

Dimeric piperidino-alane and -gallane: metal hydrides with a cyclic $M(\mu-N)_2M$ core ($M = Al$ or Ga)

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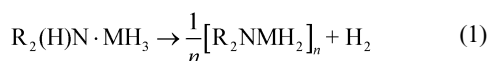
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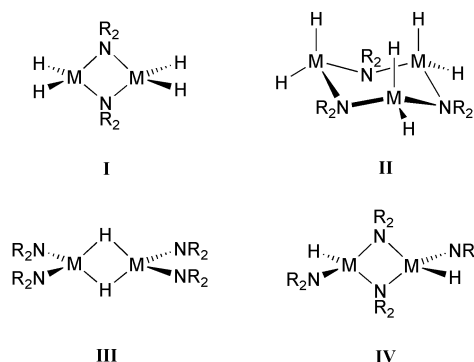
The crystal structures of piperidino-alane and -gallane at 150 K have each been shown to consist of dimeric molecules $[\overline{CH_2(CH_2)_4NMH_2}]_2$ centred on a planar, nearly square $M(\mu-N)_2M$ core ($M = Al$ or Ga). The molecular structures thus contrast with the hydrogen-bridged units favoured by the sterically encumbered piperidino derivatives $\{\overline{CMe_2(CH_2)_3CMe_2N}AlH_2\}_3$ and $\{\overline{CMe_2(CH_2)_3CMe_2N}AlH\}_2$ and are also compared with those of other amido derivatives of the Group 13 hydrides.

Amido compounds of the types R_2NMH_2 and $(R_2N)_2MH$ are among the most robust derivatives of the Group 13 hydrides MH_3 , where $M = B, Al$ or Ga .^{1–3} Access to them is usually gained *via* the adducts of the secondary amines $R_2(H)N \cdot MH_3$ and $R_2(H)N \cdot M(H)_2(NR_2)$. These eliminate dihydrogen to form the corresponding amidometal derivatives [as in eqn. (1)], with a facility that increases in the order $B < Ga < Al$.³ The derivatives are noteworthy for the diversity of structures they adopt and for their possible application as precursors to the binary nitrides MN .^{2,4}



The monomeric molecules R_2NMH_2 and $(R_2N)_2MH$ normally gain extra stability through augmenting the coordination of the metal centre in cyclic oligomers. The metal atoms are then bridged, usually by the amido but occasionally by hydrido⁵ ligands. A sufficiently bulky amido group may yet result in kinetic suppression of oligomerisation, but although the homoleptic amides $Al(NPr^t)_3$ and $Al[N(SiMe_3)_2]_3$ are indeed monomeric,¹ no examples of monomeric hydrido derivatives that are long-lived under normal conditions have been reported, so far as we are aware. Depending on the substituents R , oligomerisation yields either dimeric or trimeric products, usually with a cyclic M_2N_2 or M_3N_3 core, respectively. Increasing the bulk of R favours the dimeric structure **I**, as exemplified by $[Et_2NGaH_2]_2$ ⁶ and $[Me_2N(H)NGaH_2]_2$,⁷ or **IV**, as exemplified by $[HAl(NMe_2)_2]_2$,⁸ since these allow a greater separation between the substituents bound to M and those bound to nitrogen. When R is relatively compact, however, the trimeric structure **II** is preferred, as in $[Me_2NAlH_2]_3$ ⁹ and $[H_2NGaH_2]_3$,⁴ typically with a chairlike conformation for the 6-membered M_3N_3 ring. That the balance between dimeric and trimeric options may be a fine one is shown by dimethylamidogallane, Me_2NGaH_2 , which crystallises as a trimer¹⁰ yet vaporises at low pressure as a dimer.¹¹

The amido function may be a heterocyclic unit. Thus, various compounds of the type $[\overline{CH_2(CH_2)_xNMH_2}]_n$ ($x = 1–4$; $M = B, Al$ or Ga) were reported by Storr *et al.* in 1972.¹² Cryoscopic measurements on benzene solutions indicated degrees of association in the range $n = 2–3$. The gallium compound $\overline{CH_2CH_2NGaH_2}$ has been shown to crystallise as a trimer based on a cyclic chairlike Ga_3N_3 framework,¹³ but definitive structural information is otherwise quite sparse. Methyl groups have



been deliberately introduced into the 2 and 6 positions of the piperidine ring with the aim of increasing the bulk of the amido group in piperidinoalane derivatives.⁵ 2,6-Dimethylpiperidinoalane, $\overline{CHMe(CH_2)_3CHMeN}AlH_2$, is then reported to be a dimer in the solid state but disorder has prevented a fuller structural characterisation. By contrast, 2,2,6,6-tetramethylpiperidinoalane, $\overline{CMe_2(CH_2)_3CMe_2N}AlH_2$ [(tmp)AlH₂] appears on the evidence of its IR and NMR spectra⁵ to be a trimer, but with an Al_3H_3 cyclic skeleton akin to that found in $[Me_2AlH]_3$,¹⁴ rather than the normal Al_3N_3 unit. Such hydrogen-bridging has been confirmed in the bis(piperidino)alane, $(tmp)_2AlH$, the crystal structure of which⁵ is composed of dimeric units with a central $Al(\mu-H)_2Al$ framework (**III**) similar to that in $[Me_2AlH]_2$.¹⁴

Here we report the synthesis and X-ray structure analysis of the simple piperidino derivatives $\overline{CH_2(CH_2)_4NMH_2}$ for $M = Al$ and Ga which we show to be dimers with the piperidino ligands fulfilling the bridging role to produce cyclic $M(\mu-N)_2M$ skeletons.

Experimental

Synthesis of piperidino-alane and -gallane

Piperidinoalane, $\overline{CH_2(CH_2)_4N}AlH_2$, **1**, was prepared from freshly recrystallised $LiAlH_4$ (0.31 g, 8.1 mmol) and piperidinium chloride (0.78 g, 7.5 mmol) by the procedure used for the synthesis of dimethylamidogallane.⁹ The cold solution was filtered and the filtrate kept at 253 K over 3 weeks to give colourless crystals of **1**, which were stable *in vacuo* at temperatures up to *ca.* 273 K but decomposed rapidly at higher

Table 1 Crystal data, data collection and structure refinement for piperidinoalane, **1**, and piperidinogallane, **2**

Property	1	2
Space group	$P2_1/c$	$P2_1/c$
$a/\text{\AA}$	8.7898(12)	8.7830(18)
$b/\text{\AA}$	6.1163(8)	6.1200(12)
$c/\text{\AA}$	12.9233(17)	12.930(3)
$\beta/^\circ$	92.009(2)	92.87(3)
$V/\text{\AA}^3$	694.34(16)	694.1(2)
Z	2	2
Data/restraints/parameters	1419/1/70	1223/1/70
Conventional $R [F > 4\sigma(F)]$	R_1 0.0412 (1189 data)	R_1 0.0441 (1098 data)
Weighted $R (F^2$ and all data)	0.1202	0.1134
Largest difference peak and hole/ $e \text{\AA}^{-3}$	0.56, -0.24	1.08, -1.22

temperatures with the formation of dihydrogen and an aluminium mirror.

The corresponding gallium compound, **2**, was formed in a similar manner from freshly prepared¹⁵ LiGaH_4 (0.65 g, 8.1 mmol) and recrystallised piperidinium chloride (0.78 g, 7.5 mmol). Filtering of the solution and evaporation of the solvent gave the adduct $\overline{\text{CH}_2(\text{CH}_2)_4(\text{H})\text{N}}\cdot\text{GaH}_3$ as a white solid; heating this to 333 K *in vacuo* produced dihydrogen and colourless crystals of **2** which condensed on the walls of the reaction vessel.

The identities and purities of the two products **1** and **2** were checked by reference to their IR and Raman spectra and to the ^1H NMR spectra of $[\text{}^2\text{H}_8]$ toluene solutions and comparison with previous reports.¹² For X-ray analysis, crystals of **2** were selected and transferred under dry nitrogen at ambient temperatures; crystals of **1** were selected from under cold perfluoropolyether RS3000 oil.

X-Ray diffraction measurements

X-Ray data for **1** were collected on a Bruker SMART APEX diffractometer with a CCD area detector, those for **2** on a Stöe Stadi-4 four-circle diffractometer. In both cases, measurements were made with graphite-monochromated Mo- $K\alpha$ radiation, the crystals each being held at 150 K. Details of the data and data collection for crystals of **1** and **2** are given in Table 1.

Absorption corrections were performed using the program SADABS¹⁶ for **1** and ψ -scans for **2**, and both the crystal structures were solved by direct methods (SHELXTL).¹⁷ Hydrogen atoms attached to carbon were placed in calculated positions. The hydrogens attached to the metal atoms were readily located in a difference map in the case of the aluminium structure (see Fig. 1, top).¹⁸ The corresponding region in the map calculated for the gallium compound was much noisier (Fig. 1, bottom); the positions we propose for the hydrides in **2** are based on this map, but are evidently rather less certain than for the Al analogue. The hydride positions in both structures were refined with a similarity restraint placed on the M–H distances. All non-hydrogen atoms were modelled with anisotropic displacement parameters. The refinements proceeded by full-matrix least squares against F^2 (SHELXTL).

CCDC reference numbers 194729 and 194730.

See <http://www.rsc.org/suppdata/dt/b2/b209669m/> for crystallographic data in CIF or other electronic format.

Results and discussion

The conditions of formation of piperidinoalane and piperidinogallane illustrate well the enhanced susceptibility of secondary amine complexes of alane, compared with their gallane counterparts, to eliminate H_2 .^{3,10} Thus, $\overline{\text{CH}_2(\text{CH}_2)_4(\text{H})\text{N}}\cdot\text{AlH}_3$ eliminates H_2 spontaneously at sub-ambient temperatures (*ca.* 250 K), whereas the corresponding gallane can be isolated and is long-lived at ambient temperatures, H_2 elimination setting in

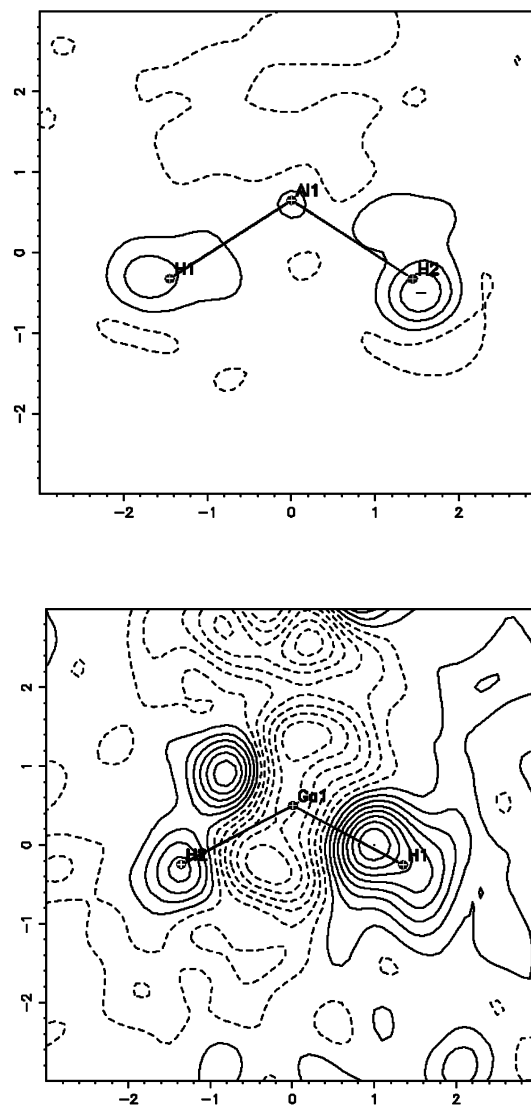


Fig. 1 Slant plane difference maps illustrating hydride location in **1** (top) and **2** (bottom). Both were obtained using phases based on all atoms except hydridic H1 and H2, and the final refined positions of these atoms are superimposed. Contours are drawn at an interval of $0.16 e \text{\AA}^{-3}$ for both maps; positive and negative contours are shown as solid and dashed lines, respectively.

at an appreciable rate only at temperatures in excess of 323 K. The elimination reaction appears not to be intramolecular but to depend on association between the N–H bond of one adduct molecule and the M–H bond of another, with non-classical hydrogen bonding^{10,19} through the resulting M–H...H–N interactions giving the first sign of H_2 formation. Such H...H interactions have been shown by both experiment and theory to be stronger for M = Al than for M = Ga, mainly because of the greater polarity of the Al–H bond.^{4,10,19}

Table 2 Selected bond distances (Å) and angles (°) for crystalline piperidinoalane, **1**, and piperidinogallane, **2**, at 150 K^a

Parameter	1 (M = Al)	2 (M = Ga)
M(1)–N(1)	1.9449(14)	2.011(3)
M(1)–N(1)#1	1.9410(14)	2.007(3)
M(1) ⋯ M(1)#1	2.7599(10)	2.8714(11)
M(1)–H(1)	1.751(16)	1.55(3)
M(1)–H(2)	1.745(16)	1.56(3)
N(1)–C(2)	1.496(2)	1.492(5)
N(1)–C(6)	1.489(2)	1.478(5)
C(2)–C(3)	1.521(3)	1.520(6)
C(3)–C(4)	1.516(3)	1.531(7)
C(4)–C(5)	1.514(3)	1.517(6)
C(5)–C(6)	1.520(2)	1.524(5)
N(1)–M(1)–N(1)#1	89.49(6)	88.79(13)
N(1)–M(1) ⋯ M(1)#1	44.69(4)	44.34(9)
N(1)#1–M(1) ⋯ M(1)#1	44.80(4)	44.45(9)
M(1)–N(1)–M(1)#1	90.51(6)	91.21(13)
H(1)–M(1)–H(2)	112.1(8)	122(2)
C(2)–N(1)–C(6)	109.13(13)	109.8(3)
C(6)–N(1)–M(1)#1	114.69(10)	114.5(2)
C(2)–N(1)–M(1)#1	115.33(11)	114.5(2)
C(6)–N(1)–M(1)	112.67(10)	112.5(2)
C(2)–N(1)–M(1)	113.61(10)	113.4(2)
N(1)–C(2)–C(3)	111.82(14)	111.7(3)
C(2)–C(3)–C(4)	111.24(16)	110.7(3)
C(3)–C(4)–C(5)	110.16(15)	110.1(3)
C(4)–C(5)–C(6)	110.58(15)	110.5(3)
N(1)–C(6)–C(5)	112.48(14)	112.1(3)

^a Atom numbering scheme as shown in Fig. 2. Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y, -z$. For the CH₂ groups, the C–H bond distances were fixed at 0.99 Å.

The two crystalline piperidino derivatives **1** and **2** are isomorphous, with very similar unit cell parameters and molecular dimensions. The molecular structure of **1** is illustrated in Fig. 2, and salient bond distances and angles for both **1** and **2** are listed

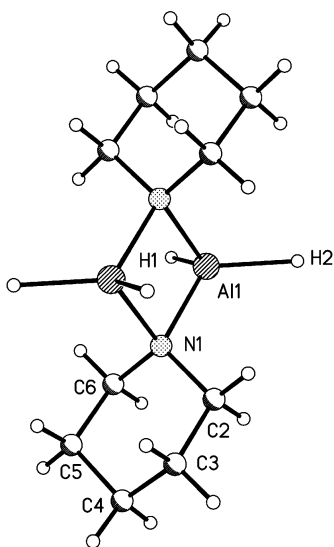


Fig. 2 Structure of the dimeric $[\overline{\text{CH}_2(\text{CH}_2)_4\text{NAlH}_2}]_2$ molecule in crystalline piperidinoalane, **1**, at 150 K as determined by X-ray diffraction.

in Table 2. Hence it is clear that the crystals are each composed of dimeric molecules $[\overline{\text{CH}_2(\text{CH}_2)_4\text{NMH}_2}]_2$ (M = Al or Ga) in which the central unit is a planar 4-membered $\text{M}(\mu\text{-N})_2\text{M}$ ring. The piperidino functions provide symmetrical bridges between the metal atoms to generate a $\text{H}_2\text{M}(\mu\text{-N})_2\text{MH}_2$ skeleton with a symmetry close to D_{2h} (see Fig. 2). The dimeric structure of the gallane is in keeping with that suggested by Storr *et al.*¹² on the evidence of solution studies. On the other hand, cryoscopic

measurements suggest that both dimeric and trimeric forms of the alane may coexist in benzene solutions.¹² Between the dimeric molecules of **1** and **2** there are no significantly short contacts to suggest secondary interactions comparable with those observed, for example, in crystalline cyclotrigallazane, $[\text{H}_2\text{NGaH}_2]_3$,⁴ and dimethylamine-alane, $\text{Me}_2(\text{H})\text{N}\cdot\text{H}_2\text{Al}(\mu\text{-H})_2\text{AlH}_2\cdot\text{N}(\text{H})\text{Me}_2$.¹⁰

The dimeric molecular structures thus contrast with the trimeric structure assumed in the crystalline state by the aziridinogallane, $[\overline{\text{CH}_2\text{CH}_2\text{NGaH}_2}]_3$,¹³ the compound most closely related to **1** and **2** for which definitive information is available. Presumably the greater spatial requirements of the piperidino compared with the relatively compact aziridino ligand are responsible for this change. Interestingly, therefore, increasing still further the spatial demands of the piperidino ligand by replacing all the hydrogens at the 2 and 6 positions with methyl groups is believed to result in a switch from amido- to hydrogen-bridging in the alane $[(\text{tmp})\text{AlH}_2]_3$.⁵

The dimensions of the central $\text{M}(\mu\text{-N})_2\text{M}$ cores of **1** and **2** conform to the pattern established for other amido-aluminium and -gallium derivatives featuring structures of this type. Thus, the cores appear in each case to be planar but slightly asymmetric, or rhombic, with one pair of M–N bonds differing in length by 0.003–0.004 Å from the other pair. In fact, with N–M–N bond angles of 89.49(6)° for **1** and 88.79(13)° for **2**, both central units are almost square. The average M–N distances [1.943(2) and 2.009(3) Å for **1** and **2**, respectively] fall well within the ranges observed for other neutral amido compounds containing $\text{M}(\mu\text{-N})_2\text{M}$ units, *viz.* 1.90–2.03 Å for Al and 1.96–2.10 Å for Ga.²⁰ Shorter distances are found when electron-withdrawing substituents, *e.g.* halogens, are attached to the metal; longer distances are typically the mark of bulky substituents at one or both centres. That the Ga–N bonds should also be slightly longer (0.066 Å) than the Al–N bonds is also consistent with the normal pattern, the average Al–N distance for 45 structures being 1.97(3) Å compared with an average Ga–N distance for 12 structures of 2.04(4) Å. By contrast, Al–P and Ga–P distances in analogous phosphido molecules containing $\text{M}(\mu\text{-P})_2\text{M}$ cyclic frameworks are not significantly different {2.43(3) Å for Al *vs.* 2.44(4) Å for Ga²⁰}.

Despite the decrease in the non-bonding interactions between the substituents on adjacent metal and nitrogen atoms, the M–N distances in the four-membered M_2N_2 ring are typically *longer* than those in the six-membered M_3N_3 ring. For example, the Ga–N bond in $[\text{Me}_2\text{NGaH}_2]_2$ is 0.046 Å longer than that in $[\text{Me}_2\text{NGaH}_2]_3$.¹⁰ It seems likely that cross-ring non-bonded repulsions between the nitrogen atoms, and possibly also between the metal atoms, play a significant part here. **1** and **2**, wholly representative dimeric amides, feature N ⋯ N distances of 2.736(3) and 2.811(6) Å and M ⋯ M distances of 2.7599(10) and 2.8714(11) Å, respectively, *i.e.* significantly short of the sums of the relevant van der Waals radii (namely, 3.10 Å for N and *ca.* 3.8 Å for both Al and Ga²¹). The N ⋯ N and M ⋯ M distances then contrast with those in the 6-membered M_3N_3 rings of $[\text{Me}_2\text{NAlH}_2]_3$ ⁹ and $[\text{Me}_2\text{NGaH}_2]_3$,¹⁰ which are typical trimeric amides. Here we find N ⋯ N distances averaging to 3.147(3) Å (M = Al) and 3.209(3) Å (M = Ga), *i.e.* slightly in excess of twice the van der Waals radius of N, and M ⋯ M distances averaging to 3.263(3) Å (M = Al) and 3.329(3) Å (M = Ga). Hence it seems that repulsive N ⋯ N interactions are the main factor counteracting the reduced interactions between the substituents and opposing the adoption of a dimeric rather than a trimeric structure.

The issue of potential non-bonded interactions has led us also to consider the effect of replacing by methyl groups all the hydrogen atoms at the 2 and 6 positions of the piperidino rings. As things stand, the shortest intramolecular C(2,6)–H ⋯ H–M contacts measure 3.06 and 2.97 Å for crystalline **1** and **2**, respectively; these are therefore greater than twice the van der Waals radius of H (2.40 Å²¹) and so give no hint of undue steric

congestion. Replacing the hydrogens at the 2,6-carbon atoms by four methyl groups which are assumed to take up a staggered orientation about the newly established C–C bonds is then calculated to give intramolecular M–H...H(methyl) contacts of 1.89 Å and 1.94 Å for M = Al and Ga, respectively. Such short distances clearly imply relatively strong repulsion between the hydrogen atoms bound to the metal and those of the methyl groups since there is little opportunity for H...H bonding.¹⁹ It is perfectly understandable therefore that (tmp)AlH₂ and (tmp)₂AlH should opt not for N-bridged but for H-bridged oligomeric forms.⁵

The M–H distances determined from Fourier difference maps also warrant some comment. The H atoms are not particularly obvious in difference maps of **2**, but give best estimates of the Ga–H distances of 1.55(3) Å. By contrast, the H atoms are clearly defined in the corresponding maps of **1**, giving a mean Al–H distance of 1.75(2) Å. As illustrated by the results of a search of the Cambridge Database²⁰ (see Fig. 3), Al–H and

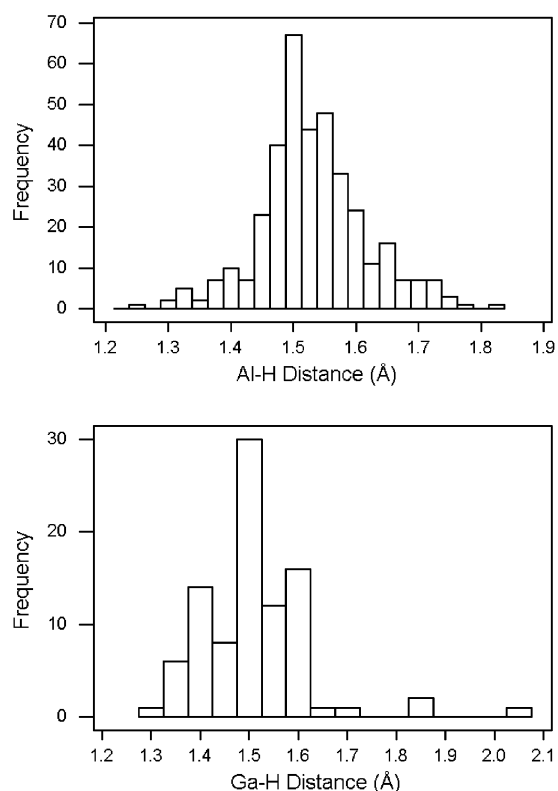


Fig. 3 Histograms of Al–H and Ga–H distances based on information held in the Cambridge Structural Database (version 5.23, April 2002 release).²⁰ The search fragment used consisted of a four-coordinate metal atom attached to a singly-coordinate hydrogen atom.

Ga–H distances are still relatively poorly defined. Admittedly some of the data carry large uncertainties, but the scale of the problem is made clear by the finding that redetermination of the same structure, e.g. that of [Me₂NAlH₂]₃,⁹ has been known to yield quite different results. According to the Database, the average (unweighted) Al–H and Ga–H distances are 1.53(9) and 1.51(11) Å, respectively. It follows that the results for the gallane, **2**, are quite unremarkable, but that the alane, **1**, appears to feature quite long Al–H bonds. Significantly, perhaps, the H–M–H angles are also different, being 112(1)° for **1** and 122(2)° for **2**. Unfortunately the high scatter observed for these parameters in the Cambridge Database meant that no meaningful systematic correlation could be derived from the structural data on related molecules. However, the difference in the MH₂ geometries observed here for **1** and **2** may imply reduced metal ns character in the Al–H bonds of **1** and the accumulation of

an appreciable negative charge on the (μ-N)₂AlH₂ units, charge transfer undoubtedly being enhanced by the polar environment of the molecules in the solid.^{19,22} Unfortunately the reactivity, thermal instability and involatility of the compound have combined to frustrate attempts to measure the IR or Raman spectrum of the crystalline solid. A resolution of this potentially interesting feature must, it appears, await neutron diffraction studies.

The geometries of the piperidino fragments in **1** and **2** relay little additional information. There is no significant difference between them, and the chair conformation and dimensions are, within experimental error, similar to those in other bridging piperidino derivatives,²⁰ although the CN bonds [1.478(5)–1.496(2) Å] are somewhat longer than in piperidine itself [1.4608(8) Å].²³

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