\mu\text{-}S)(\mu_3\text{-}CO)$, 37328-31-7; $Ni_3Cp_3(\mu_3\text{-}S)_2$, 58396-47-7; $[Ni_3Cp_3(\mu_3\text{-}CO)_2]^-$, 81205-88-1; $Ni_3Cp_3(\mu_3\text{-}CO)_2$, 12194-69-3.

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Reevaluation of the Crystal Structure Data on the Expanded-Metal Compounds $Li(NH_3)_4$ and $Li(ND_3)_4$

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Existing X-ray diffraction data (Mammano and Sienko, 1968) and neutron diffraction data (Chieux, Sienko, and DeBaecker, 1975) on the solid lithium–ammonia compounds have had to be reevaluated in the light of recent magnetic studies which indicate absence of the 82 K solid–solid transition in the deuterated compound. X-ray reflections observed at 77 K, which were previously interpreted as a mixture of hexagonal and body-centered-cubic phases, are better indexed as a single body-centered-cubic phase. Solid-phase II of $Li(NH_3)_4$, stable below 82 K, appears to belong to space group $I\bar{4}3d$, $a = 14.93$ Å, with 16 lithium atoms and 16 nitrogen atoms on Wyckoff position c and 48 nitrogens on Wyckoff position e. The same structure holds for $Li(ND_3)_4$. Below 25 K, extra reflections appear, corresponding to formation of a superstructure with period $2a$. This coincides with onset of what appears to be antiferromagnetic ordering below this temperature.

Introduction

A most remarkable feature of the lithium–ammonia phase diagram (Figure 1) is an extraordinarily deep eutectic at 20 MPM (mole percent metal) and 89 K.[1] A great deal of indirect evidence has accumulated which suggests that a compound, $Li(NH_3)_4$, is formed at or near this composition. Such evidence includes the following: the enthalpy of solution of Li in NH_3 is relatively large and negative (−38 kJ/mol), like that of Ca in NH_3 (−80 kJ/mol) and unlike that of Na in NH_3 (~0 kJ/mol);[2] the vapor pressure of the saturated $Li\text{-}NH_3$ solution is very small (32 torr at 0 °C) compared to that of $Na\text{-}NH_3$ (1700 torr at 0 °C);[3] the conductivity of solid lithium–ammonia is considerably greater than that of liquid $Li\text{-}NH_3$, whereas the reverse is true for $Na\text{-}NH_3$;[4] the heat capacity of the $Li\text{-}NH_3$ mixture is in excess of that computed from the sum of the components, an excess which peaks at 20 mole % Li;[5] solid $Li\text{-}NH_3$ shows a thermal transition at 82 K, corresponding to a break in the conductivity–temperature curve.[4] More direct evidence comes from X-ray diffraction patterns on solid $Li\text{-}NH_3$ that are neither those of Li nor NH_3.[6] Mammano and Sienko examined powder samples of 20 mol % lithium-in-ammonia solutions at 77 K and concluded that $Li(NH_3)_4(s)$ exists in two phases: a cubic form with $a_0 = 9.55$ Å stable between 82 and 89 K, and a hexagonal form having $a = 7.0$ Å and $c = 11.1$ Å, stable below 82 K.[6] Kleinman et al. found similar results but disagreed on the possible choice of space group for the hexagonal phase, claiming $P6_3$ rather than $P6_3mc$.[7]

Recently, in a magnetic investigation of lithium–methylamine solutions,[8] we remeasured the low-temperature magnetic susceptibility of $Li(NH_3)_4$ in order to verify certain unusual features of the temperature dependence as reported by Glaunsinger, Zolotov, and Sienko.[9] Not only were the gross features of temperature dependence, discontinuities at 89 and 82 K, and tendency to antiferromagnetism at very low temperatures reproduced, but the quantitative values themselves were duplicated. This last was no small feat since the forces involved were tiny and large corrections for core diamagnetism and sample container had to be applied. Fortunately, in collaboration with Landers and Dye,[10] we had worked out in the meantime a method of decomposing lithium–cryptate electride in situ in the magnetic apparatus so corrections for bucket and core diamagnetism could be made by direct measurement. Applying this technique to $Li\text{-}NH_3$, we were able to measure the *net electronic susceptibility* of $Li(NH_3)_4$ and also that of $Li(ND_3)_4$ with great accuracy. A most surprising result was that, although the susceptibilities of $Li(NH_3)_4$ and $Li(ND_3)_4$ were identical within experimental error (e.g., $(60 \pm 3) \times 10^{-6}$/mol of Li at 89 K) in the liquids above 89 K and in the solids below 82 K, there was no trace of solid phase I in the magnetic behavior of $Li(ND_3)_4$. In other words, deuteration apparently suppresses the solid–solid transition at 82 K of $Li(NH_3)_4$. Confirmation of this fact is given by the DTA studies of DeBaecker,[11] who found with $Li(ND_3)_4$ no heat effect at 82 K.

Chieux, Sienko, and DeBaecker[12] have done low-temperature neutron diffraction studies on powder samples of $Li(ND_3)_4$ and $Li(NH_3)_4$. They found that the pattern of the deuterated compound could be indexed uniquely as a body-centered-cubic phase ($a = 14.83$ Å at 30 K; $a = 14.93$ Å at 60 K). Because the electronic magnetic susceptibility of $Li(NH_3)_4$ is identical in magnitude and temperature dependence with that of Li-

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(1) Mammano, N.; Coulter, L. V. *J. Chem. Phys.* **1967**, *47*, 1564.

(2) Coulter, L. V.; Monchik, L. *J. Am. Chem. Soc.* **1951**, *73*, 5867.

(3) Marshall, P. R.; Hunt, H. *J. Phys. Chem.* **1956**, *60*, 732.

(4) Morgan, J. A.; Schroeder, R. L.; Thompson, J. C. *J. Chem. Phys.* **1965**, *43*, 4494.

(5) Mammano, N.; Coulter, L. V. *J. Chem. Phys.* **1969**, *50*, 393.

(6) Mammano, N.; Sienko, M. J. *J. Am. Chem. Soc.* **1968**, *90*, 6322.

(7) Kleinman, L.; Hyde, S. B.; Thompson, C. M.; Thompson, J. C. In "Metal-Ammonia Solutions, Colloque Weyl II"; Lagowski, J. J., Sienko, M. J., Eds.; Butterworths: London, 1970; p 229.

(8) Stacy, A. M.; Sienko, M. J. *J. Chem. Phys.*, in press.

(9) Glaunsinger, W. S.; Zolotov, S.; Sienko, M. J. *J. Chem. Phys.* **1972**, *56*, 4756.

(10) Landers, J. S.; Dye, J. L.; Stacy, A.; Sienko, M. J. *J. Phys. Chem.* **1981**, *85*, 1096.

(11) DeBaecker, F. Thesis, Diplomes d'Etudes Approfondies, Universite Paris-Sud, Faculte des Sciences d'Orsay, 1973.

(12) Chieux, P.; Sienko, M. J.; DeBaecker, F. *J. Phys. Chem.* **1975**, *79*, 2996.

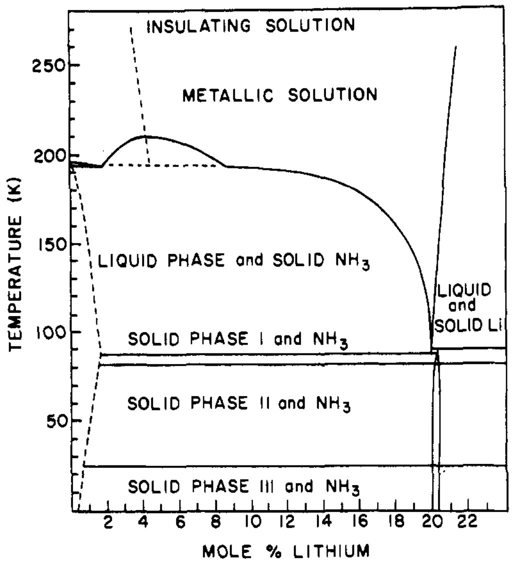

Figure 1. Phase diagram for lithium in ammonia. The details of the diagram in the vicinity of the eutectic are uncertain. It is assumed here that peritectic melting of crystalline $Li(NH_3)_4$ occurs slightly higher than the freezing point of the eutectic mixture. Recent experiments[17] suggest that there may be two closely spaced eutectics, one at 88.80 K and the other at 88.91 K, on alternate sides of congruent melting $Li(NH_3)_4$.

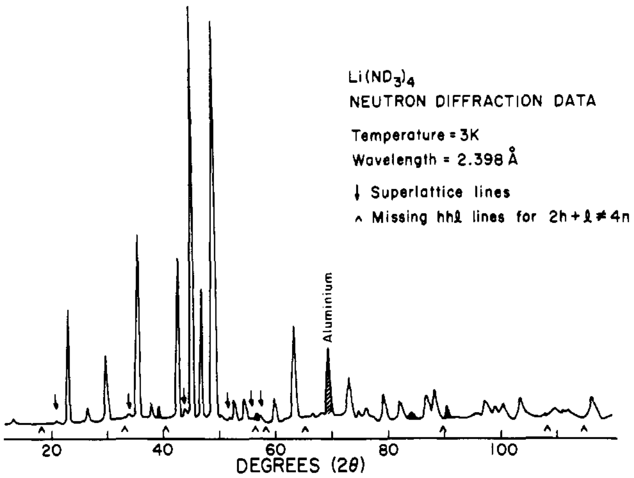

Figure 2. Neutron diffraction pattern of $Li(ND_3)_4$ at 3 K.[12] Black peaks correspond to excess ND_3, and arrows show superlattice lines disappearing at higher temperature ($T > 30$ K). Carets indicate expected positions of *hhl* lines with $2h + l \neq 4n$. Neutron wavelength is 2.398 Å.

$(ND_3)_4$ below 82 K, it is reasonable to assume that the two materials are similar in structure. For that reason, the low-temperature "hexagonal" structure of $Li(NH_3)_4$ was reexamined.

Procedure and Results

Chieux et al.[12] published neutron diffraction data on $Li(ND_3)_4$ at 3 K, $Li(NH_3)_4$ at 60 K, and $Li(NH_3)_4$ at 85 K but did not report index assignments. Our first step was to assign Miller indices to the observed reflections and compare the observed reflections with those expected from the condition $h^2 + k^2 + l^2 = 2n$ for a body-centered-cubic lattice. It was found for $Li(ND_3)_4$ and for $Li(NH_3)_4$ at 60 K that all the observed *hhl* lines, except for a single, very weak 110 line for $Li(ND_3)_4$, satisfied the condition $2h + l = 4n$. All the other *hhl* lines, which did not satisfy this condition, were either missing or occurred as accidental degeneracies with other lines. This enabled us to fix the space group, as there are only two possible space groups that have the restriction $2h + l = 4n$ on *hhl*, $Ia3d$ and $I\bar{4}3d$. The former can be ruled out on the basis that it has further conditions on *hkl* which do not hold true; the latter therefore was taken as the space group of $Li(ND_3)_4$ and the low-temperature form of $Li(NH_3)_4$.

Table I. Neutron Diffraction Data on $Li(NH_3)_4$ and $Li(ND_3)_4$[12]

		$Li(ND_3)_4$ at 3 K		$Li(NH_3)_4$ 60 K		$Li(NH_3)_4$ 85 K	
hkl	d_{calcd}[a]	d_{obsd}	intens	d_{obsd}	intens	d_{obsd}	intens
110[b]	10.47	10.47	vw				
*200	7.40						
211	6.04	6.05	m	6.06	vw	6.23	s
220	5.23	5.24	vw			5.33	vw
310	4.68	4.69	w				
222	4.27						
321	3.96	3.96	ms	3.94	vw		
400	3.70	3.70	vw				
*411, 330	3.49						
420	3.31	3.31	m	3.34	vw		
332	3.16	3.16	s	3.17	vw	3.20	w
422	3.02	3.02	ms				
431, 510	2.90	2.91	vs	2.91	s		
521	2.70	2.71	w	2.72	w	2.74	s
440	2.62	2.62	w	2.63	w		
+530, 433	2.54					2.56	s
*442, 600	2.47					2.50	vw
532, 611	2.40	2.40	w	2.41	s		
620	2.34	2.34	vvw			2.38	ms
541	2.28	2.29	m	2.30	m		
*622	2.23					2.26	s
631	2.18	2.19	vw	2.20	m	2.21	vw
444	2.14			2.15	m		
640	2.05	2.06	vvw	2.07	vw	2.08	vw
633, 721, 552	2.01	2.02	w	2.03	ms	2.03	vw
642	1.98	1.98	vw	2.00	vw		
730	1.94	1.94	w				
651, 732	1.88	1.88	w				
800	1.85						
+741, 554, 811	1.82	1.82	w	1.83	ms		
+820, 644	1.79						
653	1.77						
822, 660	1.74	1.75	w				
743, 831, 750	1.72	1.72	w	1.73	s		
*662	1.70						
752	1.68						
840	1.65						
+910, 833	1.63			1.64	vw		
842	1.61	1.62	vvw				
761, 921, 655	1.60	1.60	w	1.61	w		
664	1.58	1.58	vw				
930, 754, 851	1.56	1.56	w				
763, 932	1.53	1.52	w	1.53	w		
844	1.51	1.51	vvw				
+853, 941, 770	1.50	1.50	vvw	1.51	w		
+10,0,0, 860	1.48						
10,1,1, 772	1.47	1.47	vw				
10,2,0, 862	1.45	1.45	vw				
943, 950	1.44	1.43	vvw				
*10,2,2, 666	1.42						
10,3,1, 952, 765	1.41	1.41	w				

[a] Calculated spacings (given in A) with $a = 14.80$ A at 3 K.
[b] Asterisks represent missing *hhl* reflection with $2h + l \neq 4n$, and plus signs represent one of the reflections of the set is an *hhl* line with $2h + l \neq 4n$. [b] For the space group $I\bar{4}3d$, the 110 line should not appear.

Table I shows our assigned indices; asterisks indicate missing *hhl* lines for which $2h + l \neq 4n$, and pluses mark those cases where such lines coincide with others. Figure 2 shows the neutron diffraction pattern of $Li(ND_3)_4$ with carets to designate missing *hhl* lines with $2h + l \neq 4n$. Figure 2 also shows (with arrows) several weak reflections that disappeared at temperatures higher than 30 K. Chieux et al.[12] took these as

Table II. X-ray Data for $Li(NH_3)_4$ at 77 K[a]

			2-phase indexing[a]		1-phase indexing[b]	
2θ	intens	d_{obsd}	d_{calcd}	*hkl*	d_{calcd}	*hkl*
13.35	vvw	6.63	6.75 c	110		
14.55	s	6.09	6.09 h	100	6.13	211
16.70	vw	5.26	5.31 h	101	5.31	220
18.75	w	4.73	4.78 c	200	4.75	310
21.80	m	4.06	4.10 h	102	4.01	321
26.52	w	3.36	3.37 h	111	3.35	420
27.93	m	3.20	3.18 c	300	3.20	332
30.55	ms	2.93	2.93 h	201	2.94	431, 510
32.44	vw	2.76	2.77 h, c	004, 222	2.74	521
35.14	vw	2.55	2.55 h, c	113, 321	2.58	530, 433
38.95	mw	2.31	2.30 h	210	2.32	541

[a] Cubic (c) a = 9.55 Å; hexagonal (h) a = 7.0 Å, c = 11.1 Å. [b] Body-centered-cubic, a = 15.02 Å.

Table III. Structures of the Solid Phases of $Li(NH_3)_4$ and $Li(ND_3)_4$

phase	$Li(NH_3)_4$	$Li(ND_3)_4$	comments
solid-phase I (89–82 K)	a = 14.98 Å (85 K)	does not form	bcc,[a] different space group from solid-phase II
solid-phase II (82–~25 K)	a = 14.93 Å (60 K)	a = 14.93 Å (60 K), a = 14.83 Å (30 K)	bcc; probable space group $I\bar{4}3d$; a proportional to temp
solid-phase III	no data	a = 14.80 Å (20 K)	bcc; superstructure with period $2a$; a is constant with temp

[a] bcc = body-centered cubic.

evidence of a new low-temperature phase, but they can be accounted for by a superstructure of period $2a$.

The data for $Li(NH_3)_4$ at 60 K were of poor quality, because of the large background due to incoherent proton scattering, but they can be fitted to the same space group as $Li(ND_3)_4$. However, the data for $Li(NH_3)_4$ at 85 K, although corresponding to a body-centered-cubic structure, violate the condition on *hhl* of $2h + l = 4n$, so this phase cannot belong to the $I\bar{4}3d$ space group.

Once we were convinced that $Li(NH_3)_4$ at 60 K had the same space group as $Li(ND_3)_4$, it was a simple matter to reinterpret the previous powder X-ray diffraction studies of Mammano and Sienko.[6] Table II shows the X-ray data for $Li(NH_3)_4$ at 77 K and how it can be interpreted in terms of a single body-centered-cubic phase.

Discussion

Pooling together all the electrical, magnetic, thermal, and structural investigations that have been performed in order to elucidate the nature of solid $Li(NH_3)_4$, we come to the conclusion that there are three solid phases, as noted in Table III. The solid–solid transition at 82 K is clearly marked by differential thermal analysis in $Li(NH_3)_4$;[13] it does not occur in $Li(ND_3)_4$.[11] There is a clear break in the magnetic properties of $Li(NH_3)_4$ at 82 K;[9] there is no such break in $Li(ND_3)_4$.[14] The solid–solid transition at ~25 K shows up not only in the downturn of magnetic susceptibility of $Li(NH_3)_4$ and of $Li(ND_3)_4$ below this temperature, but a heat effect has been observed by differential thermal analysis for $Li(ND_3)_4$ at 27 ± 5 K.[12]

The absence of a phase change for $Li(ND_3)_4$ at 82 K is not surprising in view of other differences between NH_3 and ND_3. For example, the boiling and melting points of ND_3 are about three degrees higher than those of NH_3, indicating a change in the strength of hydrogen bonding upon deuteration. Furthermore, the critical temperature for liquid–liquid phase separation is higher by about ten degrees for lithium in ND_3 as compared to lithium in NH_3.[15] It is also interesting to note that the solid–solid phase transition at 82 K in $Li(NH_3)_4$ has an unusually large pressure dependence. All this information

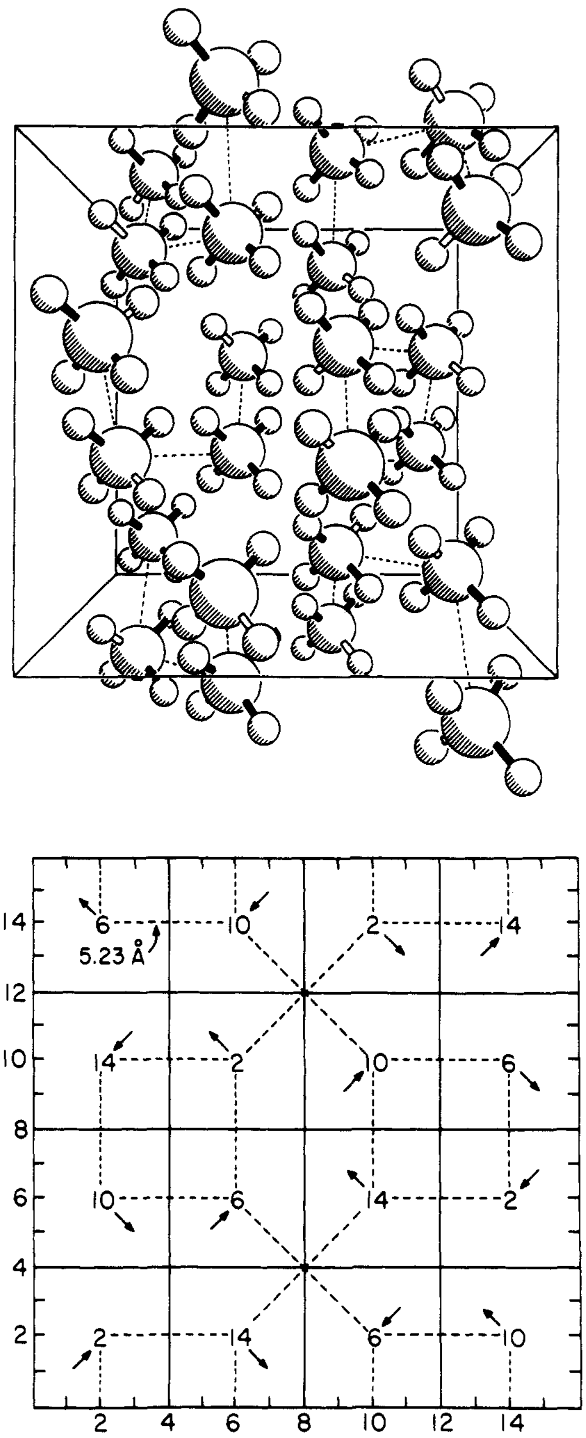

Figure 3. One possible structure of $Li(ND_3)_4$, solid-phase II. The $Li(ND_3)_4$ tetrahedra are shown positioned in the space group $I\bar{4}3d$ with the lithium atoms on Wyckoff position c at (x, x, x) = (0.125, 0.125, 0.125). The numbers on the drawing at the bottom indicate the coordinates of the lithium atoms in divisions of $^1/_{16}$. The clear bonds (top) and arrows (bottom) designate the ND_3 group that is on a special position. The dashed lines in this figure connect spiral chains of nearest-neighbor lithium atoms.

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(13) David, T.; Glaunsinger, W. S.; Zolotov, S.; Sienko, M. J. In "Electrons in Fluids, Colloque Weyl III"; Jortner, J., Kestner, N. R., Eds.; Springer-Verlag: Heidelberg, 1973; p 321.

(14) Stacy, A. Ph.D. Thesis, Cornell University, 1981.

(15) Katsumoto, M.; Damay, P. *J. Phys. Chem.* **1975**, *79*, 2928.

indicates that the phase changes are quite sensitive to the strength of the microscopic interactions between the solvent molecules. It is likely that the missing phase change in $Li(ND_3)_4$ occurs so near its melting point that the transition has not been observed.

Although no phase change is observed for $Li(ND_3)_4$ at 82 K, there are significant changes in the neutron diffraction pattern for $Li(NH_3)_4$ above and below this temperature. Only 11 reflections are observed for solid-phase I above the background scattering, making an unambiguous determination of the structure impossible. The data fit reasonably well to a body-centered-cubic phase with $a = 14.98$ Å at 85 K. While the positions of the reflections at 85 K for solid phase I are rather similar to those of solid-phase II near 82 K, there are striking differences in the line intensities. It is suggested that the phase transition at 82 K retains the body-centered-cubic symmetry with a similar lattice parameter. However, a distortion changes the space group and therefore the line intensities.

Given that there are relatively few body-centered-cubic space groups and few ways of ordering tetrahedra in a body-centered-cubic pattern, we can make a fairly good guess at the structure of solid-phase II. The density of this phase is about 0.60 g/cm^3[13], and with $a = 14.93$ Å at 60 K, the number of $Li(NH_3)_4$ molecules per unit cell must be 16. In body-centered-cubic symmetry, other possibilities are 12 and 24, both of which yield unreasonable densities, 0.44 and 0.88 g/cm^3, respectively. All of the body-centered-cubic space groups with 16 symmetry equivalent sites require a minimum symmetry of a 3-fold axis. Therefore, one NH_3 group per $Li(NH_3)_4$ molecule must be unique and on the same Wyckoff position as the lithium atoms. The other NH_3 groups can be placed on 48 general positions. In space group $I\bar{4}3d$, the 16 lithium atoms and 16 nitrogen atoms would be on Wyckoff position c and 48 nitrogens on Wyckoff position e. One possible choice for the positions of the molecules is shown in Figure 3.

The flaw in the above analysis is that it does not account for the very weak, lowest angle line observed by neutron diffraction in $Li(ND_3)_4$ at 3 K (Table I) and, at the same angle, by X-ray diffraction in $Li(NH_3)_4$ at 77 K (Table II). This line may be spurious. It did not appear in all the X-ray specimens. Also, a reexamination of some preliminary data taken on $Li(ND_3)_4$ by M.J.S. with neutron diffraction at Grenoble in 1971 showed the line recorded on one of the counters but not on the other!

That the three solid phases of $Li(NH_3)_4$ and the two phases of $Li(ND_3)_4$ are body-centered-cubic with similar lattice parameters is not unexpected. Many studies have shown that body-centered-cubic structures have the lowest electrostatic energy in the limit of low electron densities,[16] as are represented here by these "expanded-metal" compounds.

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Registry No. $Li(NH_3)_4$, 19453-81-7; $Li(ND_3)_4$, 81097-62-3.

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(16) Herring, C. In "Magnetism"; Rado, G. T., Suhl, H., Eds.; Academic Press: New York, 1966; p 71.

(17) Coulter, L. V.; Lee-Bechtold, S. H.; Madhvaraja, V. *J. Chem. Thermodyn.* **1981**, *13*, 815.

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A New Model of Structure and Bonding in the Boron Hydrides

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Tensor surface harmonic theory, recently developed by one of us, is used to describe the structure and bonding in the boron hydrides. The theory is extended to cover the *nido-* and *arachno-*boranes in a general way. The model yields the characteristic structural and electron-counting rules obeyed by *closo-*, *nido-*, and *arachno-*boranes in a direct and simple manner. *Nido-* and *arachno-*boranes are found to have pairs of high-energy occupied orbitals localized around the open (nontriangular) face. These orbitals are similar in form to those found in the cyclic planar hydrocarbons, thus explaining chemical similarities between these hydrocarbons and some nido clusters. In most nido and arachno clusters these orbitals are stabilized by the extra hydrogen atoms around the open face.

1. Introduction

The nature of bonding in the boron hydrides (or boranes) has been of interest for over 25 years. The group forms one of the largest and most coherent groups of cluster molecules, with members containing up to 15 boron–hydrogen units bonded in a closo, nido, or arachno structure.

Experience has led to the formulation of structural and electron-counting rules[1–4] for the boranes and their isoelectronic derivatives (such as the carboranes). The primary structural and electron-counting rules are summarized in Table I; they govern the boron atom skeleton of the borane. Williams[4] has formulated secondary rules dealing with hydrogen atom and heteroatom positioning; his article complements this one.

Table I. Primary Structural Rules in the Boranes

type	skeleton	formula	no. of skeletal electron pairs
closo	deltahedron	$B_pH_p^{2-}$	$p + 1$
nido	as closo with HCV[a] missing	$[B_pH_p^{4-}]$ B_pH_{p+4}	$p + 2$
arachno	as nido with an adjacent HCV[a] missing	$[B_pH_p^{6-}]$ B_pH_{p+6}	$p + 3$

[a] HCV = highest coordination vertex.

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(1) Wade, K. *J. Chem. Soc. D* **1971**, 792; *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(2) Mingos, D. M. P. *Nature (London), Phys. Sci.* **1972**, *236*, 99.

(3) Rudolph, R. W.; Pretzer, W. R. *Inorg. Chem.* **1972**, *11*, 1974.

(4) Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67.