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Neutron Diffraction Study of $[Nd(AlMe_4)_3]\cdot 0.5\,Al_2Me_6$ at 100 K: The First Detailed Look at a Bridging Methyl Group with a Trigonal-Bipyramidal Carbon Atom**

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Pentacoordinate carbon is an unusual entity. When it is observed, it exists in the form of a bridging alkyl group[1] or, in a few rare cases, as an interstitial atom in a metal cluster complex.[2] Although several examples of bridging alkyl groups have been structurally characterized,[3–15] the hydrogen atoms associated with such bridges have not always been located in the X-ray diffraction studies. We describe here the first example of a bridging methyl group structurally characterized with neutron diffraction[4] and show that it can adopt a trigonal-bipyramidal-like geometry.

The title compound **1** is the mixed-metal complex $[Nd(AlMe_4)_3]$ (isolated as a cocrystalite with Al_2Me_6),[8] which contains asymmetrical methyl bridges between neodymium and aluminum atoms. Pale purple-blue crystals of **1** were produced by the reaction of excess Al_2Me_6 with $[Nd(NMe_2)_3(LiCl)_3]$[8] and recrystallized from hexane. The transportation and mounting of the crystals for neutron diffraction was challenging because of the moisture and temperature sensitivity of the sample (it decomposes above −40°C).[16] The crystal was mounted in a specially designed anaerobic coldbox. A crystal with approximate volume 1.0 mm^3 was sealed in an aluminum container under a helium atmosphere and cooled to 100 K for neutron data collection. A total of 4535 reflections were scanned and refinement of the structure with 4013 independent F_o^2 values yielded final agreement factors of $R = 0.142$ and $R_w = 0.139$ based on 3σ data.[17] Despite the fact that these values are relatively high (due to the small size of the crystal and also possibly due to partial decomposition during the difficult crystal-mounting procedure), the final geometrical results (distances, angles, and their esd's) are quite respectable.

A molecular plot of the structure (Figure 1) shows the sixfold coordination of carbon atoms around neodymium. Each $AlMe_4$ unit is coordinated to the central Nd atom through two bridging methyl groups, which in turn are oriented such that two of their three H atoms are directed at the Nd atom. The coordination number around Nd is either six (if only Nd–C bonds are counted) or eighteen (if Nd⋯H interactions are included). Apparently, it is the steric unsaturation of the larger Nd^{III} atom rather than the enhanced Lewis

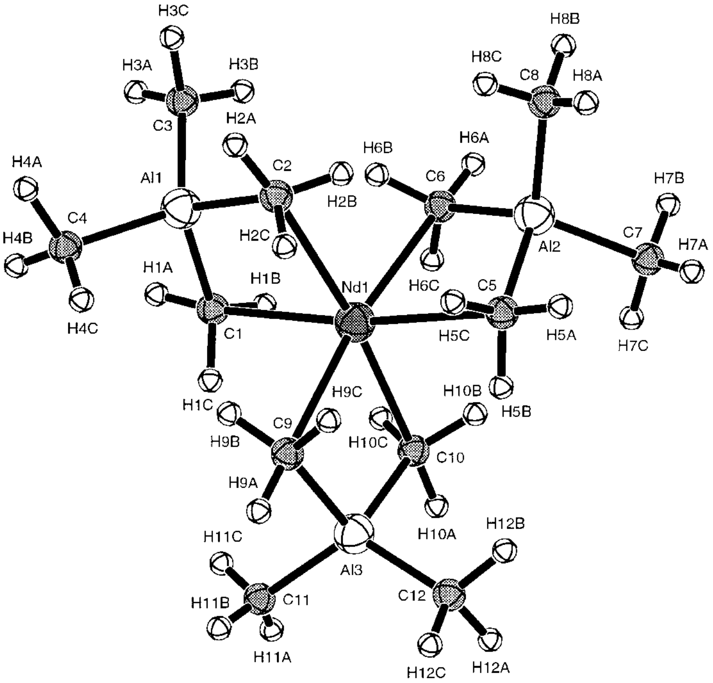

Figure 1. Stucture of $[Nd(AlMe_4)_3]$ as determined by single-crystal neutron diffraction. Each methyl group is oriented such that one hydrogen atom (labeled $H1_A$, $H2_A$, etc.) is essentially *trans* to the Nd atom. Average distances [Å] and angles [°]: Nd–C 2.598(11), Nd–H 2.649(13), Nd–Al 3.138(10), Al–C(bridge) 2.087(11), Al–C(terminal) 2.006(11), C–H_A 1.09(1), C–$H_{B,C}$ 1.08(1); Nd-C-H_A 173.8(8), H_B-C-H_C 107.4(9), Al-C-$H_{B,C}$ 123.2(9), Nd-C-Al 83.4(4), Nd-C-$H_{B,C}$ 80.3(4), Al-C-H_A 91.2(10), H_A-C-$H_{B,C}$ 102.2(14).

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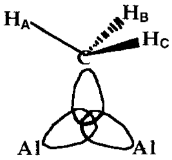
acidity of the Al^{III} center, which directs the methyl hydrogen atoms towards neodymium rather than aluminum.

The most significant feature about the structure of **1** is the fact that the carbon atoms of the bridging methyl groups adopt approximately trigonal-bipyramidal (tbp) configurations. In each of the six methyl bridges, one of the three hydrogens (labeled $H1_A$, $H2_A$, etc.) is essentially trans to the Nd atom (average Nd-C-H_A angle 173.8(8)°). Thus, Nd and H_A take up the axial positions of the tbp, while Al, H_B, and H_C occupy the equatorial positions (Figure 1). All other molecular parameters are as expected.[18]

The present structure determination is the first neutron diffraction study of a compound with bona fide *intramolecular* methyl bridges. As mentioned in reference [4], a weak intermolecular methyl interaction of the type $Si{-}CH_3\cdots Mg$ was observed in polymeric $[Mg\{CH(SiMe_3)_2\}_2]$ by single-crystal neutron diffraction.[6] In that case, the carbon atoms were also found to be distorted trigonal-bipyramidal, but of a different type with equatorial H atoms and axial positions occupied by Si and a relatively long C$\cdots$Mg interaction (2.535(4) Å). Another example is illustrated by the neutron analysis of tetrameric $[Li(BMe_4)]$ in which intermolecular $B{-}CH_3\cdots Li$ interactions were found.[7]

Low-temperature X-ray analysis of the heteroleptic complex $[Nd(N\mathit{i}Pr_2)\{(\mu\text{-}N\mathit{i}Pr_2)(\mu\text{-}Me)AlMe_2\}\{(\mu\text{-}Me)_2AlMe_2\}]$[10] revealed an analogous orientation of the hydrogen atoms of the bridging methyl groups as in **1**. In contrast, the methyl bridge found in the low-temperature X-ray analysis of Al_2Me_6 adopts a symmetric (and hence different) geometry, whereby the pseudo-C_3 rotation axis of the bridging CH_3 group bisects the Al-C-Al angle (**I**).[9] The bonding in Al_2Me_6 is generally accepted to be of the usual three-center two-electron type, involving a three-center overlap of two Al orbitals and an sp^3 hybrid orbital from carbon. In $[\{(C_5H_5)_2Y(CH_3)\}_2]$ the H atoms in the symmetrical Y-CH_3-Y bridge are arranged in a manner similar to **I**,[11] while in other complexes of the type $[(C_5R_5)_2Ln(AlMe_4)]$ (with Ln-CH_3-Al bridges) the H atoms were not located.[3, 12] Related structures include compounds with linear symmetric Zr-CH_3-Zr[13] and Lu-CH_3-Lu[14] bridges, and one compound with a linear asymmetrical $Yb{-}CH_3\cdots Be$[15] bridge, all involving C atoms in tbp configurations with equatorial hydrogen atoms.

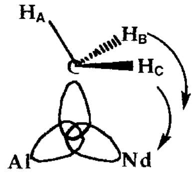


I

It is interesting to note that the tbp geometry of the carbon atom in $[Nd(AlMe_4)_3]$ bears a superficial resemblance to a carbon atom in an S_N2 transition state. Although there is a fundamental difference (the S_N2 transition state being a ten-electron system while the bridging methyl group in **1** represents an eight-electron system), the validity of the atomic geometry for this type of five-coordinate carbon is established.

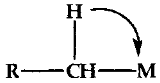
The main Nd-C bonding in $[Nd(AlMe_4)_3]$ is almost certainly augmented by Nd$\cdots$H interactions involving the H_B and H_C atoms. These interactions are presumably weak: a normal bridging Nd–H bond length can be estimated from the Nd^{III} ionic radius[19] to range from 2.23–2.36 Å, based on the value for Th–H of 2.29(3) Å measured from the neutron analysis of $[\{ThH_2Cp^*_2\}_2]$.[21] In contrast, the Nd–H distances in **1**, ranging from 2.58(2) to 2.75(2) Å, are quite long and correspond to weaker-than-covalent bonding forces, probably of the agostic variety (vide infra).[23]

The apparent tbp coordination of the carbon atom is intriguing. Trigonal-bipyramidal coordination normally corresponds to sp^3d hybridization, but this is obviously not an option for carbon. In **1** the "axial" C–H_A distances (average 1.09(1) Å) are not perceptibly different from the "equatorial" C–$H_{B,C}$ distances (average 1.08(1) Å), which would have been expected for a normal tbp geometry. Perhaps one way of rationalizing the bonding in **1** is to start with the "normal" symmetric bridge (as found in **I**) and then to imagine the CH_3 group being "tipped" towards Nd to accommodate additional C–H$\cdots$Nd agostic interactions (**II**), Nd-C-$H_{B,C}$ 80.3(4)°).



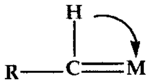
II

This "tipping" (or tilting) towards the large Lewis acidic Nd center results in a nearly linear Nd-C-H_A angle of 173.8°, as opposed to an angle of 147.5° expected for a symmetrical bridge of type **I**. Such a "tipped" geometry has been found in several structures suspected to have C–H$\cdots$M agostic interactions, mostly metal–alkyl (**III**) or metal–alkylidene (**IV**) complexes involving the early transition metals Ti and Ta.[24] In those molecules, the existence of agostic interactions between C–H bonds and electron-deficient metal atoms is manifested by highly distorted and unusually small M-C-H angles.



$R{-}\overset{H}{CH}{-}M$

III



$R{-}\overset{H}{C}{=}M$

IV

Finally, we should include a few words about the Al_2Me_6 "solvate" molecule present in the crystal. The terminal Al4–C14 and Al4–C15 distances are similar to those found in $[Nd(AlMe_4)_3]$, but the bridging Al4–C13 distance is longer (2.17(3) Å). The Al4-C13-Al4′ angle is 72.8(13)°, close to the value of 75.7° observed in the low-temperature X-ray study of Al_2Me_6.[9c] However, only two out of the three H atoms could be located at the bridging position C13. Given their location, this strongly suggests that the Al_2Me_6 solvate molecule is disordered—a feature of the structure that unfortunately could not be conclusively resolved in this study. Our attempts to model this disorder are described in the details of the structure analysis.[17]

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[17] Full details (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-100847. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

[18] The principal distances and angles in **1** are similar to those reported earlier in the X-ray study.[8] From the present neutron study, the six Nd–C distances range from 2.58(2) to 2.64(2) Å, and the Al–C distances range from 1.97(3) to 2.12(3). The angles involving the nonbridging methyl groups, C3-Al1-C4, C7-Al2-C8, and C11-Al3-C12 (119.2(15), 116.8(13), and 119.0(13)°, respectively), are considerably larger than the other C-Al-C angles.

[19] The bridging Nd–H distance can be estimated from the difference between Nd–C (2.77 Å)[20] and Th–C (2.83 Å)[21] bond lengths in various Nd and Th cyclopentadienyl complexes, combined with the bridging Th–H distance (2.29 Å) in $[\{ThH_2Cp^*_2\}_2]$.[21] This yields a value for Nd–H bond distance of 2.23 Å. Alternatively, if the difference between the ionic radii[22] of Nd^{III} (1.16 Å, nine-coordinate) and Th^{IV} (1.09 Å) is used, an estimated Nd–H distance of 2.36 Å is obtained.

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Two-Dimensional Nitroxide-Based Molecular Magnetic Materials[**]

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The temperature at which molecular solids exhibit macroscopic magnetic properties is strongly dependent on the dimensionality of the structure and on the magnitude of the exchange interactions between the spin carriers.[1] Only a few species meet the criteria at room temperature, namely, hexacyanometalates[2, 3] and an adduct of vanadium and tetracyanoethylene;[4] they exhibit ferro- or ferrimagnetic ordering. In these compounds a three-dimensional structure and a fairly strong exchange coupling are probably the cause of high-temperature magnetic ordering.

Most strategies for designing molecular magnetic materials involve antiferromagnetically coupled alternating metal ions with different spins that do not compensate one another. These ferrimagnetic structures are assembled with polydentate bridging ligands such as oxalato, oxamato, oxamido, oximato, and dithiooxalato groups.[5] The use of these ligands has been fruitful, and several structures of high dimensionality have been reported. These include a few three-dimensional structures in which control over the chirality of the coordination sphere of the metal was achieved.[6–8] However, the Curie temperatures of these materials are low because the compounds contain either diamagnetic bridging ligands, which are poor mediators of the magnetic interactions, or diamagnetic metal ions.

In contrast, the metal-radical approach[9, 10] exploits the direct coordination of a ligand atom of high spin density to the

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