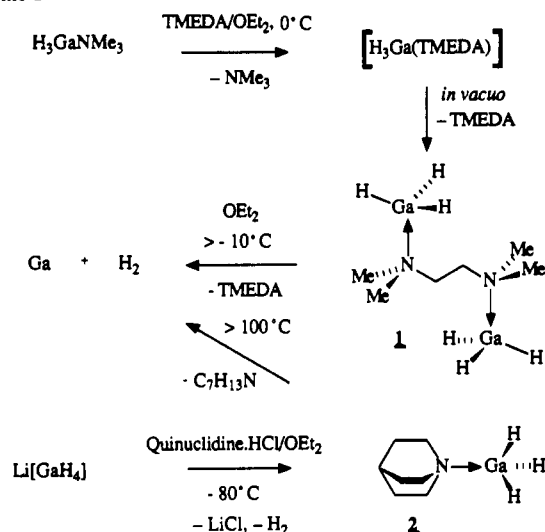


Scheme I



Compound **1** slowly decomposes in solution above  $-10^\circ\text{C}$  and in the solid at ca  $20^\circ\text{C}$  to gallium metal, hydrogen and amine, as for the related compound,  $\text{H}_3\text{GaNMe}_3$ .<sup>8</sup> In contrast, the 1:1 adduct is stable for days at room temperature in solution and in the solid. We have also attempted to prepare other gallane/polydentate tertiary amine adducts, namely those based on (-)-sparteine and  $N,N,N',N'',N'''$ -pentamethyldiethylenetriamine. Although adducts are formed at low temperatures they rapidly decompose to gallium close to ca.  $20^\circ\text{C}$ . Overall, polydentate amines seemingly destabilize gallane; the opposite prevails for alane.<sup>10</sup> Quinuclidine is a unidentate amine that enhances the stability of gallane relative to  $\text{H}_3\text{GaNMe}_3$ , most likely because it is a stronger base. Its adduct, **2**, has remarkable thermal stability, being stable for months at room temperature, subliming in vacuo at  $65$ – $70^\circ\text{C}$ , and decomposing only above ca.  $100^\circ\text{C}$ .

Results of the X-ray structure determinations of **1** and **2**<sup>11</sup> are presented in Figure 1. Both are comprised of discrete molecules possessing a crystallographic inversion center, *i*, or mirror plane,  $\sigma$ , so that the metal centers in **1** are remote, ruling out intramolecular hydride bridging. The Ga–N distances, 2.094 (4) Å in **1** and 2.063 (4) Å in **2**, reflect the differences in thermal stability of the two compounds and amine base strength, and compare with 2.124 (7) Å for the analogous distance derived from the gas-phase structure determination of  $\text{H}_3\text{GaNMe}_3$ .<sup>12</sup> (An inaccurate and incomplete X-ray structure determination on this compound yielded Ga–N = 1.97 (9) Å.<sup>4</sup>) Given that aluminum and gallium have the same covalent radius, it is interesting to note that an Al–N distance of 2.063 (8) Å in the related compound  $\text{H}_3\text{AlNMe}_3$  (2.063 (8) Å gas phase)<sup>13</sup> is consistent with it possessing similar thermal stability relative to **2** yet greater thermal stability relative

to **1**. The hydrido groups and *N*-alkyl substituents are staggered in both compounds.

**Acknowledgment.** We gratefully acknowledge support of this work by the Australian Research Council.

**Supplementary Material Available:** Tables listing atomic positional parameters, ligand hydrogen atom parameters, anisotropic thermal parameters, extended metal core geometries, and ligand non-hydrogen geometries (5 pages); tables of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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## Synthesis and X-ray Crystal Structure of a $\text{C}_2\text{B}_4$ "Carbons Apart" Carborane Dianion.

### 2,4-Bis(trimethylsilyl)-2,4-dicarbido-*nido*-hexaborate(2-): A New Synthron in Organometallics

The dianions of the *nido*-carboranes, particularly of the  $\text{C}_2\text{B}_4$ ,  $\text{C}_2\text{B}_5$ , and  $\text{C}_2\text{B}_{10}$  systems, have been the building blocks of a wide variety of metallocarboranes of main group and transition metals.<sup>1</sup> However, X-ray structural information is available for only a few selected monoanions<sup>2–6</sup> and for an unusual bis[triphenylmethylphosphonium] salt of the bis(carborane), which is, in fact, closely related to the structure of the most stable isomer of  $[\text{nido-C}_2\text{B}_{10}\text{H}_{13}]^-$  anion with 0941 *styx* topology.<sup>7</sup> Unlike the *nido-C}\_2\text{B}\_9 and *nido-C}\_2\text{B}\_{10} carborane systems, only the dillithium and sodium lithium salts of the "carbons adjacent" *nido-C}\_2\text{B}\_4* carborane dianions have been synthesized, and the corresponding disodium salt could not be made.<sup>8</sup> However, the new dianion  $[\text{nido-2,4-(Me)}_2\text{-2,4-C}_2\text{B}_4\text{H}_4]^{2-}$  (I) was made recently via the two-electron reduction of *closo*-1,6-(Me)<sub>2</sub>-1,6- $\text{C}_2\text{B}_4\text{H}_4$  (II) in the presence of lithium naphthalide in THF, and its "carbons apart" geometry was assigned on the basis of <sup>11</sup>B NMR spectroscopy and ab initio/IGLO calculations.<sup>9</sup> Nevertheless, the crystal structures**

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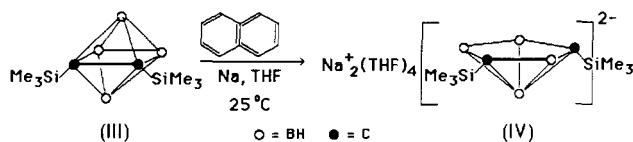
(11) Crystallographic data ( $T = 296\text{ K}$ ; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries): for compound **1**,  $\text{C}_7\text{H}_{22}\text{Ga}_2\text{N}_2$ ,  $M = 261.7$ , monoclinic, space group  $P2_1/n$ ,  $a = 5.891$  (6) Å,  $b = 17.073$  (2) Å,  $c = 6.728$  (1) Å,  $\beta = 114.161$  (9)°,  $V = 617.5$  (27) Å<sup>3</sup>,  $F(000) = 268$ ,  $Z = 2$ ,  $D_c = 1.413\text{ g cm}^{-3}$ ,  $\mu(\text{Cu K}\alpha) = 49.5\text{ cm}^{-1}$ ,  $A^* = 0.71$ – $0.92$ , specimen dimensions  $0.08 \times 0.31 \times 0.42\text{ mm}$ , 821 unique reflections, 737 with  $I > 3\sigma(I)$  used in the refinement,  $2\theta_{\text{max}} = 110^\circ$ ; for compound **2**,  $\text{C}_7\text{H}_{16}\text{GaN}$ ,  $M = 184.0$ , monoclinic, space group  $P2_1/m$ ,  $a = 6.1276$  (7) Å,  $b = 9.058$  (1) Å,  $c = 8.226$  (1) Å,  $\beta = 98.24$  (1)°,  $V = 451.9$  (6) Å<sup>3</sup>,  $F(000) = 192$ ,  $Z = 2$ ,  $D_c = 1.357\text{ g cm}^{-3}$ ,  $\mu(\text{Cu K}\alpha) = 29.7\text{ cm}^{-1}$ ,  $A^* = 0.75$ – $0.98$ , specimen dimensions  $0.06 \times 0.21 \times 0.24\text{ mm}$ , 861 unique reflections, 680 with  $I > 3\sigma(I)$  used in the refinement,  $2\theta_{\text{max}} = 110^\circ$ . The structures were solved with the heavy-atom method and refined by full-matrix least-squares refinement with non-hydrogen atoms anisotropic. Hydrogen atoms were located on difference maps and included as invariants for **1** or refined in  $x, y, z$  for **2**. Unit weights were used and the final residuals were  $R = 0.042$  and  $0.029$  and  $R' = 0.046$  and  $0.030$ , for **1** and **2**, respectively.

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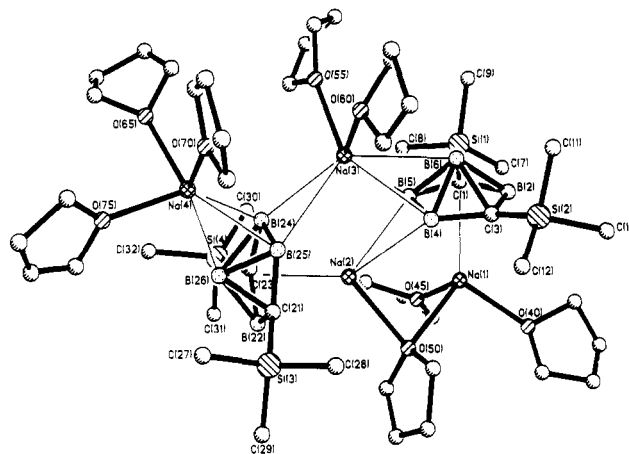
Scheme I



of dianions of the *nido*- $\text{C}_2\text{B}_4$  carborane systems have not been reported to date.<sup>10</sup>

Noting that II possesses the anticipated thermodynamically most stable structure,<sup>11</sup> the question arose whether a "carbons adjacent" analogue, *closo*-1,2- $\text{C}_2\text{B}_4\text{H}_6$ , would also yield the same "carbons apart" configuration. A comparable reduction of such an analogue *closo*-1,2-( $\text{SiMe}_3$ )<sub>2</sub>-1,2- $\text{C}_2\text{B}_4\text{H}_4$  (III)<sup>12</sup> with lithium naphthalide gave the similar "carbons apart" dianion [*nido*-2,4-( $\text{SiMe}_3$ )<sub>2</sub>-2,4- $\text{C}_2\text{B}_4\text{H}_4$ ]<sup>2-</sup> (IV) in virtually quantitative yield. Here, we report (i) the high-yield synthesis of the disodium salt of the dianion IV and (ii) the X-ray crystal structure of this compound to confirm the previously proposed "carbons apart" structure.<sup>9</sup>

The instantaneous two-electron reduction of *closo*-1,2-( $\text{SiMe}_3$ )<sub>2</sub>-1,2- $\text{C}_2\text{B}_4\text{H}_4$  (III) with sodium naphthalide in THF produced the novel, dimeric cluster  $\{\text{Na}_2^+(\text{THF})_4[2,4-(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]^{2-}\}_2$  (V) as a transparent crystalline solid in almost quantitative yield (see Scheme I).<sup>13</sup> The loss of all the THF molecules from V during the washing with dry *n*-hexane and then drying in vacuo resulted in the conversion of the crystalline solid into the amorphous powder  $\text{Na}_2^+[2,4-(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]^{2-}$  (IV). This posed a challenging task of determining the crystal structure of V since the THF's are likely to be desolvated from the crystal lattice that could result in disordering of these molecules, and consequently, increasing the *R* factor. As indicated in the crystallographic data, some of the



**Figure 1.** Perspective view of V showing the atom-numbering scheme. Pertinent parameters: Na(1)–C(1) = 2.667 (15), Na(1)–B(2) = 2.751 (18), Na(1)–C(3) = 2.796 (15), Na(1)–B(4) = 2.795 (18), Na(1)–B(5) = 2.708 (17), Na(1)– $\text{C}_2\text{B}_3$  centroid(1) = 2.38, Na(1)–O(40) = 2.299 (13), Na(1)–O(45) = 2.354 (14), Na(1)–O(50) = 2.530 (12), Na(2)–C(21) = 2.661 (14), Na(2)–B(22) = 2.676 (19), Na(2)–C(23) = 2.679 (14), Na(2)–B(24) = 2.765 (18), Na(2)–B(25) = 2.761 (17), Na(2)– $\text{C}_2\text{B}_3$  centroid(2) = 2.34, Na(2)–B(4) = 2.647 (17), Na(2)–B(5) = 2.801 (16), Na(2)–O(50) = 2.487 (12), Na(3)–B(4) = 2.799 (16), Na(3)–B(5) = 2.774 (18), Na(3)–B(6) = 3.103 (20), Na(3)–B(24) = 2.736 (19), Na(3)–B(25) = 3.064 (17), Na(3)–O(55) = 2.356 (14), Na(3)–O(60) = 2.357 (16), Na(4)–B(24) = 2.875 (19), Na(4)–B(25) = 2.743 (17), Na(4)–B(26) = 2.740 (18), Na(4)–O(65) = 2.325 (17), Na(4)–O(70) = 2.325 (15), and Na(4)–O(75) = 2.316 (14) Å; centroid(1)–Na(1)–O(40) = 125.5, centroid(1)–Na(1)–O(45) = 126.7, centroid(1)–Na(1)–O(50) = 113.6, and centroid(2)–Na(2)–O(50) = 132.5°.

carbon atoms of THF molecules are, in fact, disordered without significantly affecting the thermal parameters of their oxygens, the polyhedral cage atoms, and the sodiums (see Supplementary Table 5). These are precisely the atoms that constitute the carborane cage geometry, and give the locations of the sodium cations and the THF molecules. Therefore, Figure 1 represents the reasonable structure for the compound as found in the X-ray analysis of V.<sup>14</sup>

The crystal structure reveals that V is a dimeric  $\{\text{Na}_2^+(\text{THF})_4[2,4-(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]^{2-}\}_2$  cluster that is packed as discrete units in the unit cell. One of the sodium atoms [Na(1) or Na(2)] in each dianionic cluster within the dimeric unit adopts an essentially  $\eta^5$ -bonding posture with respect to the  $\text{C}_2\text{B}_3$  face with the metal to cage distances ranging from 2.661 to 2.796 Å and metal to  $\text{C}_2\text{B}_3$ -centroid distances of 2.34–2.38 Å that indicate that a significant interaction exists between the sodium and cage atoms. However, these distances are greater than those expected for covalent bonding, indicating that the interactions are all essentially ionic. It is also clear from Figure 1 that Na(2) interacts with the two nonunique boron atoms [B(4) and B(5)] of the neighboring cage as well, with distances of 2.647 (17) and 2.801 (16) Å. The Na(3) and Na(4) represent exopolyhedral cations of carborane cages 1 and 2, respectively. Although each of them interacts with

(10) More recently, the X-ray structures of *closo*-lanthanacarboranes such as 1,1,1,1-(THF)<sub>4</sub>-1,2,3-LnC<sub>2</sub>B<sub>9</sub>H<sub>11</sub> and 1,1,1,1-(THF)<sub>4</sub>-1,2,4-LnC<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (Ln = Sm or Yb), and *closo*-alkaline-earth metallacarboranes, 1,1,1,1-(MeCN)<sub>4</sub>-1,2,4-CaC<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, and polymeric 1,1,1-(MeCN)<sub>3</sub>-1,2,4-SrC<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, have been determined. On the basis of the splitting of the B–H stretching bands in their IR spectra, it was concluded that strong ionic interactions, in addition to covalent bonding, exist between the cationic metal center and the anionic carborane unit: Manning, M. J.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1988, 110, 4458; Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1990, 112, 4962; *Inorg. Chem.* 1990, 29, 2191 and references therein. However, the previously reported X-ray structures of metallacarboranes, derived from  $\text{C}_2\text{B}_4$  carborane dianions, involved strongly complexed metal systems.<sup>1</sup>

(11) Carbons are found in lowest coordinated sites and separated if alternative sites are available: Williams, R. E.; Gerhart, F. J. *J. Am. Chem. Soc.* 1965, 87, 3513.

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(13) A 2.34-mmol (0.51-g) sample of *closo*-1,2-( $\text{SiMe}_3$ )<sub>2</sub>-1,2- $\text{C}_2\text{B}_4\text{H}_4$  (III) was allowed to react with 5.85 mmol (0.134 g) of freshly cut sodium metal and 4.68 mmol of anhydrous naphthalene (0.599 g) in dry THF (10 mL) at room temperature for few minutes during which time the heterogeneous mixture of the reactants turned dark green. The <sup>11</sup>B NMR spectrum of this mixture, which was run after 10 min of reaction at room temperature, indicated that the *closo*-carborane III was completely consumed in the reaction. At this point, the green solution in the flask was filtered in vacuo and all the volatiles including naphthalene were removed from the filtrate at 60 °C, leaving behind a yellow-brown solid of the dianion, which was later identified as moderately air-stable  $\text{Na}_2^+[2,4-(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]^{2-}$  (0.594 g, 2.25 mmol; 96% yield; mp 263 °C; soluble in polar solvents only). This solid was washed repeatedly with dry *n*-hexane and dried in vacuo and then dissolved in a minimum quantity of dry THF to obtain colorless and transparent crystals of the dimeric dianion  $\{\text{Na}_2^+(\text{THF})_4[2,4-(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]^{2-}\}_2$  (V) for X-ray analysis. The spectroscopic data for V: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, relative to external Me<sub>4</sub>Si) δ 3.67 (s (br), 8 H, THF), 1.73 (s (br), 8 H, THF), 0.22 (s, 9 H, SiMe<sub>3</sub>); <sup>11</sup>B NMR (THF-*d*<sub>8</sub>, relative to external BF<sub>3</sub>·OEt<sub>2</sub>) δ 30.02 [br, ill-defined peak, 1 B, basal BH, <sup>1</sup>J(<sup>11</sup>B–H) – unresolved], 8.12 [d (br), 2 B, basal BH, <sup>1</sup>J(<sup>11</sup>B–H) = 115.1 Hz], –45.86 [d, 1 B, apical BH, <sup>1</sup>J(<sup>11</sup>B–H) = 159.8 Hz]; <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, relative to external Me<sub>4</sub>Si) δ 127.68 [s (br), cage carbons (SiCB)], 66.73 [m, THF], 24.62 [m, THF], 1.38 [q (br), SiMe<sub>3</sub>, <sup>1</sup>J(<sup>13</sup>C–H) = 118.5 Hz]; IR [cm<sup>–1</sup>, THF-*d*<sub>8</sub> vs THF-*d*<sub>8</sub>] 2500 (vs), 2445 (sh) [ν(B–H)].

(14) Since the dimer (V) (C<sub>48</sub>H<sub>108</sub>B<sub>8</sub>O<sub>8</sub>Si<sub>4</sub>Na<sub>4</sub>, fw = 1104.15) is composed of 72 atoms excluding hydrogens and without any heavy metal atoms, the X-ray analysis of this compound was fairly difficult. Suitable crystals of V were sealed in 0.7 mm capillary tubes under an atmosphere of dry THF. A 230 K data set was collected on the crystal of orthorhombic space group *Pbca* with the following unit cell parameters: *a* = 20.241 (9) Å, *b* = 16.505 (7) Å, *c* = 42.649 (16) Å, *V* = 14248 (10) Å<sup>3</sup>, *Z* = 8, *D*<sub>calcd</sub> = 1.02 g cm<sup>–3</sup>, and *μ* = 0.142 mm<sup>–1</sup>. A total of 7179 reflections were collected on Siemens R3m/V diffractometer, and the structure was solved by direct methods programs used in SHELXTL-PLUS; Sheldrick, G. M. *Structure Determination Software Programs*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990). All non-H atoms, except eight carbon atoms of two THF molecules, were refined anisotropically, and BLOC techniques in SHELXTL-PLUS were applied. However, during the refinement the C–C and C–O bond distances of the disordered THF molecules were constrained. Final refinement of V converged at *R* = 0.097, and *R*<sub>w</sub> = 0.11 for 2741 observed (*I* > 3.0σ(*I*)) reflections.

the two nonunique borons and one apical boron of their respective cages with the distances ranging from 2.736 to 3.103 Å, the Na(3) cation bridges both the cages and coordinates with two THF molecules. The bondings of THF molecules to other sodium atoms are strange in that the exopolyhedral Na(4) is bonded to three THF's, while Na(1) is coordinated to two discrete THF's. However, both endopolyhedral sodium atoms [Na(1) and Na(2)] are bridged by O(50) of the third THF molecule with distances of 2.530 and 2.487 Å. The most significant feature of the structure of V is the location of the carbon atoms in the C<sub>2</sub>B<sub>4</sub> cages. Figure 1 confirms unambiguously that the cage carbons of each dianion IV within the dimeric unit V are separated by a boron atom, which suggests that either cage opening probably took place at the C<sub>(cage)</sub>–C<sub>(cage)</sub> bond or the cage atoms were rearranged subsequent to the initial cage opening of the *closo*-carborane precursor 1,2-(SiMe<sub>3</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (III).

Since *closo*-1,2-(SiMe<sub>3</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (III)<sup>12</sup> is prepared from the corresponding *nido*-carborane precursor, *nido*-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (VI), in almost quantitative yield, its essentially quantitative conversion to the dianion IV opens up new frontiers in the chemistry of metallocarboranes as IV is a versatile building block that has the potential to generate a wide variety of organometallic compounds. Such species should give some insight into the slip-distortion that is inherent in those metal complexes derived from the carboranes in which the two cage carbons occupy adjacent positions.<sup>1</sup> A comprehensive study<sup>15</sup> including the ab initio calculations of pyramidal and nonpyramidal structures and comparison of experimental and theoretical (IGLO<sup>16</sup>) <sup>11</sup>B and <sup>13</sup>C chemical shift values will be published in the future. The study of the reactivity of the dianion IV toward a wide variety of metal halides is currently in progress at SMU. Study of possible dimerization<sup>17</sup> by oxidation of IV to generate new isomers of *nido*-R<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub> (R = SiMe<sub>3</sub>) is underway at USC.

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**Supplementary Material Available:** Tables 1–5, listing positional and thermal parameters, bond distances, bond angles, torsion angles and anisotropic thermal parameters (9 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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## Flexible Polydentate Binding and Aggregation of a Tetramanganese Complex with a <3-Å Mn...Mn Contact from a Mononuclear Precursor. The Centrosymmetric Mn<sub>4</sub>O<sub>2</sub><sup>8+</sup> Core with Peripheral Phenolato Bridging

Synthetic N- and/or O-coordinated Mn<sub>4</sub> complexes<sup>1–5</sup> having a <3-Å Mn...Mn contact are important in photosystem II<sup>6,7</sup> bioinorganic chemistry. Herein we describe the rational assembly of a novel entity from a mononuclear precursor incorporating flexible polydentate ligation. The concerned ligand (H<sub>3</sub>L) is the salicylaldimine N(CH<sub>2</sub>CH<sub>2</sub>N=CHC<sub>6</sub>H<sub>4</sub>OH)<sub>3</sub>. The complex MnL is known.<sup>8</sup> The structure<sup>9</sup> of MnL·MeOH (1) is shown in Figure 1a. The L<sup>3-</sup> ligand could in principle enforce C<sub>3</sub> symmetry, but in practice the facial N<sub>3</sub>O<sub>3</sub> coordination sphere is strongly elongated along the N(4)MnO(1) axis probably due to Jahn–Teller activity of the Mn<sup>III</sup>(d<sup>4</sup>) ion.<sup>10,11</sup> The tripodal nitrogen N(1) is not coordinated.

Scrutiny of L<sup>3-</sup> models vis-a-vis the MnL·MeOH structure revealed that the ligand backbone is sufficiently flexible to permit one of the arms in MnL to fan out for seeking another metal ion. The presence of certain weakened (elongated) metal–donor bonds in MnL can facilitate this. The tripodal nitrogen can also help by getting “pressed” into coordination once an arm is detached. Finally, the phenolic functions are correctly placed for consolidating polynucleation via bridging. Guided in this manner, we reacted MnL with Mn<sup>3+</sup> in 1:1 proportion with OH<sup>-</sup> added for promoting possible oxidic core formation. From the reaction mixture dark green crystals of [Mn<sub>4</sub>O<sub>2</sub>L<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>·4MeCN (2) and by subsequent solvent loss [Mn<sub>4</sub>O<sub>2</sub>L<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (3) were isolated in

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