

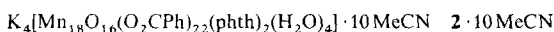
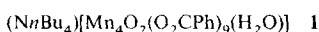
Octadecanuclearity in Manganese Carboxylate Chemistry:

$K_4[Mn_{18}O_{16}(O_2CPh)_{22}(phth)_2(H_2O)_4]$ ($phthH_2 = phthalic\ acid$)**

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Our efforts in manganese carboxylate chemistry over the last several years have been stimulated by 1) the desire to prepare models of the Mn_4 aggregate responsible for photosynthetic water oxidation,^[1] and 2) the search for molecular species with large values of spin S in the ground state to provide information on the factors responsible for the photosynthetic water oxidation and to find potential precursors to molecular ferromagnets.^[2] Our results to date have been most gratifying, because we have come across both a wide variety of high nuclearity carboxylatomanganese aggregates with aesthetically pleasing structures and complexes with large values of S and other highly unusual magnetic properties.^[3] For example, $[Mn_8O_6Cl_6(O_2CPh)_{12}(H_2O)_2]$ has an $S = 11$ ground state,^[3c,f] whereas the $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]^{z-}$ complexes have $S = 9$ or 10 ($z = 0$) or $S = 19/2$ ($z = -1$) and exhibit superparamagnet-like behavior when examined by AC susceptometry—the only *molecular* species to do so.^[3c,d,f] The latter complexes are also the highest nuclearity carboxylatomanganese species observed to date. However, we herein report a remarkable octadecanuclear Mn carboxylate aggregate, and describe its structure and magnetic properties.

The synthesis involved the reaction of **1**,^[3e] which contains a $[Mn_4(\mu_3-O)_2]^{8+}$ butterfly-like core, with the monopotassium salt of phthalic acid ($phthH_2$; benzene-1,2-dicarboxylic acid). A dark red-brown MeCN solution of complex **1** was stirred for five days with one equivalent of potassium hydrogen phthalate and yielded a similarly colored solution and an off-white precipitate of KO_2CPh . The solution was filtered, and the filtrate allowed to concentrate at ambient temperature over 10 days to give essentially black crystals of **2**·10 MeCN in about 30% yield.^[4] Increase of the storage time by a factor of 2 leads to further product crystallization (total yield about 40%).



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The structure of **2** (Fig. 1)^[4] has crystallographically imposed C_2 symmetry and idealized D_2 symmetry. Charge considerations indicate that the Mn centers are all in the Mn^{III} oxidation state. There is a central, almost linear Mn_4 unit (Mn1, Mn1', Mn2, Mn2') and seven Mn atoms above and below this unit, all held together by 16 μ_3-O^{2-} ions. The peripheral ligation is provided by 22 $PhCO_2^-$ groups in their familiar *syn,syn*-bridging mode, two terminal H_2O groups on each of two Mn atoms (Mn4 and Mn8), and two μ_4-phth^{2-} groups whose O atoms each coordinate to different Mn atoms; the latter represents an unprecedented binding mode for this group. The two $phth^{2-}$ groups ligate to a total of six Mn atoms. The 16 μ_3-O^{2-} ions can be divided into four types: 1) O15, O15', O20, and O20' have distinctly pyramidal geometry with a sum-of-angles (SOA) of about 316° ; 2) O11, O11', O16, and O16' (SOA ca. 345.5°) and O13, O13', O18, O18' (SOA ca. 355°) are also pyramidal, but

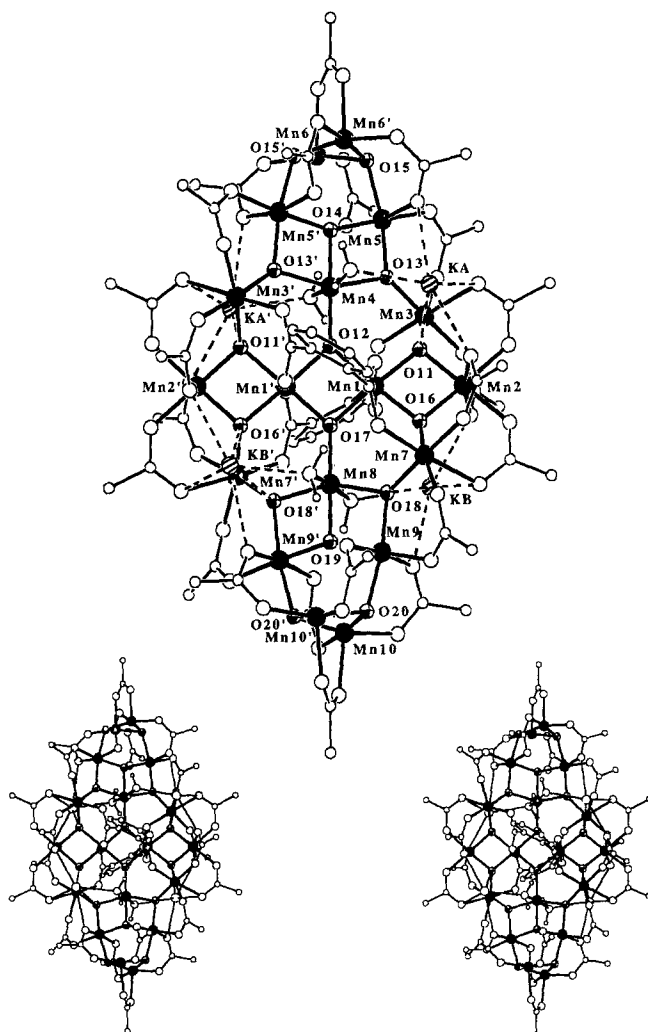


Fig. 1. ORTEP representation and stereoview of the structure of **2**; all but one of the benzoate-phenyl C atoms have been omitted for clarity. The terminal MeCN groups on the K^+ ions (KA and KB, diagonally shaded) are also omitted.

with a more flattened geometry as indicated by the SOA; 3) O12 and O17 are planar (SOA about 360°) and very approximately trigonal; and 4) O14 and O19 are planar (SOA 360°) but with an almost T-shaped geometry (Mn5-O14-Mn5' and Mn9-O19-Mn9' are $151.5(3)^\circ$ and $150.9(4)^\circ$, respectively). The Mn atoms are either five-coordinate, square-pyramidal (Mn6, Mn6', Mn10, Mn10'), or distorted octahedral displaying the Jahn-Teller axial distortion (elongation) expected for a high-spin d^4 ion in near-octahedral geometry. The $[\text{Mn}_{18}\text{O}_{16}]$ core has a somewhat sheet-like appearance and is twisted slightly about the real C_2 (vertical) axis; these points are emphasized by the stereoview in Figure 2. The K^+ ions are tightly ion-paired with the tetraanion, and their positions are indicated in Figure 1; each also has a terminal MeCN ligand (not shown).

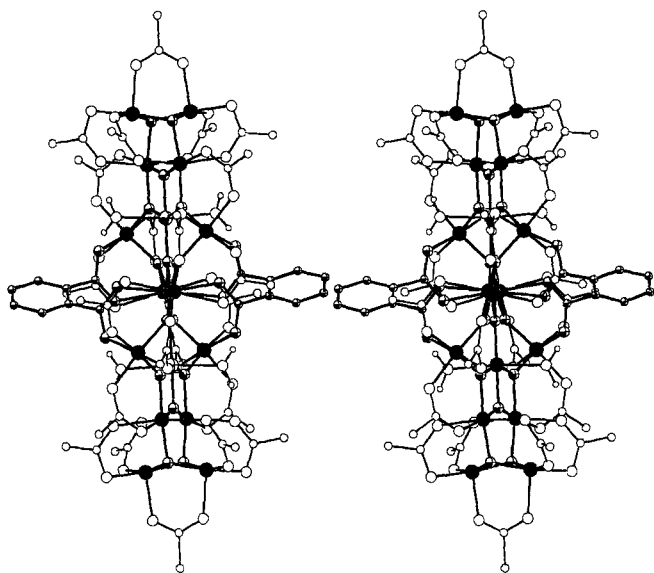
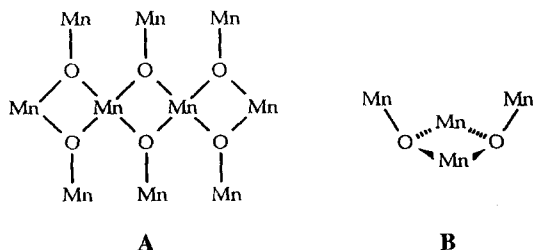


Fig. 2. ORTEP stereoview of complex **2** (without the K^+ ions) from a viewpoint essentially perpendicular to that in Figure 1 and approximately along the almost linear Mn_4 central unit. This view emphasizes the twist of the almost planar $[\text{Mn}_{18}\text{O}_{16}]$ core along the C_2 (vertical) axis.

An alternate and convenient description of **2** is as the result of fusing five $[\text{Mn}_4(\mu_3\text{-O})_2]^{8+}$ units with either a planar or bent ("butterfly") Mn_4 unit (the latter as found in **1**).^{13e, 51} The central $[\text{Mn}_{10}\text{O}_{16}]$ unit (A) represents the fusion of three such units



by sharing of "hinge" Mn atoms (Mn1 and Mn1'). Two additional $[\text{Mn}_4\text{O}_2]$ units (B) are then attached to the "wing-tip" positions of the central unit by atoms O13, O13', O14 and O18, O18', O19.

Variable-temperature, solid-state magnetic susceptibility studies were performed on powdered samples of complex **2** in the temperature range 2.00–320 K and in an applied magnetic field

of 10 kG (1 T). The $\xi_M T$ value (ξ_M is the molar DC magnetic susceptibility per Mn_{18} complex) slowly decreases from $28.67 \text{ cm}^3 \text{ K mol}^{-1}$ ($15.14 \mu_B$ per molecule) at 320.0 K to $0.376 \text{ cm}^3 \text{ K mol}^{-1}$ ($1.73 \mu_B$) at 2.00 K (Fig. 3). The spin-only value for an aggregate of eighteen noninteracting Mn^{III} ($S = 2$) ions is $54.00 \text{ cm}^3 \text{ K mol}^{-1}$ ($20.78 \mu_B$). Thus, there are appreciable antiferromagnetic exchange interactions within **2**.

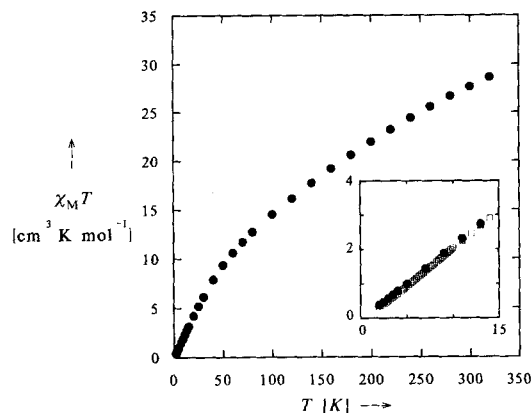


Fig. 3. Plot of $\xi_M T$ vs T data for complex **2** collected in an applied magnetic field of 10 kG. Corresponding μ_{eff} values are given in the text. The inset shows the $\xi_M T$ data in the 2–15 K range; DC data (\bullet) measured at 10 kG and AC data (\square) measured in zero DC field and 1.0 G AC field (500 Hz frequency) are shown.

AC magnetic susceptibility data were also collected for a polycrystalline sample of **2** in the 2.00–60.0 K range. These data were run in zero DC field with a 1.0 G AC field oscillating at 500 Hz. The AC susceptibility data nearly superimpose on the DC data. At the lowest temperatures (see inset in Figure 3) both $\xi_M T$ vs T plots extrapolate to $\xi_M T = 0$ at $T = 0$. Clearly, complex **2** has a $S = 0$ ground state.

Interestingly, Mn_x ($x > 3$) carboxylate complexes with ground states $S = 0$ are the exception rather than the rule. As stated earlier, one of the objectives of our program is to elucidate the various factors that lead to large S values in the ground state, and it is becoming apparent that one of these is spin frustration within certain topological arrangements.^{16j} That complex **2** with its large ensemble of paramagnetic ions should have an $S = 0$ ground state is thus somewhat surprising and of importance to this continuing search for an understanding of what is beneficial to obtaining large values of S and what is detrimental. A more detailed discussion will be presented in a full paper. From a synthetic inorganic viewpoint, the preparation of **2** shows that it is possible to generate Mn aggregates with nuclearities significantly greater than those known to date by relatively minor perturbations to the reaction system, in this case, the introduction of a dicarboxylate ligand. Further work along these lines is in progress, with the objective of increasing even further the number of high nuclearity Mn carboxylate aggregates available for study.

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[1] a) G. W. Brudvig, R. H. Crabtree, *Prog. Inorg. Chem.* **1989**, *37*, 99; b) D. Ghanotakis, C. F. Yocum, *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, **1990**, *41*, 255; c) *Manganese Redox Enzymes* (Ed.: V. L. Pecoraro), VCH, Weinheim, **1992**; d) R. J. Debus, *Biochim. Biophys. Acta* **1992**, *1102*, 269; e) Ö. Hansson, T. Wydrzynski, *Photosynth. Res.* **1990**, *23*, 131; f) G. Christou, *Acc. Chem. Res.* **1989**, *22*, 328.

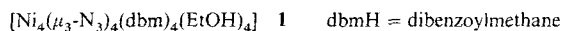
- [2] a) J. S. Miller, A. J. Epstein, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 385; b) *Magnetic Molecular Materials* (Eds.: D. Gatteschi, O. Kahn, J. S. Miller, F. Palacio) (NATO ASI Ser. Ser. E **1991**, 198); c) H. Iwamura, *Pure Appl. Chem.* **1986**, *58*, 187; *ibid.* **1987**, *59*, 1595; d) J. S. Miller, A. J. Epstein, W. M. Reiff, *Chem. Rev.* **1988**, *88*, 201; e) D. P. Goldberg, A. Caneschi, S. J. Lippard, *J. Am. Chem. Soc.* **1993**, *115*, 9299; f) A. Caneschi, D. Gatteschi, J. Laugier, P. Ray, R. Sessoli, C. Zanchini, *ibid.* **1988**, *110*, 2795; g) A. Caneschi, D. Gatteschi, R. Sessoli, A. L. Barra, L. C. Brunel, M. Guillaud, *ibid.* **1991**, *113*, 5873.
- [3] a) E. Libby, K. Folting, C. J. Huffman, J. C. Huffman, G. Christou, *Inorg. Chem.* **1993**, *32*, 2549, and references therein; b) M. W. Wemple, H.-L. Tsai, W. E. Streib, D. N. Hendrickson, G. Christou, *J. Chem. Soc. Chem. Commun.* **1994**, 1031; c) R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 1804; d) H.-L. Tsai, H. Eppley, N. de Vries, K. Folting, G. Christou, D. N. Hendrickson, *J. Chem. Soc. Chem. Commun.* **1994**, 1745; e) S. Wang, J. C. Huffman, K. Folting, W. E. Streib, E. B. Lobkovsky, G. Christou, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1672; *Angew. Chem.* **1991**, *103*, 1681; f) H.-L. Tsai, S. Wang, K. Folting, W. E. Streib, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.*, in press; g) H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou, D. N. Hendrickson, *ibid.* **1994**, *116*, 301.
- [4] Solid dried under vacuum has lost all MeCN groups. Elemental analysis: calcd (found) for $C_{170}H_{126}O_{72}K_4Mn_{18}$: C 45.72 (45.50), H 2.84 (2.80), N 0.00 (0.00), Mn 22.14 (21.98), K 3.49 (3.50)%. Crystal data: $C_{190}H_{156}N_{10}O_{72}K_4Mn_{18}$, monoclinic, $C2/c$, $T = -167^\circ\text{C}$, $a = 22.673(5)$, $b = 33.426(7)$, $c = 27.991(8)$ Å, $\beta = 105.06(1)^\circ$, $V = 20484 \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.57 \text{ g cm}^{-3}$, $6^\circ \leq 2\theta \leq 45^\circ$, 10441 unique reflections with $F > 3\sigma(F)$. All non-hydrogen atoms were refined anisotropically: hydrogen atoms were included in fixed, calculated positions. Final $R(R_w) = 0.00607(0.00606)\%$. Further details are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2, 1EZ (UK), on quoting the complete journal citation.
- [5] a) J. B. Vincent, C. Christmas, H.-R. Chang, Q. Li, P. D. W. Boyd, J. C. Huffman, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **1989**, *111*, 2086; b) E. Libby, J. K. McCusker, E. A. Schmitt, K. Folting, J. C. Huffman, D. N. Hendrickson, G. Christou, *Inorg. Chem.* **1991**, *30*, 3486; c) E. Bouwman, M. A. Bolear, E. Libby, J. C. Huffman, K. Folting, G. Christou, *ibid.* **1992**, *31*, 5185.
- [6] a) D. N. Hendrickson, G. Christou, E. A. Schmitt, E. Libby, J. S. Bashkin, S. Wang, H.-L. Tsai, J. B. Vincent, P. D. W. Boyd, J. C. Huffman, K. Folting, Q. Li, W. E. Streib, *J. Am. Chem. Soc.* **1992**, *114*, 2455; b) J. K. McCusker, J. B. Vincent, E. A. Schmitt, M. L. Mino, K. Shin, D. K. Coggin, P. M. Hagen, J. C. Huffman, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1991**, *113*, 3012; c) E. Libby, J. K. McCusker, E. A. Schmitt, K. Folting, D. N. Hendrickson, G. Christou, *Inorg. Chem.* **1991**, *30*, 3486; d) J. K. McCusker, H. G. Jang, S. Wang, G. Christou, D. N. Hendrickson, *ibid.* **1992**, *31*, 1874; e) S. Wang, H.-L. Tsai, W. E. Streib, G. Christou, D. N. Hendrickson, *J. Chem. Soc. Chem. Commun.* **1992**, 677; f) D. N. Hendrickson in *Research Frontiers in Magnetochemistry* (Ed.: C. J. O' Connor) World Scientific, Singapore, **1993**.

A Nickel(II) Azide Cubane: Characterization of the Magnetic Exchange Interactions Mediated by a Triply Bridging Azide Group Bound End-On**

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We have a long-standing interest in manganese carboxylate aggregates as models for the Mn_4 cluster in the active center of green plants and cyanobacteria for photosynthetic water oxidation.^[1] We prepared several $Mn_3^{III}Mn^{IV}$ complexes containing the distorted cubane $[Mn_4O_3X]^{6+}$ core (X = halide, carboxylate),^[2] and also the cubane $[Co_4O_4]^{4+}$ core, together with protonated versions of the latter.^[3] As an extension to this work, we

recently turned our attention to cubane complexes containing other metal ions, to investigate the electronic and magnetic properties of this interesting class of compound further. We report here the cubane complex **1**; this is the first paramagnetic



molecule to contain end-on-coordinated, triply bridging azide ligands,^[4-6] and thus provides an opportunity to characterize the magnetic exchange interactions mediated by azide in this rare bridging mode. The structure of one other $[M_4(N_3)_4]^{n+}$ cubane species is known, namely diamagnetic $[Pt_4(N_3)_4(CH_3)_{12}]^{15}$.

A one-pot reaction of $Ni(ClO_4)_2 \cdot 6H_2O$, NaN_3 , and $Na(dbm)$ (in a 1:1:1 molar ratio) in EtOH at room temperature yields a bright green precipitate containing **1** and a little $NaClO_4$. Recrystallization from $CH_2Cl_2/EtOH$ affords large green crystals of pure **1** in 78% overall yield. The IR spectrum of **1** as a Nujol mull shows, in addition to bands arising from dbm^- and coordinated EtOH, a very strong absorption at 2087 cm^{-1} attributable to the $\nu_{\text{asym}}(N-N-N)$ stretching vibration of coordinated azide;^[7] this band appears at 2089 cm^{-1} in $CHCl_3$ solution. The $\nu_{\text{sym}}(N-N-N)$ and $\delta(N-N-N)$ vibrations also expected from a metal-bound azide^[7] were masked by absorptions from the dbm^- ligand and could not be positively identified. The UV/Vis spectrum of **1** in $CHCl_3$ is typical of an octahedral Ni^{II} complex,^[8] while the 1H NMR spectrum of **1** in $CDCl_3$ shows the paramagnetically shifted resonances of only a single environment for dbm^- and EtOH.

The structure of the bis(toluene) solvate of **1** (Fig. 1)^[9] contains a tetranuclear $[Ni_4(\mu_3-N_3)_4]^{4+}$ cubane core; the molecule has virtual C_3 symmetry and lies on a general position within the unit cell. Each Ni ion is octahedrally coordinated by three end-on-coordinated, triply bridging azide ligands, one chelating dbm^- ligand, and one ethanol ligand. Each ethanol ligand is intramolecularly hydrogen-bonded to an O atom in a dbm^- ligand that is

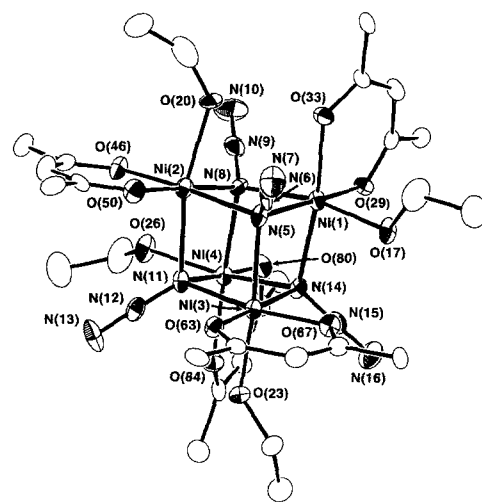


Fig. 1. ORTEP representation of complex **1** (ellipsoids at the 50% probability level). For clarity, only the *ipso* carbon atoms of the dbm^- phenyl rings are shown. Selected distances [\AA] and angles [$^\circ$]: $Ni(1) \cdots Ni(2)$ 3.168(1), $Ni(1) \cdots Ni(3)$ 3.146(1), $Ni(1) \cdots Ni(4)$ 3.231(1), $Ni(2) \cdots Ni(3)$ 3.239(1), $Ni(2) \cdots Ni(4)$ 3.177(1), $Ni(3) \cdots Ni(4)$ 3.156(1), $Ni(1)-N(5)$ 2.141(5), $Ni(1)-N(8)$ 2.136(6), $Ni(1)-N(14)$ 2.094(5), $Ni(2)-N(5)$ 2.117(5), $Ni(2)-N(8)$ 2.111(5), $Ni(2)-N(11)$ 2.138(6), $Ni(3)-N(5)$ 2.132(6), $Ni(3)-N(11)$ 2.100(5), $Ni(3)-N(14)$ 2.132(5), $Ni(4)-N(8)$ 2.109(6), $Ni(4)-N(11)$ 2.150(5), $Ni(4)-N(14)$ 2.113(6), $Ni(1)-N(5)-Ni(2)$ 96.1(2), $Ni(1)-N(5)-Ni(3)$ 94.8(2), $Ni(2)-N(5)-Ni(3)$ 99.4(2), $Ni(1)-N(8)-Ni(2)$ 96.5(2), $Ni(1)-N(8)-Ni(4)$ 99.1(2), $Ni(2)-N(8)-Ni(4)$ 97.7(2), $Ni(2)-N(11)-Ni(3)$ 99.7(2), $Ni(2)-N(11)-Ni(4)$ 95.6(2), $Ni(3)-N(11)-Ni(4)$ 95.9(2), $Ni(1)-N(14)-Ni(3)$ 96.2(2), $Ni(1)-N(14)-Ni(4)$ 100.4(2), $Ni(3)-N(14)-Ni(4)$ 96.1(2).

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