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_2B_4 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 $C_{(cage)}$–$C_{(cage)}$ bond or the cage atoms were rearranged subsequent to the initial cage opening of the *closo*-carborane precursor 1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ (III).

Since *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ (III)[12] is prepared from the corresponding *nido*-carborane precursor, *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ (VI), in almost quantitative yield, its essentially quantitative conversion to the dianion IV opens up new frontiers in the chemistry of metallacarboranes 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.[1] A comprehensive study[15] including the ab initio calculations of pyramidal and nonpyramidal structures and comparison of experimental and theoretical (IGLO[16]) ^{11}B and ^{13}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[17] by oxidation of IV to generate new isomers of *nido*-$R_4C_4B_8H_8$ (R = $SiMe_3$) is underway at USC.

Acknowledgment. The work at SMU was supported by grants from the National Science Foundation (CHE-9100048), the Robert A. Welch Foundation (N-1016), and the donors of the Petroleum Research Fund, administered by the American Chemical Society. Support for the work at USC was provided by the Loker Hydrocarbon Research Institute. The work at CSU was supported by the National Science Foundation (Grant CHE-8922339).

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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(15) Williams, R. E.; Bausch, J. W.; Prakash, G. K. S.; Hosmane, N. S.; Jia, L.; Onak, T. P. Geometrical Systematics of Nido-6-vertex Carboranes and Selected Heteroatom Analogs. To be submitted for publication.

(16) (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919.

(17) Koster, R.; Seidel, G.; Wrackmeyer, B. *Angew. Chem.* **1985**, *97*, 317.

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Received May 8, 1991

Flexible Polydentate Binding and Aggregation of a Tetramanganese Complex with a <3-Å Mn···Mn Contact from a Mononuclear Precursor. The Centrosymmetric $Mn_4O_2^{8+}$ Core with Peripheral Phenolato Bridging

Synthetic N- and/or O-coordinated Mn_4 complexes[1-5] having a <3-Å Mn···Mn contact are important in photosystem II[6,7] bioinorganic chemistry. Herein we describe the rational assembly of a novel entity from a mononuclear precursor incorporating flexible polydentate ligation. The concerned ligand (H_3L) is the salicylaldimine $N(CH_2CH_2N{=}CHC_6H_4OH)_3$. The complex MnL is known.[8] The structure[9] of MnL·MeOH (**1**) is shown in Figure 1a. The L^{3-} ligand could in principle enforce C_3 symmetry, but in practice the facial N_3O_3 coordination sphere is strongly elongated along the N(4)MnO(1) axis probably due to Jahn–Teller activity of the $Mn^{III}(d^4)$ ion.[10,11] The tripodal nitrogen N(1) is not coordinated.

Scrutiny of L^{3-} 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^{3+} in 1:1 proportion with OH^- added for promoting possible oxidic core formation. From the reaction mixture dark green crystals of $[Mn_4O_2L_2](PF_6)_2{\cdot}4MeCN$ (**2**) and by subsequent solvent loss $[Mn_4O_2L_2](PF_6)_2$ (**3**) were isolated in

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(1) Vincent, J. B.; Christmas, C.; Chang, H.-R.; Li, Q.; Boyd, P. D. W.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1989**, *111*, 2086–2097. Vincent, J. B.; Christmas, C.; Huffman, J. C.; Christou, G.; Chang, H.-R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 236–238. Christmas, C.; Vincent, J. B.; Huffman, J. C.; Christou, G.; Chang, H.-R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 1303–1305.

(2) Kulawiec, R. J.; Crabtree, R. H.; Brudvig, G. W.; Schulte, G. K. *Inorg. Chem.* **1988**, *27*, 1309–1311.

(3) Bashkin, J. S.; Chang, H.-R.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1987**, *109*, 6502–6504. Li, Q.; Vincent, J. B.; Libby, E.; Chang, H.-R.; Huffman, J. C.; Boyd, P. D. W.; Christou, G.; Hendrickson, D. N. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1731–1733.

(4) Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1990**, *112*, 4985–4986.

(5) A few Mn_4 species having all Mn···Mn contacts >3 Å are also known: Wieghardt, K.; Bossek, U.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 328–329. Wieghardt, K.; Bossek, U.; Nuber, B.; Weiss, J.; Bonvoisin, J.; Corbella, M.; Vitols, S. E.; Girerd, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 7398–7411. McKee, V.; Shepard, W. B. *J. Chem. Soc., Chem. Commun.* **1985**, 158–159. McKee, V.; Tandon, S. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1334–1336. Brooker, S.; McKee, V. *J. Chem. Soc., Chem. Commun.* **1989**, 619–620. Brooker, S.; McKee, V.; Shepard, W. B. Pannel, L. K. *J. Chem. Soc., Dalton Trans.* **1987**, 2555–2562. Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 9121–9122. Suzuki, M.; Sugisawa, T.; Senda, H.; Oshio, H.; Uehara, A. *Chem. Lett.* **1989**, 1091–1094. Stibrany, R. T.; Gorun, S. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1156–1158.

(6) Amesz, J. *Biochim. Biophys. Acta* **1983**, *726*, 1–12. Dismukes, G. C. *Photochem. Photobiol.* **1986**, *43*, 99–115. George, G. N.; Prince, R. C.; Cramer, S. P. *Science* **1989**, *243*, 789–791. Yachandra, V. K.; Guiles, R. D.; McDermott, A. E.; Cole, J. L.; Britt, R. D.; Dexheimer, S. L.; Sauer, K.; Klein, M. P. *Biochemistry* **1987**, *26*, 5974–5981.

(7) Vincent, J. B.; Christou, G. *Advances in Inorganic Chemistry*; Academic Press Inc.: San Diego, CA, 1989 Vol. 33, pp 197–257. Pecoraro, V. L. *Photochem. Photobiol.* **1988**, *48*, 249–264. Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153–1172.

(8) Cook, D. F.; Cummins, D.; McKenzie, E. D. *J. Chem. Soc., Dalton Trans.* **1976**, 1369–1375.

(9) The MnL complex was prepared as reported.[8] Green crystals of MnL·MeOH were grown from a CH_2Cl_2–MeOH mixture: space group $P2_1/n$ with $a = 10.826$ (5) Å, $b = 14.821$ (9) Å, $c = 16.348$ (9) Å, $\beta = 95.10$ (4)°, $V = 2613$ (2) Å^3, $Z = 4$, and $\rho_{calcd} = 1.38$ g cm^{-3}. Data were collected on a Nicolet R3m/V diffractometer at 23 °C with Mo Kα radiation (λ = 0.71073 Å). The 1174 reflections having $I > 2\sigma(I)$ were used to yield $R = 7.85\%$, $R_w = 6.37\%$, and GOF = 1.13.

(10) Fackler, J. P.; Avdeef, A. *Inorg. Chem.* **1974**, *13*, 1864.

(11) A chloro derivative of MnL is reported to have strict C_3 symmetry: Alcock, N. W.; Cook, D. F.; McKenzie, E. D.; Worthington, J. M. *Inorg. Chim. Acta* **1980**, *38*, 107–112. Evidently dynamic distortion is present, the observed structure being the time average.

0020-1669/91/1330-3795$02.50/0

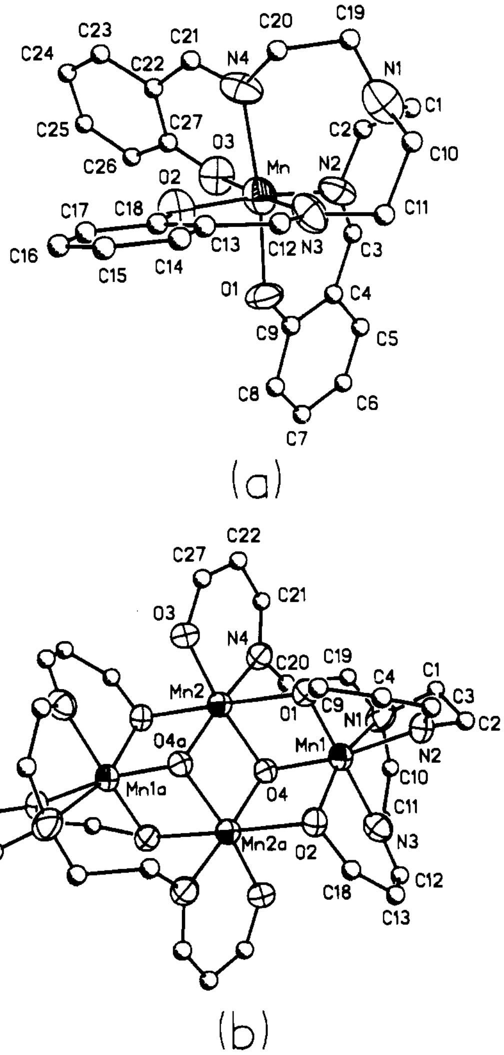

Figure 1. (a) View of MnL in MnL·MeOH. Selected bond distances (Å) and angles (deg) are as follows: Mn–O(1), 2.116 (8); Mn–O(2), 1.910 (9); Mn–O(3), 1.906 (8); Mn–N(2), 2.111 (10); Mn–N(3), 2.062 (10); Mn–N(4), 2.290 (10); O(1)–Mn–O(2), 88.1 (3); O(1)–Mn–O(3), 96.5 (3); O(1)–Mn–N(4), 172.4 (3); N(2)–Mn–N(3), 98.0 (4); N(2)–Mn–N(4), 103.0 (3). (b) View of the cation of $[Mn_4O_2L_2](PF_6)_2\cdot 4MeCN$ (four carbon atoms of each benzene ring excluded for clarity). Symmetry-equivalent atoms are not named or named with "a" added (e.g. Mn1, Mn1a). Selected bond distances (Å) and angles (deg) are as follows: Mn(1)–O(1), 1.916 (5); Mn(1)–O(2), 2.127 (6); Mn(1)–O(4), 1.909 (5); Mn(1)–N(1), 2.407 (8); Mn(1)–N(2), 1.997 (6); Mn(1)–N(3), 2.030 (7); Mn(2)–O(1), 2.301 (5); Mn(2)–O(3), 1.892 (5); Mn(2)–O(4), 1.916 (5); Mn(2)–N(4), 2.019 (7); Mn(2)–O(2A), 2.222 (5); Mn(2)–O(4A), 1.950 (5), Mn(1)···Mn(2), 3.000 (3); Mn(1)···Mn(2A), 3.042 (3); Mn(2)···Mn(2A), 2.906 (3); Mn(1)–O(4)–Mn(2), 103.3 (2); Mn(1)–O(4)–Mn(2A), 104.1 (2); O(4)–Mn(2)–O(4A), 82.5 (2); O(4)–Mn(1)–N(2), 170.7 (2); O(2)–Mn(1)–N(1), 162.0 (2); O(1)–Mn(1)–N(3), 172.6 (3); O(3)–Mn(2)–O(4), 166.7 (2); O(1)–Mn(2)–O(2A), 177.4 (2); O(3)–Mn(2)–N(4), 91.6 (2).

nearly quantitative yields.[12] The stoichiometry of the synthetic reaction is as follows:

$$2MnL + 2Mn^{3+} + 4OH^- \rightarrow [Mn_4O_2L_2]^{2+} + 2H_2O \quad (1)$$

The remarkably facile and efficient aggregation of **2** from **1** is a good indicator of how a flexible polypeptide backbone having side-chain donors (amine, carboxyl, phenol) could possibly organize oxidic Mn_4 ensembles[6,7] in PSII.

The structure[13] of $[Mn_4O_2L_2]^{2+}$ is shown in Figure 1b. The cation is centrosymmetric. The coordination spheres are of two types, MnN_3O_3 and $MnNO_5$—both axially elongated. The μ_3-O atoms are displaced from the Mn_4 plane by 0.858 Å in opposite directions. The shortest Mn···Mn contact is 2.906 (3) Å. The $[Mn_4(\mu_3\text{-}O)_2]^{z+}$ core, held by peripheral carboxylate bridging, is known in butterfly configuration[1] for $z = 8$ and in centrosymmetric configuration[1,2] for $z = 6$. By contrast the core in **2** is phenolate bridged and is centrosymmetric with $z = 8$.

Complex **3** is antiferromagnetic; the magnetic moment decreases with decreasing temperature from 7.45 μ_B at 297 K to 5.00 μ_B at 10 K. No EPR signals are observed. In MeCN four quasi-reversible one-electron cyclic responses are seen corresponding to the oxidation-state interval $Mn^{IV}{}_2Mn^{III}{}_2$ to $Mn^{III}{}_2Mn^{II}{}_2$ ($E_{1/2}$ at Pt electrode, 298 K: 0.98, 0.82, 0.03, and −0.20 V versus SCE). Only two of the couples have $E_{1/2}$ values above the water oxidation threshold. Complex **1** shows Mn^{IV}–Mn^{III} and Mn^{III}–Mn^{II} couples ($E_{1/2}$, 0.54 and −0.29 V).

In summary, flexible polydentate ligation is an excellent instrument for assembling the Mn_4 moiety—a finding of considerable interest in the context of PSII. The centrosymmetric configuration is new for the $Mn_4O_2{}^{8+}$ core, and so is phenolato bridging.

Acknowledgment. Financial support from the Department of Science and Technology, New Delhi, is acknowledged. Affiliation to the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India, is acknowledged. We are thankful to Professor C. N. R. Rao for help regarding magnetic data.

Supplementary Material Available: For **1** and **2**, text giving details of structure determination and tables listing atomic coordinates (Tables I and VI), complete bond distances (Tables II and VII) and angles (Tables III and VIII), anisotropic thermal parameters (Tables IV and IX), and hydrogen atom positional parameters (Tables V and X) (13 pages); listings of observed and calculated structure factors for the above two complexes (16 pages). Ordering information is given on any current masthead page.

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[12] MnL·MeOH was stirred with $Mn(OAc)_3\cdot 2H_2O$ in warm acetonitrile, and methanolic KOH was added (MnL:Mn^{3+}:OH^- = 1:1:2) followed by solid NH_4PF_6. Upon concentration and cooling (5 °C), crystals of $[Mn_4O_2L_2](PF_6)_2\cdot 4MeCN$ deposited. When dried in air, the crystals rapidly lost MeCN, leaving $[Mn_4O_2L_2](PF_6)_2$ as a powder (yield 93%). Anal. Calcd for $[Mn_4O_2L_2](PF_6)_2$: C, 44.66; H, 3.72; N, 7.71; Mn, 15.13. Found: C, 44.72; H, 3.70; N, 7.66; Mn, 15.10.

[13] A fresh crystal of $[Mn_4O_2L_2](PF_6)_2\cdot 4MeCN$ was covered with fast-setting epoxy to prevent solvent loss: space group $P2_1/n$, with a = 14.019 (7) Å, b = 16.165 (8) Å, c = 15.995 (7) Å, β = 102.27 (4)°, V = 3542 (3) Å^3, Z = 2, and ρ_{calcd} = 1.52 g cm^{-3}. The structure was solved by direct methods with 3020 observed ($I > 3\sigma(I)$) data collected at 23 °C, affording R = 6.81%, R_w = 7.50%, and GOF = 1.77.

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Received June 28, 1991

First Stereospecific Preparation of a Polynuclear Coordination Compound. Use of Λ-Ru^{II}(*o*-phen)$_2$ as a Chiral Building Block

The resolution of $M(L^\frown L)_3$ and $M(L^\frown L)_2(A)(B)$ complexes (where $L^\frown L$ are bidentate ligands) into optical isomers was one of the great achievements of Alfred Werner during the development of the coordination theory.[1] Although it is since clear, that octahedral coordination moieties of the above-mentioned type are chiral, stereoselective synthesis has not been developed in coordination chemistry in the same sense as in organic chemistry. Yet the chirality of the coordination centers is a major problem in the synthesis of polynuclear complexes. Recently, a method for separating enantiomers of complexes that are capable of forming dinuclear species was published.[2] The synthesis of dinuclear

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[1] Werner, A. *Z. Anorg. Chem.* **1899**, *21*, 145; Werner, A. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1887, 2445, 3132, 3272, 3279. Bailar, J. C., Jr. *Coord. Chem. Rev.* **1990**, *100*, 1.

[2] Baker, A. D.; Morgan, R. J.; Strekas, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 1411.