experiences stronger eclipsing interactions with the equatorial group and thus prefers to coordinate next to an axial substituent (Chart II).[24]

In summary, we have demonstrated a strong preference for complexation of unsymmetrical cyclic acetals and have provided an experimentally based explanation for the unidirectional ring opening of these species.

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Supplementary Material Available: Full characterization of **1–5** along with COSY and HETCOR spectra for **2**, **2**·BF_3, **5**, and **5**·BF_3 and APT spectra for **4**·BF_3 (12 pages). Ordering information is given on any current masthead page.

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Crystal Structure of the Expanded-Metal Compound $^7\mathrm{Li(ND_3)_4}$

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The structure of the expanded-metal compound $\mathrm{Li(ND_3)_4}$ has been one of the most important and elusive unsolved problems in metal–ammonia chemistry.[1,2] This unique compound has the lowest melting point of any known metal (89 K), possesses unusual electrical[3] and magnetic[4] properties, and is just on the metallic side of the metal–nonmetal transition.[5] Mammano and Sienko were the first to recognize that 20 mol% metal solutions of lithium in ammonia formed a stable crystalline solid below 90 K.[6] They concluded that there were two crystalline phases: a cubic phase with $a = 9.55$ Å, stable between 82 and 89 K, and a hexagonal phase with $a = 7.0$ Å and $c = 11.1$ Å existing below 82 K. These distinct phases will be referred to as phase I and phase II, respectively. Chieux et al.[7] performed several low-temperature neutron powder diffraction (NPD) data collections on both $^7\mathrm{Li(NH_3)_4}$ and $^7\mathrm{Li(ND_3)_4}$ over the range 3–85 K using the D1B spectrometer at the Institut Laue-Langevin. They found that the protonated compound changed from phase I to phase II upon cooling from 85 to 60 K, which corroborates the previous X-ray studies, although the assignment of the lattice for phase II was different. However, no phase change was observed in the range 60–85 K for the deuterated compound. The diffraction patterns indicated that both phases were body-centered cubic (bcc), with $a = 15.03$ Å at 85 K and $a = 14.93$ Å at 60 K. This isotope effect has been verified by careful thermodynamic measurements.[8] Below 25 K, additional reflections appear in the diffraction patterns of $^7\mathrm{Li(ND_3)_4}$ corresponding to the formation of a superstructure having a period $2a$ (phase III), which coincides with the onset of antiferromagnetic behavior below about 25 K.[5,9] Although the study of Chieux et al.[7] has been the most informative structural investigation of this intriguing compound to date, no detailed structural analysis could be performed on the data due to overwhelming preferred orientation, as evidenced by the poor reproducibility of peak intensities (>30%). Recently, Stacy and Sienko[9] reevaluated all previous structural data. They found that the X-ray data for both phases I and II are better indexed as a single bcc phase and suggested the probable space group, $I\bar{4}3d$, as well as a hypothetical structure. The elucidation of the structure of $^7\mathrm{Li(ND_3)_4}$ above the antiferromagnetic transition temperature is the subject of this investigation. These results confirm the idealized model proposed by Stacey and Sienko.[9]

Table 1. Fractional Coordinates and Isotropic Thermal Parameters for $\mathrm{Li(ND_3)_4}$[a]

atom	x	y	z	U_{iso}
Li	1094 (6)	1094	1094	1.4 (4)
N(1)	2064 (2)	2064	2064	1.8 (1)
D(1)	2614 (4)	1749 (3)	2229 (3)	5.8 (2)
N(2)	1697 (2)	−79 (2)	1328 (2)	2.8 (1)
D(11)	2324 (4)	−119 (4)	1545 (3)	5.2 (2)
D(12)	1311 (3)	−472 (3)	1689 (3)	3.5 (1)
D(13)	1794 (3)	−379 (4)	718 (4)	5.8 (2)

[a] Fractional coordinates are listed in 10^4 Å. Isotropic thermal parameters are given in 10^2 Å^2.

The sample was prepared by condensing sodium-dried ND_3 (Cambridge Isotope Laboratories, 99.5%) into 7.5 cm × 1.2 cm i.d. quartz sample cells containing ^{7}Li (Oak Ridge, 99.94%), to yield 3.84 g of $^7\mathrm{Li(ND_3)_{4.0}}$. In addition, an ample amount of quartz wool was included in the sample cell to inhibit large crystal growth. Time-of-flight (TOF) NPD data were collected on the general purpose powder diffractometer[10] at IPNS. Initial data collections showed a high degree of preferred orientation, i.e., some reflections were present in some detectors and not in others. Most of this effect was eliminated by rotating the sample in 5° intervals (360° total coverage) while data were collected for 5 min/interval.

The structure was refined by using the generalized structure analysis system (GSAS).[11] The space group was uniquely determined to be $I\bar{4}3d$, with $a = 14.8131$ (28) Å. However, the coincidence of reflections caused by the bcc lattice hampered Patterson and direct-methods solution attempts. After considering how this tetrahedrally shaped molecule would have to fit into the asymmetric unit according to the constraints imposed by space-group requirements, we decided to begin refinement by using rigid bodies. An idealized $\mathrm{Li(ND_3)_4}$ unit was assembled while the Li atom and one N atom of an ND_3 group were kept on the body-diagonal axis, as required by space-group symmetry. Fractional coordinates were refined, while isotropic temperature factors were held constant at 0.06 Å^2. After this refinement converged, the reflections for interplanar spacings >1.4 Å fit well, but those <1.4

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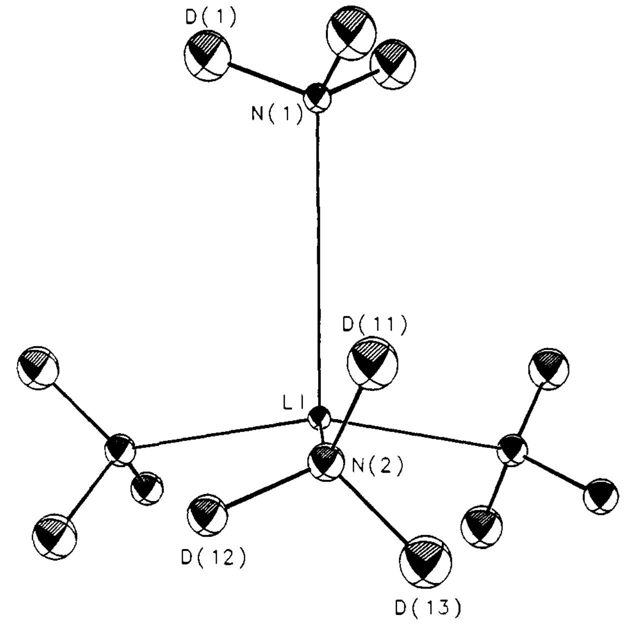

Figure 1. ORTEP drawing of $Li(ND_3)_4$. Selected bond distances and angles are as follows: Li–N(1) = 2.488 (16) Å; Li–N(2) = 1.984 (4) Å; N(1)–D(1) = 0.970 (5) Å; N(2)–D(11) = 0.985 (5) Å; N(2)–D(12) = 0.976 (4) Å; N(2)–D(13) = 1.018 (6) Å; N(1)–Li–N(2) = 98.4 (5)°; N(2)–Li–N(2) = 117.9 (2)°; D(1)–N(1)–D(1) = 108.3 (4)°; D(11)–N(2)–D(12) = 109.7 (5)°; D(11)–N(2)–D(13) = 97.4 (6)°; D(12)–N(2)–D(13) = 108.0 (5)°.

Å did not. Next, the rigid-body constraints were replaced with fractional-coordinate soft constraints while all N–D bonds were held at 1.01 (3) Å. This led to a solution having all but one D atom in chemically reasonable locations. Inclusion of data at higher *d* spacings from the 90° bank and evaluation of subsequent difference-Fourier maps led to a proper placement of the remaining D atom. A complete refinement of the structure, including absorption and neutron primary extinction corrections without the application of constraints, was then possible. Isotropic thermal parameters were refined, which led to a weighted residual (R_{wp}) of 4.66% for a combined refinement using both 148° and 90° banks of data.

The three-dimensional drawing shown in Figure 1 shows that all ammonia molecules of an individual $^7Li(ND_3)_4$ complex are coordinated to lithium. Therefore, there is not hydrogen bonding between these complexes in phase II. A most interesting aspect of this refinement is that one N atom bonds to the Li atom at a much longer distance (2.488 Å) than the other three (1.984 Å), so that the $Li(ND_3)_4$ complex has a distorted pyramidal shape. Therefore, this compound is perhaps better described by the formula $^7Li(ND_3)_3{\cdot}ND_3$. The more weakly bound ND_3 can provide some insight into the nature of the phase I–phase II transition that occurs at 82 K in $Li(NH_3)_4$. Upon warming, the weakly bound NH_3 molecules may reorient or become dissociated from the tetraamine unit, which could drive an order–disorder phase transition, as has been suggested for the phase I–phase II transition.[8] This structure determination for phase II permits band-structure and ab initio calculations to be undertaken and sets the stage for a similar refinement of the low-temperature antiferromagnetic phase III of $^7Li(ND_3)_4$. A full account of the structural refinement of phase II of $^7Li(ND_3)_4$ will be published elsewhere.[12]

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Supplementary Material Available: Final difference profile plots for the 148° and 90° detector banks, a table of intermolecular and intramolecular nonbonded distances, and TOF NPD peak profiles (23 pages); a listing of structure factors (5 pages). Ordering information is given on any current masthead page.

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Antibody Catalysis of a Diels–Alder Reaction[†]

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Recent studies have focused on the mammalian immune system as a source of highly specific, tailored catalysts. With transition-state analogues as haptens, it has been possible to elicit antibodies that promote a variety of chemical transformations, including ester and amide hydrolysis,[1,2] photochemical processes,[3] a sigmatropic rearrangement,[4] and a β-elimination.[5] We report here application of this strategy to the catalysis of a bimolecular [2 + 4] cycloaddition.

The Diels–Alder reaction is one of the most important and versatile transformations available to organic chemists for the construction of complex natural products, therapeutic agents, and synthetic materials of all kinds. It involves concerted addition of a conjugated diene to an olefin to give a cyclohexene derivative. The bimolecular process has a large entropic barrier, with activation entropies typically in the range −30 to −40 cal K^{-1} mol^{-1}.[6] Theoretical considerations suggest that it should be possible to pay for this substantial loss in translational and rotational entropy, and greatly accelerate the rate of reaction, by binding the two reactants together in an antibody combining site.[7]

The transition state of a Diels–Alder cycloaddition is highly ordered, resembling product more closely than starting material.[8]

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