

Controlled Aggregation and Deaggregation of a Polynuclear Oxido-Bridged Manganese Complex: Utility to Synthesis of the Jahn–Teller Effect in High-Spin Manganese(III)

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Received October 1, 1992

Initial results are described in a new program designed to develop various synthetic procedures for the covalent linking of Mn carboxylate aggregates into aggregates-of-aggregates and polymers-of-aggregates. Treatment of $(\text{NBu}^n)_4[\text{Mn}_4\text{O}_2(\text{OAc})_7(\text{pic})_2]$ (**1**) (picH = picolinic acid) with Me_3SiCl leads to selective abstraction of the unique Jahn–Teller labilized AcO^- and the dimerization of the resulting fragment to yield $\text{Mn}_8\text{O}_4(\text{OAc})_{12}(\text{pic})_4$ (**3**). A similar reaction employing $(\text{NBu}^n)_4[\text{Mn}_4\text{O}_2(\text{OBz})_7(\text{pic})_2]$ (**4**) yields $[\text{Mn}_4\text{O}_2(\text{OBz})_6(\text{pic})_2(\text{MeCN})_2]$ (**5**), dimerization to an octanuclear complex analogous to **3** being prevented by steric repulsions. In addition, treatment of **3** with excess PhCOOH leads to clean conversion to **5**. The structure of **3** consists of two $[\text{Mn}_4\text{O}_2(\text{OAc})_6(\text{pic})_2]$ fragments held together by two interfragment Mn–O linkages involving pic oxygen atoms formerly uncoordinated in **1**. The structure of **5** is similar to **4**; the seventh BzO[−] group is replaced by two MeCN groups. Crystal data for **3** at -157°C : monoclinic, $P2_1/n$, $a = 11.276(5) \text{ \AA}$, $b = 26.159(11) \text{ \AA}$, $c = 11.671(5) \text{ \AA}$, $\beta = 93.11(2)^\circ$, $Z = 2$, $V = 3437.39 \text{ \AA}^3$, $R(R_w) = 8.71\%$ (8.28%) using 1364 unique data with $F > 3.0\sigma(F)$. Crystal data for **5** at -173°C : monoclinic, $C2/c$, $a = 22.312(4) \text{ \AA}$, $b = 21.725(3) \text{ \AA}$, $c = 12.657(2) \text{ \AA}$, $\beta = 90.81(1)^\circ$, $Z = 4$, $V = 6134.69 \text{ \AA}^3$, $R(R_w) = 7.35\%$ (6.86%) using 2964 unique data with $F > 2.33\sigma(F)$.

Introduction

Most efforts in the development of higher oxidation state ($\geq\text{II}$), oxide-bridged manganese chemistry have been primarily directed toward di- and tetranuclear species to obtain potential models for the Mn units within Mn biomolecules.^{1,2} In the process, we and others have somewhat frequently encountered higher nuclearity products, encompassing an impressive range of nuclearities and structural types; to date, structurally-characterized species include Mn_6 ,³ Mn_7 ,⁴ Mn_8 ,⁵ Mn_9 ,^{5a,6} Mn_{10} ,⁷ Mn_{11} ,⁸ Mn_8Fe_4 ,⁹ and Mn_{12} .^{9,10} In parallel, high-nuclearity Fe carboxylates have also been reported, comprising Fe_6 ,¹¹ Fe_8 ,¹² Fe_{10} ,¹³ Fe_{11} ,¹⁴ Fe_{16}M ($\text{M} = \text{Co}$, Mn),¹⁵ Fe_{17} ,¹⁶ and Fe_{19} .¹⁶ In all cases, the various authors involved would probably agree that the precise nuclearity and structure

could not have been predicted from the reagents and stoichiometries employed, even though some reactions were certainly directed toward the formation of higher nuclearity species. In this respect, the reactions cannot be described as “under operator control” but instead within the realm of “spontaneous self-assembly”.

Higher nuclearity species are important for a variety of reasons, including providing insights into the assembly of the polynuclear core of the ferritin protein¹⁷ and understanding the variation of magnetic exchange interactions as a function of nuclearity, metal oxidation state, and structural details. The latter reason has been particularly important for Mn because ferromagnetic exchange interactions have frequently led to high-spin ground-state values. For example, $\text{Mn}_4\text{O}_3\text{Cl}_4(\text{OAc})_3(\text{py})_3$ and related complexes have $S = 9/2$ ground states,¹⁸ whereas $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{-CR})_{16}(\text{H}_2\text{O})_4$ species have ground states of $S = 9$ or 10 , depending

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on the R group and other factors.^{9,10,19} such species have potential application as precursors to molecular ferromagnets if methods can be developed to link them together in a manner that encourages 3D ferromagnetic ordering.

Given the above importance of higher nuclearity species and the unpredictable nature of their discovery to date, it was considered timely and, indeed, essential to attempt to overcome this lack of control and develop methodology for their rational synthesis. One attractive approach is to link together, in a controlled manner, smaller nuclearity "building blocks" derived from available smaller nuclearity species, retaining the structural identity and attractive magnetic properties of the precursor molecule. The latter objective is an important one, especially since the longer-term aim is to access new molecular ferromagnets, and it has demanded employment of mild, low-temperature solution methods. We herein report our first success in a new program directed toward controlled covalent linkage of Mn_x complexes to yield aggregates-of-aggregates and polymers-of-aggregates. We describe the reversible aggregation of a particular tetranuclear complex to an octanuclear product, the direction of nuclearity change (i.e., aggregation or deaggregation) being controlled by carboxylate abstraction and steric bulk, respectively. Portions of the described work have been reported in preliminary form.^{20a}

Experimental Section

Syntheses. All operations were performed under aerobic conditions except where noted. Materials were used as received. Reactions involving Me₃SiCl were performed with standard Schlenk techniques under a nitrogen atmosphere using distilled MeCN (CaH₂) and ether (Na/benzophenone). The complexes (NBuⁿ)₄[Mn₄O₂(OAc)₇(pic)₂] (1; picH = picolinic acid), Mn₂O₂(pic)₄ (2), and (NBuⁿ)₄[Mn₄O₂(OBz)₇(pic)₂] (4; OBz = benzoate) were available from previous work.²¹ Manganese(III) acetate, "Mn(OAc)₃·2H₂O", was prepared as described elsewhere.²²

Mn₈O₄(OAc)₁₂(pic)₄ (3). Method A. To a stirred dark-red solution of (NBuⁿ)₄[Mn₄O₂(OAc)₇(pic)₂] (0.58 g, 0.50 mmol) in MeCN (30 mL) was added Me₃SiCl (0.19 mL, 1.5 mmol). The solution turned purple-brown. Storage of the undisturbed flask for 1 week at room temperature gave well-formed purple-brown crystals of the title complex; these were collected by filtration, washed with MeCN (4 × 10 mL) and dried in air. The yield was 0.13 g (32% based on Mn). Dried crystals slowly lose interstitial solvent, and the solid also appears to be hygroscopic. This has made obtaining good analytical data difficult. An analysis sample gave results consistent with 3⁷/2MeCN·4H₂O. Anal. Calcd for C₅₅H_{70.5}N₇O₄₀Mn₈ (fw 1916.18): C, 34.47; H, 3.71; N, 5.48; Mn, 22.94. Found: C, 35.1; H, 3.3; N, 4.8; Mn, 22.4. To obtain crystals suitable for diffraction, the reaction mixture was layered with one volume of ether and the crystals, isolated and washed as before, were kept under MeCN to avoid solvent loss. Selected IR data (Nujol mull): 3400 (br), 2255 (w), 1682 (m), 1644 (m), 1595 (s), 1568 (s), 1341 (s), 1327 (s), 1294 (s).

Method B. A slurry of Mn₂O₂(pic)₄ (0.16 g, 0.25 mmol) and Mn(OAc)₃·2H₂O (0.54 g, 2.0 mmol) in MeCN (50 mL) containing glacial HOAc (0.50 mL) was stirred for 1 h. The resulting purple-brown solution was filtered to remove a brown residue, and the filtrate was stored for 1 week at room temperature. The product formed as small purple-brown crystals that were isolated by filtration, washed with MeCN (3 × 10 mL) and dried in air. The yield was 0.34 g (75% based on total available Mn). The experiments with other reagent ratios were carried out by varying the amount of Mn(OAc)₃·2H₂O employed. The analytical sample analyzed for 3³/2MeCN·5H₂O. Anal. Calcd for C₅₁H_{66.5}N_{5.5}O₄₁Mn₈ (fw 1852.09): C, 33.07; H, 3.62; N, 4.16; Mn, 23.73. Found: C, 33.2; H, 3.4; N, 4.0; Mn, 23.2. The IR spectrum was identical to that of a sample prepared by method A.

[Mn₄O₂(OBz)₆(pic)₂](MeCN)₂ (5). Method A. To a red-brown solution of (NBuⁿ)₄[Mn₄O₂(OBz)₇(pic)₂] (0.79 g, 0.50 mmol) in MeCN

Table I. Crystallographic Data for Complexes 2 and 3

param	3	5
formula	C ₄₈ H ₅₂ N ₄ O ₃₆ Mn ₈ ^a	C ₆₂ H ₅₀ N ₆ O ₁₈ Mn ₄
M _r	1700.45 ^a	1386.86
space group	P2 ₁ /n	C2/n
temp, °C	-157	-173
a, Å	11.276(5) ^b	22.312(4) ^d
b, Å	26.159(11)	21.725(3)
c, Å	11.671(5)	12.657(2)
β, deg	93.11(2)	90.81(1)
V, Å ³	3437.39	6134.69
Z	2	4
ρ _{calc} , g·cm ⁻³	1.643 ^a	1.502
range colcd	6° ≤ 2θ ≤ 45°	6° ≤ 2θ ≤ 45°
tot. data	4685	4401
unique data	4461	4011
averaging R	0.071	0.055
obsd data	1364 ^c	2964 ^e
R (R _w), %	8.71 (8.28)	7.35 (6.86)

^a Excluding solvent molecule. ^b Using 38 unique reflections at -157 °C. ^c F > 3.0σ(F). ^d Using 80 unique reflections at -173 °C. ^e F > 2.33σ(F).

(30 mL) was added Me₃SiCl (0.19 mL, 1.5 mmol). The resulting dark brown solution was layered with ether (40 mL); after 1 week, brown crystals of the product were collected by filtration, washed with MeCN (3 × 10 mL), and dried in air. The yield was 0.20 g (30% based on Mn). The crystals were found to lose solvent readily, and they were kept in the mother liquor until a suitable crystal had been found for X-ray crystallography. The latter established the formulation 5·2MeCN; the dried solid lost the interstitial MeCN molecules and appeared to be hygroscopic. The analysis sample analyzed for 5·6H₂O. Anal. Calcd for C₅₈H₅₆N₄O₂₄Mn₄ (fw 1412.86): C, 49.31; H, 4.00; N, 3.97. Found: C, 49.2; H, 3.8; N, 3.9. Selected IR spectrum (Nujol mull): 3400 (br), 2294 (w), 2249 (w), 1678 (s), 1603 (s), 1568 (s), 1489 (m), 1396 (s), 1321 (s), 1308 (s), 1292 (s), 1258 (m), 1238 (m).

Method B. A slurry of complex 3 (0.32 g, 0.17 mmol) in MeCN (50 mL) was stirred with benzoic acid (0.25 g, 2.0 mmol) for 1 day to give a red suspension. More benzoic acid (0.25 g, 2.0 mmol) was added and the mixture stirred for one more day to give a brick-red solid that was isolated by filtration, washed with MeCN (3 × 10 mL), and dried in air. The yield was 0.33 g (70%). The identity of the product was confirmed by IR spectroscopic comparison with samples from method A.

X-ray Crystallography. Data were collected for complexes 3 and 5 on a Picker four-circle diffractometer; details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere.²³ Crystallographic data are collected in Table I. For both complexes, the structures were solved by a combination of direct methods (MULTAN) and Fourier technique and refined by full-matrix least-squares.

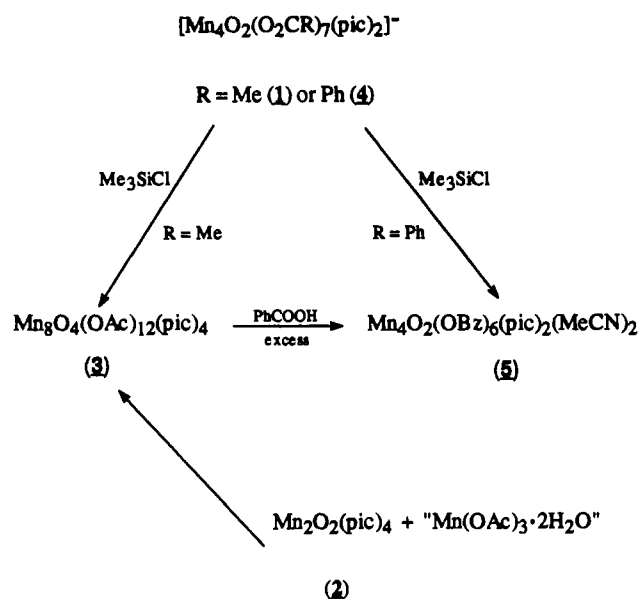
For complex 3, a systematic search of a limited hemisphere of reciprocal space yielded a set of diffraction maxima with symmetry and systematic extinctions that uniquely identified the space group as P2₁/n. Unfortunately, the crystal diffracted only weakly, and intensities decreased significantly above 2θ = 30°. Nevertheless, the structure solution proceeded uneventfully and all non-hydrogen atoms were readily located. After convergence of the isotropic refinement, only the Mn atoms were assigned anisotropic thermal parameters; other atoms were refined isotropically in the final cycles. Hydrogen atoms were also included in fixed, calculated positions. Five atoms from disordered interstitial solvent molecules were also located in a difference Fourier map and included as C atoms in the final cycles (C49 to C53). The final difference map was essentially featureless, the maximum peak being 0.78 e/Å³. The interstitial solvent area displayed several residual peaks, as expected.

For complex 5, a systematic search for a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to space groups C2/c or Cc. Subsequently solution and successful refinement of the structure confirmed the centrosymmetric choice C2/c. All non-hydrogen atoms of the Mn₄ molecule were readily located, were well behaved, and were refined with anisotropic thermal parameters. At this point, one interstitial MeCN molecule per asymmetric unit was located in a difference Fourier map but it was disordered. A satisfactory model was obtained comprising two sites for the MeCN

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Scheme I

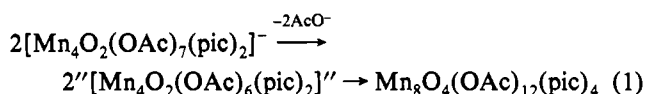


molecule, each with 50% occupancy. There also appears to be additional disorder at each site, but no attempt was made to resolve this. For the final cycles, all hydrogen atoms (except those on the interstitial MeCN molecules) were included in calculated and fixed positions. A final difference Fourier was essentially featureless, with the largest peak being $0.72 \text{ e}/\text{\AA}^3$.

Final values of conventional discrepancy indices R and R_w for both complexes are listed in Table I.

Results

Syntheses. For convenience, the various transformations described below are summarized in Scheme I. The first molecule chosen for aggregation studies was $[\text{NBu}^n_4][\text{Mn}_4\text{O}_2(\text{OAc})_7(\text{pic})_2]$ (1); this is readily prepared in high yield and purity, is soluble in a number of donor organic solvents, and has been characterized in detail.²¹ One potential means of aggregation, and the first one explored, was considered to be abstraction of a peripheral ligand to give a coordinatively-unsaturated fragment that *might* aggregate to an octanuclear product (eq 1); our hope was that a



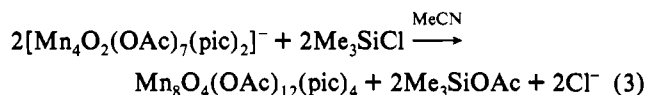
remaining acetate group would convert from μ_2 to μ_3 or μ_4 , both of which are known in Mn chemistry,^{3,10} and thus provide the required interfragment linkages. After several years of experience with mercurial manganese chemistry, we also recognized, however, that such a reaction need not proceed as logically as it might appear on paper.²⁴ A proven carboxylate-abstracting reagent is Me_3SiCl ,²⁵ forming the silyl ester (eq 2), but how can a particular



carboxylate be abstracted selectively? We felt it important to achieve this regioselectivity, if possible, because random attack of Me_3SiCl on the seven AcO^- groups of complex 1 seemed likely to lead to a messy mixture of products. In fact, such considerations represented an ulterior motive behind the decision to employ complex 1. Shown in Figure 1 is the structure of 1. Octahedral high-spin Mn^{III} (d^4) is a textbook example of a system that exhibits a Jahn-Teller (JT) distortion; in our many Mn^{III} -containing systems, this has invariably been a JT axial elongation, and 1 is

no exception. Also shown in Figure 1 are the relative orientations of the four JT axes. Close examination reveals that only one of the seven AcO^- groups has *both* its oxygen atoms (O27 and O29) lying on JT axial sites (with two "long" ($>2.2 \text{ \AA}$) Mn-O linkages), namely the acetate bridging the "body" or "backbone" Mn atoms (Mn1 and Mn3) of the Mn_4 butterfly. We suspected that this relatively weaker-bound AcO^- group might thus be more labile than the others, and we have described elsewhere that, in the presence of excess $\text{CD}_3\text{CO}_2\text{D}$, ^1H NMR indicates that only this AcO^- group undergoes acetate exchange rapidly on the NMR time scale.²¹ Its resonance rapidly and completely disappears to be replaced by a new resonance assigned to an average environment of free and bound AcO^- groups. Thus, exchange is fast on the NMR time scale. In contrast, the other AcO^- resonances are hardly affected until longer time periods have elapsed. We subsequently suspected that this more labile acetate, exposed as it is to external reagents (Figure 1), might also be the most susceptible to electrophilic attack by Me_3SiCl and that selective AcO^- abstraction from this site might therefore be possible. Subsequent observations appeared to support this thinking.

Treatment of complex 1 with 1 equiv of Me_3SiCl under N_2 in MeCN led to a color change to purple-brown and slow crystallization over several days of well-formed crystals of 3. To our great satisfaction, AcO^- loss had indeed induced dimerization of a tetranuclear unit to an octanuclear product (eq 3). Structural



characterization (*vide infra*) clearly confirmed a "dimer-of-tetramers" structure; i.e., an alternative formulation of 3 as $[\text{Mn}_4\text{O}_2(\text{OAc})_6(\text{pic})_2]_2$ is quite accurate. The low yield (18%) suggested that either a competing reaction was consuming Me_3SiCl or other Mn products were present in solution. Once formed, 3 is essentially insoluble in MeCN; however, slow kinetics of precipitation could be affecting the yield. Layering of the solution with a little ether increased the yield of 3 slightly; layering of the filtrate with more ether produced starting material (complex 1). This suggested competing reactions of Me_3SiCl , probably with H_2O ; the concentration of 1 employed (ca. 0.02 M) makes its molar amount comparable to that of the water impurities in the relatively large volume of MeCN used (60 mL/mmol of 1). Therefore, the molar ratio of Me_3SiCl was systematically increased, and the variation in yield of 3 is shown in Table II. Differences between yields in neat MeCN *vs* MeCN/ Et_2O are small, probably due to experimental variations; the Et_2O appears to increase the rate of precipitation rather than the amount. The yield optimizes at a 3:1 ratio. Higher ratios decrease the yield, and attempts to isolate and identify other products from the filtrates have proven fruitless; IR data have suggested mixtures, and we have not been able to separate a pure fraction. It is possible these mixtures contain molecules in which more than two $[\text{Mn}_4\text{O}_2(\text{OAc})_6(\text{pic})_2]$ fragments have been linked together, but it is also possible that the additional AcO^- abstraction has led to destabilization of the Mn_4O_2 core and its conversion to other units. Note, for example, that treatment of $[\text{Mn}_4\text{O}_2(\text{OAc})_7(\text{bpy})_2](\text{ClO}_4)$ with 3 or 4 equiv of Me_3SiCl leads to identification of at least two products, $\text{MnCl}_2(\text{bpy})$ and $[\text{Mn}_{11}\text{O}_{10}\text{Cl}_2(\text{OAc})_2(\text{bpy})_2(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, indicating that both disproportionation and drastic nuclearity changes have taken place.⁸

More recently, an alternative preparative route to 3 has been discovered. The reaction between $\text{Mn}^{\text{IV}}\text{O}_2(\text{pic})_4$ (2) and $\text{Mn}(\text{OAc})_3\cdot 2\text{H}_2\text{O}$ has been under investigation as a potential route to Mn/O/OAc/pic complexes containing Mn^{IV} ; instead, complex 3 (8Mn^{III}) is the product. A ratio-dependence study (Table III) shows an optimum yield of 3 (66% based on total Mn) at a 1:8 ratio of $2:\text{Mn}(\text{OAc})_3\cdot 2\text{H}_2\text{O}$. This is consistent with eq 4. On the

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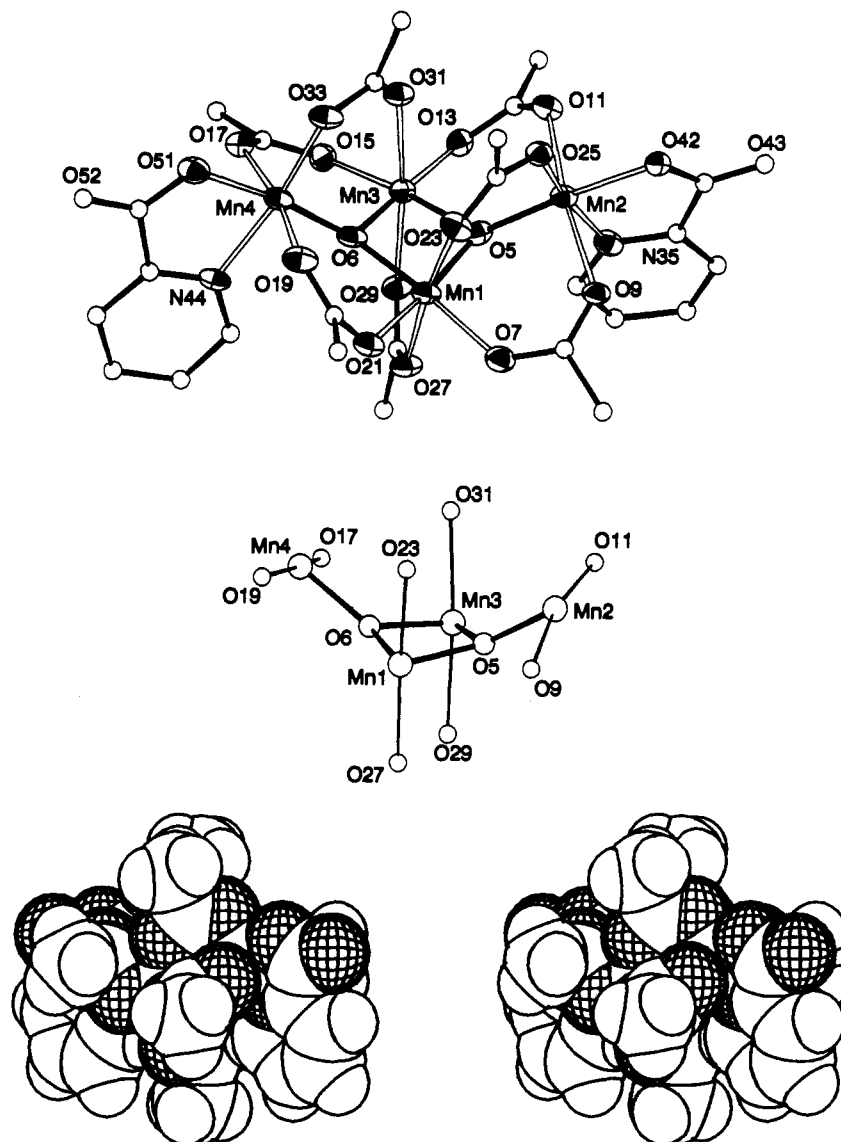
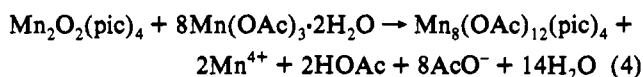


Figure 1. Structure of complex 1: (top) ORTEP representation (50% probability ellipsoids) with atoms not bound to Mn being deemphasized by depiction as spheres of arbitrary size; (middle) Mn_4O_2 core showing the relative disposition of the four Jahn-Teller axes; (bottom) space-filling stereoview showing the accessibility of the seventh AcO^- at the bottom to Me_3SiCl . The three viewpoints are slightly different.

Table II. Variation of Yield of Complex 3 as a Function of Me_3SiCl Ratio and Other Parameters

ratio ^a	yield, % ^b	conditions ^c	ratio ^a	yield, % ^b	conditions ^c
1:1	18	MeCN	3:1	34	MeCN
1:1	24	MeCN/Et ₂ O	3:1	43	MeCN/Et ₂ O
2:1	32	MeCN	3:1 ^d	0 ^e	MeCN/py
2:1	24	MeCN/Et ₂ O	4:1	19	MeCN/Et ₂ O

^a Me_3SiCl : 1; 0.50 mmol of 1 in distilled MeCN (30 mL). ^b $\pm 3\%$; the product was washed copiously with MeCN to remove any starting material and dried; the formulation $3 \cdot 7/2 \text{MeCN} \cdot 4\text{H}_2\text{O}$ was employed. ^c Layering employed an equal volume of Et₂O. ^d Plus 1.0 mmol of py. ^e A small quantity of $\text{Mn}_2\text{O}_2(\text{pic})_4$ (2) was obtained.



basis of this model, 2 supplies the pic^- and $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ supplies the Mn^{III} and AcO^- ; the filtrate is still colored, confirming the presence of Mn^{IV} and/or Mn^{III} in solution. This high yield route to 3 is particularly convenient for bulk syntheses (method B in the Experimental Section).

The formation of 3 from 1 with Me_3SiCl is thought to proceed *via* abstraction of the unique AcO^- group to form the $[\text{Mn}_4\text{O}_2(\text{OAc})_6(\text{pic})_2]$ fragment that then dimerizes (eq 1). The rapidity of the reaction and the paramagnetic nature of the species preclude monitoring of the reaction by NMR, and so some

Table III. Effect of the Complex 2: $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ Ratio on the Yield and Purity of Complex 3

2: $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ ratio	yield of 3 ^a	purity ^b	2: $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ ratio	yield of 3 ^a	purity ^b
1:10	44	pure	1:4	<21 ^c	impure ^d
1:8	66	pure	1:2	^e	very impure ^e
1:6	50	pure			

^a Yield based on total available Mn using the formulation $3 \cdot 3/2 \text{MeCN} \cdot 5\text{H}_2\text{O}$ indicated by elemental analysis. ^b Assessed by IR. ^c The number indicates the yield if all isolated solid were 3, which it is not. ^d The impurity is complex 2. ^e Heavily contaminated with 2.

alternative support for the formation of the fragment has been sought. Addition of py (Table II), hopefully to trap the fragment as $\text{Mn}_4\text{O}_2(\text{OAc})_6(\text{pic})_2(\text{py})_2$, suppressed formation of 3 but gave instead small amounts of 2, a Mn^{IV} species, presumably *via* pyridine-induced disproportionation of Mn^{III} . Addition of Et₂O to the filtrate merely gave more 2 (but containing a little 3 as judged by IR). An alternative approach to trapping the putative fragment therefore seemed necessary.

Inspection of space-filling diagrams of 3 indicated that the Mn_8 "dimer-of-tetramers" could not form if $\text{R} = \text{Ph}$ owing to steric repulsions, suggesting that a $\text{Mn}_4\text{O}_2(\text{OBz})_6(\text{pic})_2$ fragment should not aggregate. Thus, $(\text{NBu}^n)_4[\text{Mn}_4\text{O}_2(\text{OBz})_6(\text{pic})_2]$ (4) was treated with Me_3SiCl and the isolated product was indeed the hoped-for tetranuclear complex $\text{Mn}_4\text{O}_2(\text{OBz})_6(\text{pic})_2(\text{MeCN})_2$ (5)

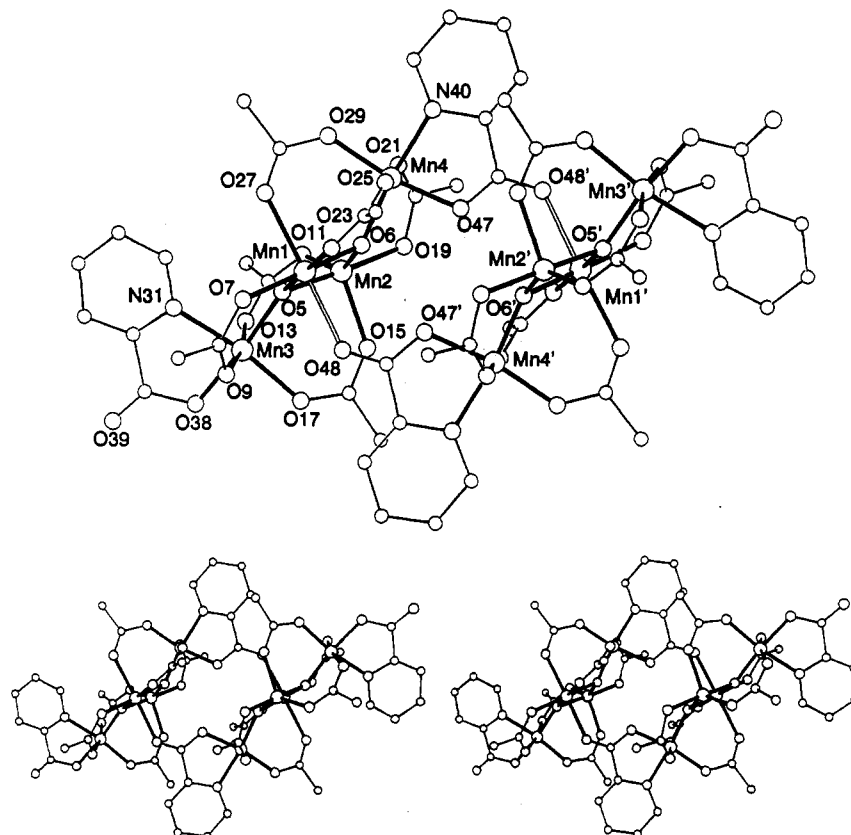
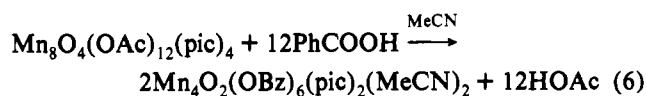
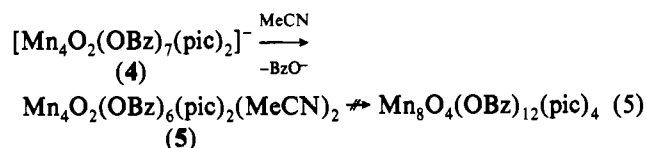


Figure 2. Labeled structure and stereoview of complex 3. To avoid congestion, not all symmetry-equivalent atoms have been labeled. The μ_3 -O atoms are O5, O5', O6, and O6'. The two interfragment linkages (Mn1-O48 and Mn1'-O48') are unshaded to assist in their location.

possessing two MeCN molecules instead of a seventh BzO⁻ (eq 5). Further, treatment of complex 3 with excess PhCOOH led



to BzO⁻/AcO⁻ exchange and formation of complex 5 (eq 6). Thus, 3 can be "deaggregated" by incorporation of a bulkier R group. We feel that structural confirmation of 5 (*vide infra*) lends strong support to the overall sequence of eq 1 for the formation of 3 from 1.

It has been argued that the location of the unique carboxylate on two JT axes provides the extra lability to ensure selective AcO⁻ abstraction. If so, one might expect the analogous iron complex (NBuⁿ)₄[Fe₄O₂(OAc)₇(pic)₂] not to react with Me₃SiCl as cleanly as complex 1, since high-spin Fe^{III} (d⁵) is not susceptible to Jahn-Teller distortion. Treatment of (NBuⁿ)₄[Fe₄O₂(OAc)₇(pic)₂]^{20b} with 1 equiv of Me₃SiCl led to slow precipitation of a red powder over several hours. The IR spectrum of this material clearly did not correspond to that of an Fe analogue of 3 and appeared to consist of a mixture of products. The elemental analysis was inconsistent with any reasonable formulation, and attempts to obtain a pure, crystalline material were unsuccessful. Although all that can be said with certainty is that clean conversion to the Fe analogue of 3 had not occurred, our suspicion is that nonselective AcO⁻ abstraction has led to a variety of products.

Description of Structures. The structures of complexes 3 and 5 are shown in Figures 2-4. Fractional coordinates for 3 and 5 are listed in Tables IV and V, respectively. Selected metric parameters are collected in Tables VI and VII. Complex 3

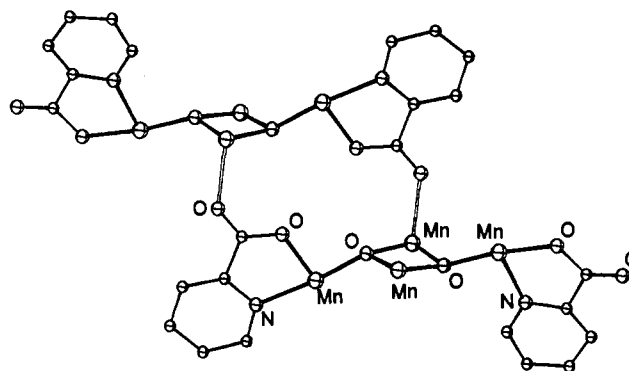
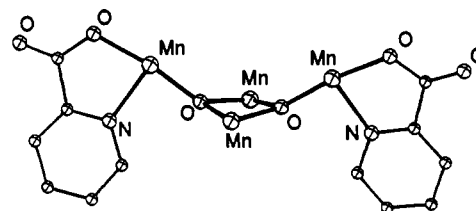


Figure 3. The core structures of complexes 1 (top) and 3 (bottom) showing changes to the Mn₄O₂ cores and pic⁻ ligation on aggregation and the location of the two interfragment bonds.

crystallizes in monoclinic space group $P2_1/n$ and contains Mn₈ molecules lying on inversion centers. The asymmetric unit thus contains half the molecule. The structure of 3 consists of two [Mn₄O₂(OAc)₆(pic)₂] fragments that have dimerized *via* the formation of two interfragment linkages. The latter involve picolate oxygen atoms O48 and O48', which were not bound to Mn in the starting material, complex 1 (i.e., oxygen atoms O43 and O52 in Figure 1). Only these two bonds, Mn1-O48 and its symmetry-related partner, hold the fragments together, and they are left unshaded in Figure 2 to emphasize their location. The interfragment linkages are 2.236(19) Å long, comparable with

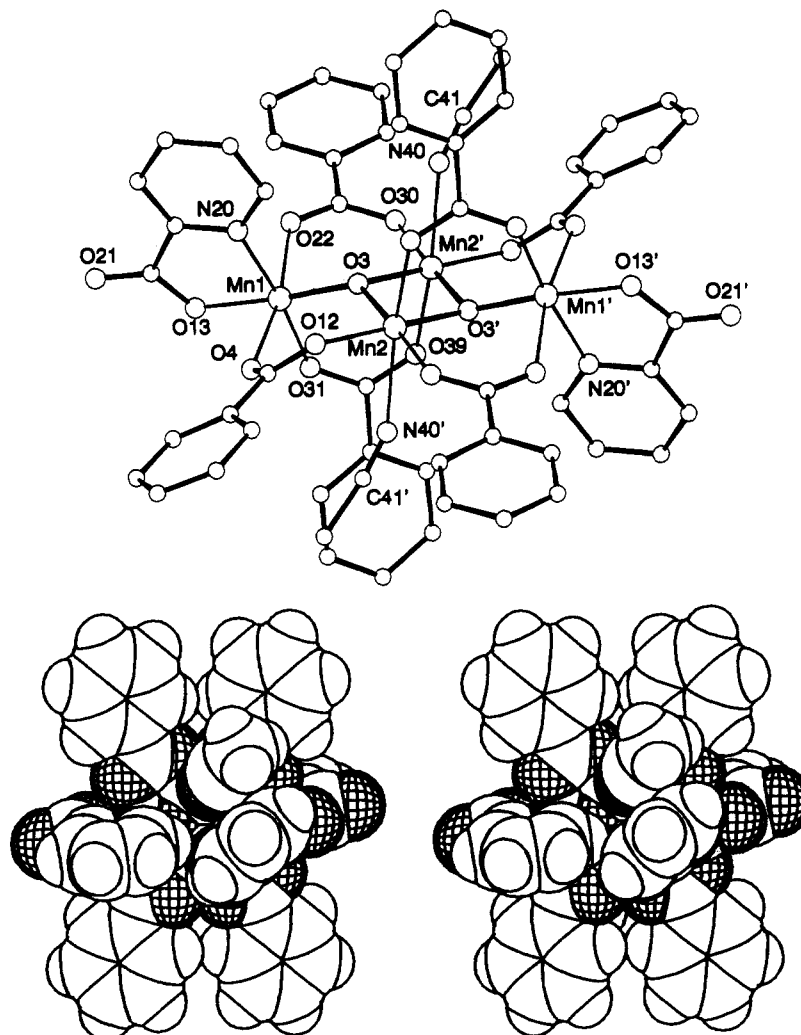


Figure 4. Structure of complex 5: (top) Atom labeling scheme, with not all symmetry-related atoms labeled to avoid congestion; (bottom) space-filling stereoview emphasizing the steric bulk that prevents aggregation and the MeCN groups (viewpoint approximately perpendicular to the central Mn_2O_2 rhomb).

Table IV. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10$) for Complex 3

atom	x	y	z	B_{iso}^a	atom	x	y	z	B_{iso}^a
Mn1	4195(4)	1216(2)	8888(4)	16	O25	6598(17)	521(8)	8428(16)	20(4)
Mn2	2357(5)	493(2)	8237(4)	20	C26	7902(31)	994(13)	9645(29)	35(8)
Mn3	1265(4)	1586(2)	8981(4)	18	O27	4606(17)	1370(8)	7080(17)	21(5)
Mn4	5077(4)	152(2)	7655(4)	16	C28	4973(27)	1113(12)	6311(26)	18(6)
O5	2518(16)	1196(7)	8456(15)	14(4)	O29	5135(17)	613(8)	6370(16)	20(4)
O6	4016(17)	510(8)	8519(16)	17(4)	C30	5318(26)	1339(12)	5215(24)	17(6)
O7	4232(20)	1950(8)	9205(18)	29(5)	N31	1445(22)	2129(9)	7724(20)	16(5)
C8	3405(34)	2214(14)	9726(31)	35(8)	C32	2180(28)	2146(13)	6869(28)	24(7)
O9	2438(18)	2071(7)	9981(16)	17(4)	C33	2220(36)	2514(16)	6078(34)	51(8)
C10	3853(33)	2757(14)	10009(31)	40(8)	C34	1371(35)	2871(15)	6156(33)	45(8)
O11	1031(18)	555(8)	7038(16)	21(4)	C35	529(30)	2865(13)	7006(30)	30(7)
C12	188(31)	841(14)	7062(29)	30(7)	C36	561(29)	2465(13)	7698(27)	28(7)
O13	9999(19)	1191(9)	7764(18)	32(5)	O38	-271(28)	2421(12)	8673(26)	19(6)
C14	-783(33)	794(14)	6081(31)	43(8)	O39	-21(17)	2018(8)	9342(16)	18(4)
O15	1468(17)	377(7)	9711(16)	17(4)	O40	8866(20)	2683(9)	8764(18)	31(5)
C16	1046(26)	660(12)	10440(25)	15(6)	N40	3835(20)	330(9)	13170(19)	11(5)
O17	919(17)	1143(8)	10287(16)	17(4)	C41	3379(24)	253(10)	14177(22)	5(5)
C18	657(26)	461(12)	11506(25)	20(6)	C42	2646(29)	639(13)	14593(27)	27(7)
O19	2284(18)	9758(8)	7986(17)	22(5)	C43	2370(28)	1093(13)	14000(27)	25(7)
C20	2822(24)	-456(11)	7154(22)	8(6)	C44	2848(29)	1136(13)	12920(27)	25(7)
O21	3590(20)	-263(9)	6711(19)	35(5)	C45	3597(27)	771(12)	12572(25)	18(6)
C22	2451(34)	9017(15)	6979(33)	49(8)	C46	4145(23)	771(11)	11419(22)	4(5)
O23	5884(19)	1184(9)	9292(18)	28(5)	O47	5168(18)	-399(8)	8775(16)	20(4)
C24	6704(24)	886(11)	9122(22)	7(5)	O48	3905(16)	1106(7)	10752(15)	12(4)

^a B_{iso} values for atoms refined anisotropically are calculated using the formula in: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

other JT elongated Mn–O(acetate) bonds in 3 (2.126(20)–2.237(23) Å. Although Figure 2 may suggest that there is a channel through 3, a space-filling model indicates that this is not the case; the two fragments are close-fitting.

The conversion of 1 to 3 can be rationalized as follows: removal of the AcO⁻ group bridging the central Mn atoms generates two coordinatively-unsaturated, five-coordinate Mn centers, one of which is converted back to six-coordination *via* the new inter-

Table V. Fractional Coordinates ($\times 10^4$)^a and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10$) for **5**

atom	x	y	z	B_{iso}^b
Mn1	3335(1)	1981(1)	1658(1)	16
Mn2	2917(1)	3005(1)	-110(1)	16
O3	2891(2)	2204(2)	465(4)	16
O4	2645(3)	1376(3)	2256(4)	22
C5	2252(4)	1086(4)	1751(7)	20
O12	2897(3)	3812(2)	-789(4)	20
O13	3809(3)	1659(3)	2801(4)	19
C14	4090(4)	1138(4)	2646(7)	19
C15	4045(4)	892(4)	1535(6)	20
C16	4338(4)	380(4)	1184(7)	23
C17	4252(4)	196(4)	139(8)	27
C18	3876(4)	548(4)	-495(7)	24
C19	3589(4)	1059(4)	-108(7)	23
N20	3680(3)	1228(3)	909(5)	17
O21	4359(3)	860(3)	3329(5)	27
O22	4143(3)	2457(3)	1150(5)	24
C23	4180(4)	2939(4)	645(6)	21
O30	3748(3)	3216(3)	183(4)	22
O31	3041(2)	2653(2)	2523(4)	17
C32	2745(4)	3145(4)	2293(7)	18
O39	2699(3)	3379(2)	1393(4)	18
N40	3340(3)	2630(3)	-1682(6)	21
C41	3525(5)	2721(5)	-2458(9)	40
C42	3728(9)	2910(9)	-3504(12)	97
C43	9851(6)	3375(5)	496(11)	55
C44	9914(10)	3801(9)	1512(18)	34
N45	10065(13)	4138(8)	2826(13)	43
C46	9950(10)	2937(11)	1188(20)	44
N47	10063(12)	2570(10)	1925(17)	67

^a Phenyl rings omitted. ^b See Table IV, footnote.

fragment linkages; the other one remains five-coordinate. Thus, Mn1, Mn3, and Mn4 are six-coordinate and essentially octahedral, whereas Mn2 has distorted trigonal bipyramidal geometry (O5–Mn2–O19 = 176.7(9)°). There are also some structural changes to the Mn₄O₂ core of the fragments as a result of the need to accommodate the interfragment linkages. This is best seen by inspection of Figure 3, where complexes **1** (top) and **3** (bottom) are shown devoid of their AcO⁻ ligands. Complex **1** is clearly seen to have a central Mn₄ butterfly unit with pic⁻ oxygen atoms *trans* to the μ_3 -O²⁻ groups. In complex **3**, however, note that two pic⁻ groups have swung into positions that allow the formerly noncoordinated oxygen atom to ligate to a Mn in the other fragment. As a result, a pic⁻ nitrogen atom is now *trans* to the μ_3 -O²⁻ group. Also, the Mn atom to which this pic⁻ group is attached has relocated to a position that makes the Mn₄ unit now almost planar rather than butterfly.

The structure of complex **5** is shown in Figure 4 together with a space-filling stereoview. The molecule again lies on an inversion center. The seventh AcO⁻ is gone and is replaced by two MeCN groups, which, however, bind on opposite sides of the central Mn₂O₂ rhomb, as required by the inversion center. The Mn₄ unit is now rigorously planar rather than in a butterfly arrangement. The two pic⁻ groups keep their oxygen atoms (O13, O13') *trans* to the μ_3 -O²⁻ groups (O3, O3'), but again as required by the inversion center, one of the pic⁻ groups has rotated such that the pyridine rings are *anti* rather than *syn* as in **4** and **1** (Figure 3, top). This again emphasizes the lability and structural deformability of the Mn₄O₂ complexes, as already evidenced in the structure of **3 vs 1**. The MeCN groups bind in a significantly nonlinear fashion (Mn2–N40–C41 = 149.1(8)°), and this is undoubtedly due to steric rather than electronic factors, the former probably comprising both steric pressure from adjacent BzO⁻ rings (Figure 4, bottom) and crystal packing forces.

Discussion

The present work has successfully overcome, for the particular complex employed, the two main problems in the controlled linking of Mn/O/RCO₂⁻ aggregates into higher nuclearity oligomers. First, a means of linkage has been achieved, and second, the

Table VI. Selected Interatomic Distances (Å) and Angles (deg) for Complex **3**

(a) Distances			
Mn1···Mn2	2.876(7)	Mn1···Mn3	3.450(7)
Mn1···Mn4	3.309(7)	Mn2···Mn3	3.248(7)
Mn2···Mn4	3.300(7)	Mn3–O5	1.872(19)
Mn1–O5	1.932(19)	Mn3–O9	2.134(20)
Mn1–O6	1.904(20)	Mn3–O13	2.213(23)
Mn1–O7	1.956(23)	Mn3–O17	1.970(20)
Mn1–O23	1.939(23)	Mn3–O38	1.905(20)
Mn1–O27	2.222(21)	Mn3–N31	2.060(25)
Mn1–O48	2.236(19)	Mn3–N31	2.060(25)
Mn2–O5	1.863(20)	Mn4–O21	2.237(23)
Mn2–O6	1.882(20)	Mn4–O25	2.126(20)
Mn2–O11	1.997(21)	Mn4–O29	1.927(20)
Mn2–O15	2.061(20)	Mn4–O47	1.946(20)
Mn2–O19	1.947(21)	Mn4–N40	2.038(23)
(b) Angles			
Mn–O6–Mn2	98.5(9)	O5–Mn3–O9	92.7(8)
Mn1–O5–Mn3	130.2(10)	O5–Mn3–O13	90.4(8)
Mn2–O5–Mn3	120.9(10)	O5–Mn3–O17	96.8(8)
Mn1–O6–Mn2	98.9(9)	O5–Mn3–O38	173.3(9)
Mn1–O6–Mn4	123.2(10)	O5–Mn3–N31	92.1(9)
Mn2–O6–Mn4	123.8(11)	O9–Mn3–O13	170.8(8)
O5–Mn1–O6	79.9(8)	O9–Mn3–O17	94.0(8)
O5–Mn1–O7	94.9(9)	O9–Mn3–O38	89.0(8)
O5–Mn1–O23	175.9(10)	O9–Mn3–N31	84.1(8)
O5–Mn1–O27	90.5(8)	O13–Mn3–O17	94.3(8)
O5–Mn1–O48	93.3(7)	O13–Mn3–O38	87.0(8)
O6–Mn1–O7	174.8(9)	O13–Mn3–N31	87.1(9)
O6–Mn1–O23	96.0(9)	O17–Mn3–O38	89.6(9)
O6–Mn1–O27	89.2(8)	O17–Mn3–N31	171.0(10)
O6–Mn1–O48	94.4(8)	O38–Mn3–N31	81.6(9)
O7–Mn1–O23	89.2(10)	O6–Mn4–O21	91.4(8)
O7–Mn1–O27	89.9(8)	O6–Mn4–O25	94.0(8)
O7–Mn1–O48	86.8(8)	O6–Mn4–O29	99.1(9)
O23–Mn1–O27	89.2(8)	O6–Mn4–O47	91.2(9)
O23–Mn1–O48	87.2(8)	O6–Mn4–N40	171.8(9)
O27–Mn1–O48	175.2(7)	O21–Mn4–O25	174.5(8)
O5–Mn2–O6	82.3(9)	O21–Mn4–O29	88.7(9)
O5–Mn2–O11	94.6(9)	O21–Mn4–O47	88.9(8)
O5–Mn2–O15	94.5(8)	O21–Mn4–N40	85.5(9)
O5–Mn2–O19	176.7(9)	O25–Mn4–O29	89.2(8)
O6–Mn2–O11	145.1(8)	O25–Mn4–O47	92.3(8)
O6–Mn2–O15	112.4(8)	O25–Mn4–N40	89.4(9)
O6–Mn2–O19	94.7(9)	O29–Mn4–O47	169.5(9)
O11–Mn2–O15	102.5(8)	O29–Mn4–N40	88.4(9)
O11–Mn2–O19	87.2(9)	O47–Mn4–N40	81.2(9)
O15–Mn2–O19	87.7(8)		

“building-block” molecule has not undergone major changes to its intrinsic structure. The former area is under investigation by a number of groups interested in linking metal aggregates or clusters.^{26–30} The latter is, however, a particularly worrisome problem for higher (\geq II) oxidation state 3d metal aggregates where substitutional lability and the absence of metal–metal bonding often mean that the building block is quite “fragile” and prone to drastic structural and nuclearity changes. We have already seen such dramatic changes^{8,24} on several occasions. The present work thus represents a successful “test-of-feasibility” for our new program although the described procedures are by no means generally applicable; although we could not have predicted the precise *means* of interfragment linkage, we are encouraged that it has proven possible to selectively abstract a JT-labilized AcO⁻ group and thereby to dimerize an Mn₄ unit into an Mn₂ product, without significantly altering the Mn₄O₂ core.

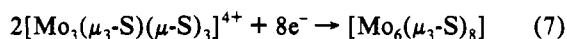
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Table VII. Selected Interatomic Distances (Å) and Angles (deg) for Complex 5

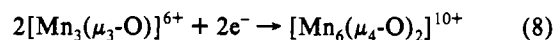
(a) Distances			
Mn1···Mn2	3.282(1)	Mn1···Mn2'	3.390(1)
Mn2···Mn2'	2.892(2)	Mn1···Mn1'	6.013(1)
Mn1-O3	1.859(5)	Mn2-O3	1.887(5)
Mn1-O4	2.169(6)	Mn2-O3'	1.905(6)
Mn1-O13	1.912(5)	Mn2-O12	1.953(5)
Mn1-O22	2.182(6)	Mn2-O30	1.942(6)
Mn1-O31	1.944(5)	Mn2-O39	2.131(5)
Mn1-N20	2.045(7)	Mn2-N40	2.361(7)
O3···O3'	2.454(12)	C41-N40	1.090(12)
(b) Angles			
O3-Mn1-O13	173.1(2)	O3-Mn2-O3'	80.6(2)
O3-Mn1-O31	94.6(2)	O3-Mn2'-O30	100.3(2)
O3-Mn1-N20	91.8(2)	O3'-Mn2-O12	175.5(2)
O3-Mn1-O4	93.9(2)	O3'-Mn2'-O39	89.9(2)
O3-Mn1-O22	94.0(2)	O3-Mn2-N40'	91.2(2)
O13-Mn1-O31	92.1(2)	O3'-Mn2'-O30	177.3(2)
O13-Mn1-N20	81.4(2)	O3-Mn2-O12	95.5(2)
O13-Mn1-O4	84.4(2)	O3-Mn2'-O39	94.3(2)
O13-Mn1-O22	87.0(2)	O3-Mn2'-N40	96.1(2)
O31-Mn1-N20	173.3(2)	O30'-Mn2-O12	83.5(2)
O31-Mn1-O4	90.7(2)	O30-Mn2'-O39	88.2(2)
O31-Mn1-O22	90.5(2)	O30-Mn2'-N40	81.4(2)
N20-Mn1-O4	87.2(2)	O12-Mn2-O39'	92.7(2)
N20-Mn1-O22	85.7(2)	O12-Mn2-N40'	86.9(2)
O4-Mn1-O22	169.5(2)	O39-Mn2'-N40	169.6(2)
Mn2-N40-C41	149.1(8)	Mn1-O3-Mn2'	128.4(3)
Mn2-O3-Mn2'	99.4(2)	Mn1-O3-Mn2	122.3(3)

The controlled linkage of fragile, paramagnetic 3d aggregates with retention of their intrinsic identity is rare. Probably the most advanced efforts to date are those by Coucouvanis and co-workers,³¹ who, for biological modeling reasons, have accomplished the controlled linking of [Fe₄S₄]²⁺ and [MoFe₃S₄]³⁺ cubane aggregates by S²⁻, either alone or in combination with additional ligands (e.g., OH⁻, CN⁻, N₂H₄, etc.). The linking of two [Fe₄S₄]²⁺ cores by S²⁻ has also been reported by Holm;^{32,33b} in addition, this group has also linked [Fe₄S₄]²⁺ cores with a variety of dithiolate ligands.³³

It should be emphasized that the aggregation of 1 to 3 does not fall within the realm of "cluster condensation" reactions. The latter are those reactions in which smaller nuclearity M_x cores are fused to higher nuclearity M_y (often y = 2x) cores, usually by conversion of μ_n-bridging groups in the starting material to μ_{n+1} modes.³⁴⁻³⁶ For example, reductive dimerization of Mo₃(μ₃-S)(μ₂-S)₃Cl₄(PEt₃)₄(MeOH) (3Mo^{IV}) leads to condensation of the [Mo₃S₄] core and formation of Mo₆S₈(PEt)₆ (2Mo^{IV}, 4Mo^{III}) (eq 7).^{35a} A related core condensation reaction is also known in



Mn chemistry *viz.* reductive dimerization of Mn₃O(O₂CPh)₆(py)₂(H₂O) (Mn^{II}, 2Mn^{III}) to Mn₆O₂(O₂CPh)₁₀(py)₂(MeCN)₂ (4Mn^{II}, 2Mn^{III}) (eq 8).^{3d} Another related but clearly different type of core condensation is seen in the conversion of the [Mn₄O₂]⁸⁺ core into a [Mn₇O₄]¹³⁺ core where two [Mn₄O₂]



butterfly units have condensed by vertex sharing at one of the "wing-tip" Mn atoms;^{4b} no oxidation-state changes have occurred this time. The above condensations are distinctly different from the conversion of 1 to 3 and the linkage of Fe₄S₄ aggregates by Coucouvanis and Holm; the latter are best described as "building-block" aggregation, the main distinguishing feature being retention of the identity of the starting material. As an additional illustrative example, contrast the building-block linkage of Mo₂(O₂CBuⁱ)₄ dimers using a variety of organic bridging groups (L) to give [Mo₂(μ-L)Mo₂] products²⁹ with the condensation reaction of, e.g., Mo₂Cl₄(PPh₃)₂(MeOH)₂ to give Mo₄Cl₈(MeOH)₄, the latter containing a rectangular metal-metal-bonded core.^{36a} Similarly, the crystal structure of a related building-block linkage product, [Ru₂(O₂CR)₄](pyz) (pyz = pyrazine), has recently appeared.³⁰

Conclusions and Prognosis for the Future. The present results serve to establish the feasibility of linking Mn_x aggregates, and future work will build on this initial success. It is evident, however, that successful formation of 3 was fortunate in several ways. The high solubility of 1 only in good donor solvents had seemed likely to doom the aggregation attempts and give, for example, the acetate version of 5. Similarly, the available Cl⁻ (eq 2) could have given [Mn₄O₂(OAc)₆(pic)₂Cl_x]^{x-} (x = 1, 2). No doubt all these species are present in equilibrium in solution, and the low solubility of 3 causes the octanuclear species to preferentially crystallize. Further, it was fortunate that the flexibility of the peripheral ligation was sufficient to allow the pic⁻ group to provide the interfragment linkage; this aspect of the formation of 3 remains, on hindsight, the point at which there was least "operator control" and the area in which future modifications to our approach must be made. In any case, very few of our Mn aggregates possess pic⁻ groups, and it is clear that future work cannot rely on pic⁻ or similar groups *already* bound to the aggregate to provide interfragment linkages. It seems unlikely that we shall continue to be fortunate and obtain aggregated products this way. Thus, future work will be and is being performed in the presence of an exogenous bridging ligand capable of forming a covalent link between two fragments generated by carboxylate abstraction and thus bringing the fragment-linkage step under better operator control. Choice of a suitable and good ligand (e.g., dicarboxylate, pyrazine, 4,4'-bipyridine, etc.) as employed by others with 4d/5d metals²⁶⁻³⁰ should allow the reaction to be directed toward the desired higher nuclearity products. For the latter objective, the selective abstraction of Jahn-Teller-labilized carboxylate groups as demonstrated in this work should prove invaluable in providing regioselectivity to linkage attempts. Since this work was completed, in fact, we have obtained additional products from reactions involving selective abstraction of Jahn-Teller-labilized carboxylate groups, and we are therefore confident of the more general applicability of this latter effect. Indeed, the combination of exogenous bridging ligand and selective carboxylate abstraction has already, at time of writing, yielded access to both additional examples of aggregates-of-aggregates and also to one-dimensional polymers of aggregates.³⁷ These results will be described in due course.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 8808019).

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, and bond distances and angles and ORTEP diagrams for complexes 3 and 5 (26 pages). Ordering information is given on any current masthead page. Complete MSC structure reports (Nos. 89182 (3) and 90225 (5)) are available on request from the Indiana University Chemistry Library.

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