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# $[Mn_3O(O_2CPh)_6(py)_2]_2(4,4'-bpy)$ and $[Mn_9O_7(O_2CC_6H_4-p-OMe)_{13}(4,4'-bpy)]_2$ : new multinuclear manganese complexes

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#### Abstract

The synthesis, X-ray crystal structures and magnetic properties of two new types of dimers of multinuclear manganese aggregates are described.  $[Mn_3O(O_2CPh)_6(py)_2]_2(4,4'-bpy)$  is prepared from the reaction of the trinuclear starting material  $[Mn_3O(O_2CPh)_6(py)_2]_2(H_2O)]$  with 4,4'-bipyridine. This compound can be described as a dimer of trinuclear units and has been characterized crystallographically as part of a unit cell which also contains a monomeric, trinuclear species. Dimers of enneanuclear manganese complexes linked by two bifunctional units (4,4'-bipyridine or *trans*-1,2-bis(4-pyridylethene)) may be prepared from the tetranuclear starting material, ("Bu<sub>4</sub>N)[Mn<sub>4</sub>O<sub>2</sub>-(O<sub>2</sub>CR)<sub>9</sub>(H<sub>2</sub>O)], where R = Ph or C<sub>6</sub>H<sub>4</sub>-p-OMe. The new octadecanuclear complex [Mn<sub>5</sub>O<sub>7</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-p-OMe)<sub>13</sub>(4,4'-byy)]<sub>2</sub> has been structurally characterized. This complex shows magnetic behavior which can be fit by considering only magnetic interactions within the individual Mn<sub>5</sub>O<sub>7</sub> units. © 1997 Elsevier Science S.A.

Keywords: Manganese complexes; Polynuclear complexes; Magnetism; Crystal structures

#### 1. Introduction

The covalent linking of molecules with large ground state spins is one possible method of promoting magnetic interactions that can lead to molecule-based magnetic materials. Networks of metals linked by multifunctional ligands have a distinct advantage over truly 'molecular' materials because the covalent bonding interactions throughout the solid generally result in stronger magnetic interactions than are possible without such interactions [1]. There is also much current interest in trying to build 2-D and 3-D polymeric networks of metals from mononuclear metal building blocks and multifunctional organic ligands such as squarate [2], 4,4'-bipyridine [3] and 1,3,5-benzenetricarboxylic acid [4]. Such polymeric materials have been touted as porous inorganic solids that may perform absorption [5], ion exchange [6] or shape selective catalysis [7]. However, despite the characterization of many new linked species built from metal monomers and small metal aggregates [8], little analogous work has been done to build polymers or oligomers through the linking of large metal clusters. The use of large or intermediate-sized metal aggregates as building blocks for such

0020-1693/97/\$17.00 © 1997 Elsevier Science S.A. All rights reserved PII \$0020-1693(97)05661-2 reactions is one potential way of working toward both magnetic and structure/function goals.

Bifunctional ligands such as 4,4'-bipyridine [9] and pyrazine [10] have been shown to mediate electron transfer [9a] and magnetic interactions [11,9b], although the magnetic interactions have generally been shown to be weak. The coordination chemistry of 4,4'-bpy with transition metals includes dimers [12] as well as linear [13,10], sheet [3c] and 3-D polymers [3a,c] of a wide variety of monomeric building blocks. Several examples of polymers of Cu [14,9b] dimers linked by 4,4'-bipyridine have been structurally characterized, and dimolybdenum [10] units have also been linked by 4,4'-bpy to give extended polymer chains. Dimers of trinuclear (M<sub>3</sub>O) ruthenium species [15] linked by 4,4'-bpy have also been isolated.

There is precedent for interesting polymerization and aggregation reactions of higher nuclearity manganese oxide aggregates [16–18,21–23]. Polymerization and dimerization of tetranuclear  $Mn_4O_2$  'butterfly' species have been demonstrated with two closely related complexes, ("Bu<sub>4</sub>N)-[ $Mn_4O_2(O_2CPh)_6(dbm)_2$ ] and ("Bu<sub>4</sub>N)[ $Mn_4O_2(O_2CPh)_6(dbm)_2$ ] [16], where Hdbm is dibenzoyImethane. Treatment of ("Bu<sub>4</sub>N)[ $Mn_4O_2(O_2CPh)_6(dbm)_2$ ] with

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4,4'-bipyridine results in a zigzag polymer of  $Mn_4$  units,  $[Mn_4O_2(O_2CPh)_6(dbm)_2(4,4'-bpy)]_2$ , while treatment of the EtOAc adduct with *trans*-1,2-bis(4-pyridyl)ethene (bpe) results in a dimer of  $Mn_4$  units,  $[Mn_4O_2(O_2CPh)_6-(dbm)_2]_2(bpe)$  [16]. Magnetic data for these complexes can be fit assuming magnetically isolated tetranuclear units, indicating that magnetic interaction between the aggregates must be small [17].

The development of rational syntheses of large multinuclear metal complexes, especially from building blocks possessing high ground state spins, has been a recent goal of coordination chemists. It has been shown that such complexes can be prepared through both linking of multinuclear units [16,17] and through structural rearrangement to form even larger aggregates [18–21,23]. The reactivity of the bifunctional ligands 4,4'-bpy and bpe with the trinuclear and tetranuclear manganese aggregates,  $Mn_3O(O_2CPh)_6(py)_2(H_2O)$ and ( $^nBu_4N$ ) [ $Mn_4O_2(O_2CPh)_9(H_2O)$ ], was investigated in order to explore the coordination chemistry of bifunctional ligands in the presence of potentially reactive aggregates.

One candidate for the isolation of discrete rather than polymeric structures is the asymmetric trinuclear species  $Mn_3O(O_2CPh)_6(py)_2(H_2O)$  [19]. This neutral,  $Mn^{II}_2Mn^{II}$ mixed-valence triangular complex has a ground state spin of S=1/2 [20]. One or more of the axial donor ligands could be replaced by bifunctional ligands such as 4,4'-bipyridine, which could bridge the multinuclear complexes and potentially mediate inter-unit interactions. Depending on the degree of substitution, however, dimers, oligomers and one- or twodimensional polymers could be formed. Characterization of the products of such reactions will be discussed, and the crystal structure of one of the resulting aggregates will be presented.

Another complex which is an ideal candidate for linking through bifunctional nitrogen-containing ligands is the tetranuclear Mn<sub>4</sub>O<sub>2</sub> 'butterfly' complex, ("Bu<sub>4</sub>N) [Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CPh)<sub>9</sub>-(H<sub>2</sub>O)]. It is well-suited for such reactivity because it does not possess strong capping chelating ligands like other Mn<sub>4</sub>O<sub>2</sub> butterfly complexes. This 'naked butterfly', as it has been designated, shows a tendency to rearrange and aggregate resulting in the formation of Mn<sub>8</sub> [21,22], Mn<sub>9</sub> [21] and even Mn<sub>18</sub> [23] complexes under appropriate reaction conditions. Thus, the products of its reactions can be exciting and novel but are often difficult to predict. In the present work reactions of ("Bu<sub>4</sub>N)[Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CPh)<sub>9</sub>(H<sub>2</sub>O)] with bifunctional N-donor ligands were investigated in order to explore the potential dimerization, polymerization or aggregation reactions that might result. These reactivity studies resulted in the isolation of several new complexes and in the structural characterization of a new octadecanuclear species that consists of two Mn<sub>9</sub> units linked by two 4,4'-bpy ligands.

#### 2. Experimental

#### 2.1. Materials and characterization

Solvents were used as purchased and reactions were performed under aerobic conditions.  $[Mn_3O(O_2CPh)_{6^-}]$ 

 $(py)_2(H_2O)$  [19] and (<sup>n</sup>Bu<sub>4</sub>N) [Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CPh)<sub>9</sub>(H<sub>2</sub>O)] [21b] were prepared as described previously. Elementai analyses were performed by Atlantic Microlab, Inc., Norcross, GA, the Microanalytical Laboratory at the University of Manchester, Manchester, UK, or in house at Indiana University using a Perkin-Elmer Series II CHNS/O analyzer 2400. IR spectra (KBr) were recorded on a Nicolet 510P spectrophotometer. <sup>1</sup>H NMR were recorded on a 300 MHz Varian Gemini 2009 spectrometer with the protio-solvent as a reference. Conductivity measurements were made using a YSI model 31A conductance bridge and a YSI model 3403 conductivity cell (1 cm<sup>-1</sup> cell constant).

Magnetic susceptibility measurements (d.c.) were carried out on powdered samples using a Quantum Design MPMS5 SQUID susceptometer equipped with a 55 kG magnet in a 10 kG applied field. Data were collected between 2 and 300 K. The samples were restrained in parafilm to prevent torquing. Alternating current (a.c.) magnetic susceptibility measurements were made using a Quantum Design MPMS2 SQUID a.c. susceptometer. The a.c. frequency used for the measurements was 1000 Hz and the a.c. field strength was 1 G. Pascal's constants were used to estimate the diamagnetic corrections, and they were subtracted from the experimental susceptibilities to give the molar paramagnetic susceptibilities.

#### 2.2. Synthesis of $[Mn_3O(O_2CPh)_6(p-CH_3C_5H_4N)_3]$

To an absolute EtOH solution (40 ml) was added Mn(O<sub>2</sub>CMe)<sub>2</sub>·4H<sub>2</sub>O (4.00 g, 16.3 mmol), benzoic acid (15.0 g, 123 mmol) and 4-picoline (5.0 ml, 56 mmol). To the resulting solution was slowly added solid, finely crushed KMnO<sub>4</sub> (1.0 g, 6.3 mmol). The solution turned black, and microcrystalline powder began precipitating out of solution. The solution was allowed to stand overnight, and then filtered. The solid was washed with  $3 \times 10$  ml of absolute EtOH, and was redissolved in 20 ml of CH2Cl2 and filtered to remove some whitish solid. The filtrate was layered with 30 ml of hexanes and the flask was allowed to stand overnight to give large X-ray quality crystals [24]<sup>1</sup>. This product was redissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered and recrystallized with 1.5 volume equivalents of hexanes, and the crystalline product was washed with Et<sub>2</sub>O. Isolated yield of the recrystallized product was 2.7 g (31% based on Mn). Anal Calc. for C<sub>60</sub>H<sub>51</sub>Mn<sub>3</sub>N<sub>3</sub>O<sub>13</sub>: C, 60.52; H, 4.33; N, 3.54. Found: C, 60.54; H, 4.37; N, 3.33%. IR spectrum (KBr, cm<sup>-1</sup>): 1617(vs), 1574(vs), 1504(m), 1491(w), 1448(m), 1394(vs, b), 1230(m), 1219(w), 1209(m), 1172(w), 1068(m), 1026(m), 839(w), 808(m), 721(s), 692(m),673(m), 584(w), 534(w), 495(m), 486(w), 449(m).

<sup>&</sup>lt;sup>1</sup> Crystallographic data for Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(*p*-MeC<sub>3</sub>H<sub>4</sub>N)<sub>3</sub>·2CH<sub>2</sub>Cl<sub>2</sub>: monoclinic, C2<sub>1</sub>/*n*, C<sub>60</sub>H<sub>51</sub>Mn<sub>3</sub>N<sub>5</sub>O<sub>12</sub>2CH<sub>2</sub>Cl<sub>2</sub>: *a* = 14.651(2), *b* = 26.491(4), *c* = 16.167(3) Å;  $\beta$  = 102.51(1)<sup>2</sup>; *T* = -170°C;  $\lambda$ (Mo K $\alpha$ ) = 0.71069 Å; of the 10837 unique intensities measured, 8232 with  $F_n > 3(F_n)$  yielded R(F) = 0.562 and  $R_{\infty}(F) = 0.0609$ . Further informin is available from Indiana Molecular Structure Center Rep. No. 95094.

### 2.3. Synthesis of $[Mn_3O(O_2CPh)_6(p-CH_3C_5H_4N)_2]_2$ -(4,4'-bpy) and derivatives

A solution of Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(p-MeC<sub>5</sub>H<sub>4</sub>N)<sub>3</sub> (0.44 g, 0.37 mmol) was prepared using 30 ml of CH2Cl2, and 4,4'bipyridine (0.029 g, 0 19 mmol) was added with stirring. The solution was filtered and the solvent removed in vacuo. The resulting product was redissolved in 40 ml of a 1:1 CH2Cl2/CH3CN mixture. Nitrogen gas was bubbled into the solution to remove CH2Cl2. Microcrystals precipitated and the solution was allowed to stand overnight. The product was filtered, washed with CH3CN, and air dried. The isolated yield from the reaction was typically 35% based on Mn. Anal. Calc. for C118H96Mn6N6O26: C, 58.85; H, 4.07; N, 3.46. Found: C, 58.72; H, 4.05; N, 3.27%. IR spectrum (KBr, cm<sup>-1</sup>): 1612(s), 1570(s), 1491(w), 1449(w), 1397(s,br), 1231(w), 1219(w), 1175(w), 1069(w), 1026(w), 808(w), 718(m), 689(w), 673(m), 625(w), 608(w), 498(w), 464(w). A similar preparation from CHCl<sub>3</sub> using Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>- $(py)_2(H_2O)$  as the starting material resulted in the analogous complex  $[Mn_3O(O_2CPh)_6(py)_2]_2(4,4'-bpy)$  (1). Anal. Calc. for C, 59.86; H, 3.88; N 3.67. Found: C, 59.42; H. 3.97: N. 3.48%. When crystallization of the pyridine derivative of this species was slowed through the addition of excess pyridine, X-ray quality crystals of [Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(py)<sub>2</sub>]<sub>2</sub>- $(4,4'-bpy) \cdot 2Mn_3O(O_2CPh)_6(py)_3 \cdot solv resulted.$ 

#### 2.4. Synthesis of Na(O2CC6H4-p-OMe) · H2O

Anisic acid (6.0 g, 39.4 mmol) was dissolved in 200 ml of absolute EtOH, and NaOH (1.5 g, 39.4 mmol) was dissolved in 7 ml of distilled  $H_2O$ . The NaOH solution was then added to the anisic acid solution and white crystals began to precipitate out of solution immediately. After several minutes, the solution was filtered, and the product was washed with EtOH ( $3 \times 20$  ml) and Et<sub>2</sub>O ( $2 \times 10$  ml), and the solid was allowed to air dry. The yield of the reaction was 69% (4.75 g). Anal. Calc. for C<sub>8</sub>H<sub>9</sub>O<sub>4</sub>Na: C, 51.77; H, 4.55. Found: C, 51.90; H, 4.35%. IR spectrum (KBr, cm<sup>-1</sup>): 1686(w), 1595(s), 1541(s), 1422(s). 1310(w), 1255(s), 1184(w), 1172(m), 1138(w), 1102(m), 1032(m), 1005(w), 855(m), 793(s), 785(s), 700(m), 634(w), 615(m), 536(w), 507(w).

#### 2.5. Synthesis of Mn(O2CC6H4-p-OMe)2

MnCl<sub>2</sub>·4H<sub>2</sub>O (2.08 g, 11.6 mmol) was dissolved in 50 ml of distilled H<sub>2</sub>O. In a second flask, NaO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-*p*-OMe (4.50 g, 25.8 mmol) was dissolved in 100 ml of warm distilled H<sub>2</sub>O. The NaO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-*p*-OMe solution was added to the MnCl<sub>2</sub>·4H<sub>2</sub>O solution, stirring vigorously. Light pink solid began precipitating out of solution immediately. The solid was filtered and washed with H<sub>2</sub>O (2×20 ml) and Et<sub>2</sub>O (2×5 ml). The solid was allowed to air dry. Yield of the reaction was 64% based on Mn (2.90 g). Anal. Calc. for C<sub>16</sub>H<sub>14</sub>O<sub>6</sub>Mn: C, 48.87; H, 4.61; Mn 13.97. Found: C, 48.88;

H, 4.97; Mn, 15.10%. IR spectrum (KBr,  $cm^{-1}$ ): 1610(s), 1593(s), 1533(s), 1508(m), 1442(w), 1417(s), 1319(w), 1302(w), 1260(s), 1177(s), 1147(s), 1103(w), 1032(s), 845(w), 801(w), 785(s), 698(w), 634(w), 617(m), 551(w), 498(w).

# 2.6. Synthesis of $({}^{n}Bu_{4}N)[Mn_{4}O_{2}(O_{2}CC_{6}H_{4}-p-OMe)_{9}+(H_{2}O)\cdot 2CH_{2}Cl_{2}(4)$

A slurry of 2.80 g (7.12 mmol) of  $Mn(O_2CC_6H_4-p-OMe)_2 \cdot 2H_2O$  and 8.43 g (55.4 mmol) of anisic acid was made. Solid ("Bu<sub>4</sub>N)MnO<sub>4</sub> (0.81 g, 2.24 mmol) was added to the slurry slowly. The solution darkened but some whitish solid remained suspended. After 10 min of stirring, the solution was filtered to remove the whitish solid. The filtrate was layered with a 2:1 Et<sub>2</sub>O/hexanes solution and the solution was set aside to crystallize. After 24 h, the red-brown solid was filtered and washed with Et<sub>2</sub>O (3×20 ml). Yield was 2.62 g (54.5% based on Mn). Anat. Caic. for C<sub>90</sub>H<sub>103</sub>NO<sub>30</sub>Cl<sub>4</sub>Mn<sub>4</sub>: C, 52.92; H, 5.18; N, 0.69. Found: C, 52.84; H, 5.00; N, 0.59%. IR spectrum (KBr, cm<sup>-1</sup>): 1607(s), 1557(m), 1509(m), 1458(w), 1390(s,b), 1312(w), 1255(s), 1171(s), 1103(w), 1028(m), 851(m), 783(m), 700(w), 637(w), 621(m), 511(w).

# 2.7. Synthesis of dimers of [Mn<sub>9</sub>O<sub>7</sub>(O<sub>2</sub>CR)<sub>13</sub>(L-L)] complexes

### 2.7.1. Synthesis of [Mn<sub>9</sub>O<sub>7</sub>(O<sub>2</sub>CPh)<sub>13</sub>(4,4'-bpy)]<sub>2</sub>. 0.5CH<sub>3</sub>CN · 3H<sub>2</sub>O (3)

A sample of ("Bu<sub>4</sub>N) [Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CPh)<sub>9</sub>(H<sub>2</sub>O)] (0.250 g, 0.156 mmol) was dissolved in CH<sub>3</sub>CN (10 ml). To this solution, 0.208 g (0.069 mmol) of 4,4'-bpy in CH<sub>3</sub>CN (1 ml) was added with stirring. The solution was stirred for several minutes and then allowed to stand undisturbed overnight. After 48 h, reddish microcrystals were isolated by filtration. The solid was washed with CH<sub>3</sub>CN (2 × 10 ml) and Et<sub>2</sub>O (2 × 10 ml). The yield was typically 72% based on Mn (~120 mg). Anal. Calc. for  $C_{202}H_{152}N_4O_{69}Mn_{18}$ · 0.5CH<sub>3</sub>CN: C, 51.34; H, 3.26; N, 1.33; Mn, 20.82. Found: C, 51.15; H, 3.15: N, 1.33; Mn, 21.33%. IR spectrum (KBr, cm<sup>-1</sup>): 1599(m), 1557(m), 1534(m), 1493(w), 1026(w), 937(w), 844(w), 808(w), 717(m), 682(m), 661(m), 623(w), 503(w,b), 441(w).

#### 2.7.2. Synthesis of $[Mn_9O_7(O_2CPh)_{13}(bpe)]_2$

A sample of ("Bu<sub>4</sub>N) [Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CPh)<sub>9</sub>(H<sub>2</sub>O)] (0.200 g, 0.125 mmol) was dissolved in CH<sub>3</sub>CN (20 ml). To this solution was added *trans*-1,2-bis(4-pyridyl)ethene (bpe) (0.0228 g, 0.125 mmol) dissolved in 10 ml of CH<sub>3</sub>CN. The solution was stirred for several minutes and allowed to stand overnight. After 48 h, the red-brown solid was isolated by filtration, and the solid was washed with CH<sub>3</sub>CN (2 × 20 ml) and El<sub>2</sub>O (2 × 20 ml). The yield of the reaction was 88.7 mg (67.7% based on Mn). Anal. Calc. for C<sub>206</sub>H<sub>150</sub>N<sub>4</sub>O<sub>66</sub>Mn<sub>18</sub>: C, 52.35; H, 3.20; N, 1.18; Mn, 20.92. Found: C, 52.42; H, 3.25; N, 1.36; Mn, 20.65%. IR spectrum (KBr, cm<sup>-1</sup>): 1599(m), 1555(m,b), 1493(w), 1449(w), 1414(s), 1307(w), 1177(w), 1069(w), 1027(w), 841(w), 823(w), 717(s), 681(m), 662(m), 552(w), 503(w), 451(w).

### 2.7.3. Synthesis of $[Mn_9O_7(O_2CC_6H_4-p-OMe)_{13}(4,4'-bpy)]_2$ (5)

 $(^{n}Bu_{4}N)[Mn_{4}O_{2}(O_{2}CC_{6}H_{4}-p-OCH_{3})_{9}(H_{2}O)] (0.500 g,$ 0.24 mmol) was added to a solution of CH<sub>3</sub>CN (40 ml). In a separate flask, 4,4'-bpy (0.0415 g, 0.26 mmol) was dissolved in 5 ml CH<sub>3</sub>CN and this solution was then added to the solution of  $(^{n}Bu_{4}N)[Mn_{4}O_{2}(O_{2}CPhOCH_{3})_{9}(H_{2}O)]$ with stirring. The solution was allowed to stand at room temperature for 48 h. Red-brown needles were filtered off and the product was washed with CH<sub>3</sub>CN (3×10 ml) and  $Et_2O(2 \times 10 \text{ ml})$ . The yield of the reaction was 0.133 g (46%) based on Mn). Anal. Calc. for C228H198N4O92Mn18: C, 50.20; H, 3.66; N, 1.03; Mn, 18.13. Found: C, 50.00; H, 3.70; N, 1.10; Mn, 18.37%. IR spectrum (KB1, cm<sup>-1</sup>): 1607(s), 1547(m), 1510(m), 1456(w), 1408(s,b), 1313(w), 1300(w), 1258(s), 1219(w), 1175(s), 1152(w), 1105(w), 1030(m), 851(w), 808(w), 783(s), 700(m), 669(w), 638(m), 629(m), 509(w), 439(w).

# 2.8. Reaction of $("Bu_4N)[Mn_4O_2(O_2CPh)_9(H_2O)]$ with excess 4,4'-bpy

A solution of ("Bu<sub>4</sub>) [Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CPh)<sub>9</sub>(H<sub>2</sub>O)] (0.250 g, 0.156 mmol) in CH<sub>3</sub>CN (10 ml) was treated with an excess (0.172 g, 1.10 mmol) of 4,4'-bipyridine in CH<sub>3</sub>CN (2 ml). After 24 h a purple–gray solid precipitated from solution. The solid was washed with CH<sub>3</sub>CN (2 × 10 ml), CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 ml) and Et<sub>2</sub>O and allowed to air dry. The yield of the reaction was 157 mg. *Anal.* for 6: Found C, 52.12; H, 3.82; N, 2.75; Mn, 20.27%. IR spectrum (KBr, cm<sup>-1</sup>): 1611(s,sh), 1570(s), 1491(w), 1449(w), 1395(vs,br), 1219(w), 1175(w), 1069(w), 1026(w), 808(w), 718(s), 688(w), 673(m), 625(w), 467(w).

#### 2.9. X-ray crystallography

X-ray crystallographic data for  $Mn_3O(O_2CPh)_6(py)_2]_2$ -(4,4'-bpy)  $\cdot 2Mn_3O(O_2CPh)_6(py)_3 \cdot py \cdot 14CH_3CN$  were collected on a Picker four-circle diffractometer at  $-170^{\circ}C$ and  $-172^{\circ}C$ , respectively. Details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere [25]. The structures were solved using direct (MULTAN) and Fourier methods. Selected crystallographic data are listed in Table 1.

# 2.9.1. $[Mn_3O(O_2CPh)_6(py)_2]_2(4,4'-bpy) \cdot 2Mn_3O(O_2CPh)_{6}-(py)_3 \cdot py \cdot 14CH_3CN (1 \cdot 2Mn_3O(O_2CPh)_6(py)_3 \cdot py \cdot 14CH_3CN)$

 $[Mn_{3}O(O_{2}CPh)_{6}(py)_{2}]_{2}(4,4'-bpy) \cdot 2Mn_{3}O(O_{2}CPh)_{6}$ (py)<sub>3</sub>·py·14CH<sub>3</sub>CN crystallizes in the orthorhombic space group *Fddd*. The four unique Mn atoms in the asymmetric unit were located in the initial best E-map using MULTAN 78. The remaining non-hydrogen atoms were located by successive iterations of least-squares and difference Fourier maps. The asymmetric unit was found to contain one fourth of a bipyridine-bridged dimer as well as one half of an Mn<sub>3</sub> monomer with terminal pyridine groups. As shown in Fig. 1, in addition to the monomer (Fig. 2) and dimer (Fig. 3), the crystal lattice also contains pyridine, as well as several partially occupied CH<sub>3</sub>CN molecules. The full-matrix leastsquares refinement was completed using anisotropic thermal parameters on the manganese atoms and isotropic thermal parameters on all other non-hydrogen atoms. Calculated fixed hydrogen atoms were introduced on the main molecules of interest. The final R(F) was 0.096 for 3467 observed reflections. The final difference map was essentially featureless, the maximum peak was 0.61 e  $Å^{-3}$  and the minimum peak was -0.42 e Å<sup>-3</sup>.

2.9.2.  $[Mn_9O_7(O_2CC_6H_4-p-OMe)]_3(4,4'-bpy)]_2 \cdot 20CH_3CN$ 

[Mn<sub>9</sub>O<sub>7</sub>(O<sub>2</sub>CPhOMe)<sub>13</sub>(4,4'-bpy)]<sub>2</sub> crystallizes in a monoclinic C2/c space group with four molecules per unit cell. Data collection problems on the large unit cell due to heat and humidity hampered initial attempts to solve the structure because frost accumulated on the crystal and appeared to cause the crystal to deteriorate and fracture. Because of this, data collection was initialized on five different crystals. The two best partial data sets gave nearly a complete set and only these two were used for the solution and refinement of the structure. The initial steps of the data reduction were carried out as usual, while the scaling and merging of the two sets of data were carried out using the XPREP section of SHELXTL Version 5.3. The structure was solved using SHELX and the full unique data set. The asymmetric unit was found to contain one-half of the dimer and several well-defined acetonitrile molecules as well as an additional seven atoms that were assumed to be parts of solvent molecules (10 total solvent molecules per unit cell was assumed for the unit cell density calculation). Due to the large number of parameters, the full-matrix, least-squares analysis was carried out in a cyclical manner. The nine unique Mn atoms were refined anisotropically, while all other atoms were refined using isotropic thermal parameters. The final R(F) was 0.118. The final difference map was reasonably clean: the largest peak (1.2 e Å<sup>-3</sup>) was located 2 Å from C(88) and the deepest hole was  $-0.7 \text{ e } \text{Å}^{-3}$ .

#### 3. Results and discussion

#### 3.1. Synthesis of $[Mn_3O(O_2CPh)_6(py)_2]_2(4,4'-bpy)$

Lability of the Mn<sub>3</sub>O species in solution created significant difficulties for isolation of well-characterized products from Table I

Formula <sup>a</sup>	Caulter Ner Oar Mare	CHN. OMn
Formula weight (g mol 1)	5231.05	6275 99
Crystal system	orthorbombic	monoclinc
Space group	Fddd	C2/c
$a(\mathbf{\hat{A}})$	40.278(8)	49.370(9)
	68.088(14)	15.991(3)
c (Å)	18.353(3)	46.859(9)
α(°)	90	90
β(°)	90	125.04(1)
μ(') ν(°)	90	90
Cell volume $(\mathring{A}^3)$	50332	30289
7	8	4
τ.(°C)	- 170	- 172
Radiation <sup>b</sup>	ΜοΚα	ΜοΚα
$D_{\rm ext} (\rm g\rm cm^{-3})$	1.38	1.376
F(100)	21568	12860
Linear absorption coefficient (cm <sup>-1</sup> )	8.062	8.062
Scan type	ω/2θ	ω/2θ
Scan speed (° min <sup>-1</sup> )	8.0	8.0
Total data	10748	23795
Reflections measured	+h, +k, +l	$\pm h$ , $+k$ , $+l$
Unique data	8268	19841
No variables	388	843
R	0.69	0.1090
Observed data <sup>c</sup>	3467	set no. 1 12395, set no. 2 11400
R(R) de	0.0963(0.0980)	0.1185(0.1176)
Goodness of fit f	1.660	1.973

 $Crystallographic collection data for [Mn_3O(O_2CPh)_6(py)_2]_2(4.4'-bpy) \cdot [Mn_3O(O_2CPh)_6(py)_3] \cdot py \cdot 14CH_3CN (1) and [Mn_9O_7(O_2CC_6H_4p-OMe)_{13} - (4.4'-bpy)]_2 \cdot 20CH_3CN (5)$ 

\* Including solvent molecules.

<sup>b</sup> Graphite monochromator.

 $^{\circ}F > 3\sigma(F).$ 

 ${}^{d}R = \sum ||F_{0}| - |F_{c}||/\sum |F_{0}|.$ 

 $R_w = [\sum w(|F_0| - |F_c|)^2 / w |F_0|^2]^{1/2}$ , where  $w = 1/\sigma^2$ .

<sup>f</sup> GOF =  $[(\sum w(|F_0| - |F_c|)^2)/(n-p)]^{1/2}$ ; n = observed reflections, p = refined parameters.

its reactions with 4,4'-bpy. In the manganese trinuclear system, the replacement of water and/or pyridine by 4,4'-bpy is so facile that great care must be taken to selectively crystallize a single species. Precipitation of a polymeric species from acetonitrile is rapid and control over the products could only be exerted through slow diffusion of the reagents. However, the insolubility of this product in all common solvents and its elemental analysis support the formulation of a one-dimensional polymer with water in the third site of the triangle. Unfortunately, the polymeric species was unsuitable for Xray structure analysis. When crystallization was slowed through addition of excess pyridine which competes with the 4,4'-bipyridine for Mn coordination sites, single crystals formed which were suitable for X-ray studies. They proved to contain a 2:1 ratio of monomeric units Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>-(py)3 to 'dimer of triangles' units linked by 4,4'-bpy. Later it was found that the dimeric unit, [Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(py)<sub>2</sub>-(H<sub>2</sub>O)]<sub>2</sub>(4,4'-bpy), could be isolated from chloroform, although various preparations seem to vary in the number of coordinated pyridine and H<sub>2</sub>O molecules in the other sites. Dimers prepared from Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(p-MeC<sub>5</sub>H<sub>4</sub>N)<sub>3</sub>, which possesses three identical axial ligands instead of the asymmetric ligation of Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(py)<sub>2</sub>(H<sub>2</sub>O), did not

exhibit this problem, and the dimer of triangular units could be readily attained.

#### 3.2. Synthesis of [Mn<sub>9</sub>O<sub>7</sub>(O<sub>2</sub>CR)<sub>13</sub>(L-L)]<sub>2</sub> complexes

When a solution of  $({}^{n}Bu_{4}N)[Mn_{4}O_{2}(O_{2}CPh)_{9}(H_{2}O)]$ (2) in CH<sub>3</sub>CN was treated with 1 equiv. of 4,4'-bipyridine in CH<sub>3</sub>CN, no significant color change occurred. Over a period of 48 h, however, a red-brown microcrystalline product precipitated as the solution stood undisturbed at 20°C. Crystals of this product (3) could be grown by layering a solution of 3 in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>ClCH<sub>2</sub>Cl, or PhCN with CH<sub>3</sub>CN. Unfortunately, the large parallelepipeds grown by this method appeared to be layered and did not diffract X-rays well. Physical characterization of the crystals via IR and NMR spectroscopies, however, indicated a potentially interesting structure (vide infra). Elemental analysis of the crystals showed very low nitrogen content, suggesting perhaps that the new complex was a 4,4'-bpy complex of a large Mn aggregate.

Because attempts to structurally characterize complex 3 were unsuccessful, the methoxybenzoate substituted 'naked butterfly' (4) was prepared in the hope that the product of its reaction with 4,4'-bpy might provide crystals that were better suited to X-ray structural characterization. Complex 4 was synthesized in an analogous fashion to  $({}^{n}Bu_{4}N)[Mn_{4}O_{2}-(O_{2}CPh)_{9}(H_{2}O)]$  (2) [21b]. The spectroscopic and microanalytical characterization of the product were consistent with the formulation  $({}^{n}Bu_{4}N)[Mn_{4}O_{2}(O_{2}CPh)_{9}(H_{2}O)] \cdot$ 2CH<sub>2</sub>Cl<sub>2</sub>.

When a solution of  $({}^{n}Bu_{4}N)[Mn_{4}O_{2}(O_{2}C_{6}H_{4}-p-OMe)_{9}-$ (H2O)] · 2CH2Cl2 (4) in CH3CN was treated with a CH3CN solution containing 1 equiv. of 4,4'-bpy, no color change occurred, but as in the case of the analogous reaction of complex 2, crystals precipitated from the reaction solution over a period of ~48 h. The crystals isolated from the initial reaction solution were unsuitable for X-ray diffraction analysis, but X-ray quality parallelepipeds of complex 5 could be grown from the filtrate of a recrystallization of 5 from PhCN/ CH<sub>3</sub>CN after the initial crop of crystals had been removed. The crystals were kept in contact with the mother liquor until they were mounted because of severe solvent loss problems. Physical characterization of 5 via IR and NMR spectroscopies and elemental analysis indicated that it was the methoxybenzoate derivative of 3. X-ray analysis of the crystals showed that complex 4 had both aggregated into a larger manganese oxide aggregate and dimerized via the 4,4'-bpy ligands to give  $[Mn_9O_7(O_2CC_6H_4-p-OMe)_{13}(4,4'-bpy)]_2 \cdot 20CH_3CN$ (5 solv), an unusual dimer of Mn<sub>9</sub>O<sub>7</sub> aggregates linked by two molecules of 4,4'-bpy, as shown in Fig. 4. Elemental analysis of a sample of 5 solv dried in vacuo indicates that the sample retains none of the lattice solvent molecules upon drying. Yield of the reaction is ~55% based on Mn. A balanced reaction for the formation of 5 is given by Eq. (1). An analogous reaction may written for the reaction of complex 2, which was formulated as [Mn<sub>9</sub>O<sub>7</sub>(O<sub>2</sub>CPh)<sub>13</sub>(4,4'-bpy)]<sub>2</sub>.

The 'naked butterfly' is oxide-poor relative to 5 and the additional oxides are probably provided by a small amount of adventitious water. Taking charge considerations into account, the reaction shows no overall change in the oxidation state of the manganese ions; all Mn appear to remain as  $Mn^{III}$  in the product. This observation is confirmed by the structural parameters of 5 (vide infra).

$$9({}^{n}Bu_{4}N) [Mn_{4}O_{2}(O_{2}CC_{6}H_{4}-p-OMe)_{9}(H_{2}O)] + 4(4,4'-bpy) + H_{2}O \rightarrow 20 p-MeOC_{6}H_{4}CO_{2}H + 2[Mn_{9}O_{7}(O_{2}CPhOMe)_{13}(4,4'-bpy)]_{2} + 9({}^{n}Bu_{4}N)(O_{2}CC_{6}H_{4}-p-OMe)$$
(1)

When the identities of products of these reactions with 4,4'bpy were known, additional variations on the synthesis were attempted to try to increase the yield. The use of a small amount of added water led to no increase in the yield of the reaction, indicating that the adventitious water in the solvent was sufficient to allow the dramatic transformation to the octadecanuclear species. Addition of benzoylperoxide to the 'naked butterfly' starting materials, as in the preparation of  $[Na_2Mn_9O_7(O_2CPh)_{15}(CH_3CN)_2]$  (5) [21a], also resulted in no increase in overall yield of complexes 4 or 5.

An investigation of the effect of the ratio of 4,4'-bpy to butterfly starting material in these reactions was initiated because some initial studies indicated a large increase in the yield of isolated solid when a large excess of the ligand was employed. As the amount of bpy is increased, no increase in overall yield occurs for 0.5 to 4 equiv. of 4,4'-bpy. However, if over 8 equiv. of the ligand are used, the amount of solid isolated increased by ~75%. The resultant solid product changes gradually from a red-brown solid at 0.5 equiv. to a purple-gray solid at 16 equiv. This solid is a new compound which by elemental analysis and IR spectroscopy appears to have more 4,4'-bpy per Mn ion than 3. Curiously, similar reactivity studies of complex 4 with an excess of 4,4'-bipyridine did not lead to the production of an analogous methoxybenzoate derivative of this new complex; only [MngO7- $(O_2CC_6H_4$ -p-OMe)<sub>13</sub>(4,4'-bpy)]<sub>2</sub> (5) can be isolated from such reactions. ("Bu<sub>4</sub>N) [Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CPh)<sub>9</sub>(H<sub>2</sub>O)] (2) also reacts with the slightly longer and less linear ligand, trans-1,2-bis(4-pyridyl)ethene (bpe), to give a complex which has IR, NMR and microanalytical data that are consistent with the formula  $[Mn_9O_7(O_2CPh)_{13}(bpe)]_2$ . The addition of 1 equiv. of pyrazine to 2 results in no noticeable reaction, presumably because the lability and smaller size of this ligand does not allow the formation of the analogous dimer of Mno species linked by pyrazine.

# 3.3. Description of structure of $[Mn_3O(O_2CPh)_{d}(py)_2]_2^{-1}$ (4,4'-bpy) $\cdot 2 Mn_3O(O_2CPh)_{d}(py)_3 \cdot py \cdot 14CH_3CN$

The results of the single crystal X-ray structure determination of  $[Mn_3O(O_2CPh)_6(py)_2]_2(4,4'-bpy)\cdot 2Mn_3O-(O_2CPh)_6(py)_3 \cdot py \cdot 14MeCN$  are shown in Figs. 1-3. Selected bond distances and angles are shown in Table 2 and fractional coordinates are given in Table 3. Especially noteworthy is the size of the unit cell (Fig. 1), which contains



Fig. 1. ORTEP representation of the unit cell of  $[Mn_3O(O_2CPh)_6(py)_2]_2$ -(4,4'-bpy)·2Mn\_3O(O\_2CPh)\_6(py)\_3·py·14CH\_3CN with the disordered pyridine and peripheral ligation of the monomer and dimer of triangles omitted for clarity.



Fig. 2. ORTEP representation of the monomer unit  $Mn_3O(O_2CPh)_6(py)_3$ of  $[Mn_3O(O_2CPh)_6(py)_2]_2(4,4'-bpy) \cdot 2Mn_3O(O_2CPh)_6(py)_3 \cdot py \cdot 14CH_3CN$ with thermal ellipsoids shown at the 25% level. Hydrogen atoms are omitted and outer atoms are de-emphasized for clarity.



Fig. 3. ORTEP representation of the dimer unit  $[Mn_3O(O_2CPh)_6(py)_2]_2$ (4,4'-bpy) of  $[Mn_3O(O_2CPh)_6(py)_2]_2(4,4'-bpy) \cdot 2Mn_3O(O_2CPh)_6(py)_3$ . py · 14CH<sub>3</sub>CN. Thermal ellipsoids are shown at the 50% level.

thirty-two manganese triangular units, half as linked dimers and the other half as monomers, in alternating layers.

The monomeric units, as shown in Fig. 2, sit on a two-fold axis which runs through one manganese atom and relates the two remaining metal atoms. On the basis of bond length considerations, the unique manganese is assigned as Mn<sup>III</sup> while the Mn<sup>II</sup> and remaining Mn<sup>III</sup> are disordered among the two equivalent sites. The monomeric triangle is unlike the previously structurally characterized compound Mn<sub>3</sub>O-(O<sub>2</sub>CPh)<sub>6</sub>(py)<sub>2</sub>(H<sub>2</sub>O) [19] on two counts. First it contains no axial water ligation and instead possesses three axial pyridine donors. Previous attempts to isolate and crystallize the fully pyridine ligated monomeric trinuclear species have been unsuccessful, although the picoline derivative has been recently structurally characterized [24]. A second salient feature of the structure of  $1 \cdot 2Mn_3O(O_2CPh)_6(py)_3 \cdot solv$  is that the pyridine rings lie in the plane of the three manganese atoms and not perpendicular to it as was observed in the structure of Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(py)<sub>2</sub>(H<sub>2</sub>O), which is likely the result of packing forces.

Mn(l)		Mn(2)	3.286(3)
Mn(2)		Mn(2b)	3.411(5)
Mn(41)		Mn(42)	3.305(4)
Mn(42)		Mn(42d)	3.391(5)
Mn(1)		0(3)	1.828(15)
Mn(1)		0(4)	2.000(13)
Mn(1)		U(4D)	2.000(13)
Mn(1)		0(13)	2.117(12)
Mn(1)		U(136)	2.117(12)
Ma(1) Ma(2)		N(31)	2.058(17)
Ma(2) Ma(2b)		0(3)	1.958(8)
Mn(20) Mn(2)		0(3)	1.906(8)
Mn(2)		0(15)	2.101(11)
Mn(2)		0(13)	2.127(12)
Mn(2)		0(22)	2.001(12)
Mn(2)		N(35)	2.110(12)
Mn(2) Mn(41)		O(43)	2.155(14)
Mn(41)		0(44)	2 121(11)
Mn(41)		O(53)	2.018(11)
Mn(41)		O(53d)	2.018(11)
Mn(41)		N(71)	2.090(18)
Mn(42)		0(43)	1 980(7)
Mn(42d)		O(43)	1.980(7)
Mn(42)		O(46)	2.079(12)
Mn(42)		O(55)	2.146(12)
Mn(42)		O(62)	2.163(11)
Mn(42)		O(64)	2.096(12)
Mn(42)		N(75)	2.179(15)
Mn(2)	Mn(1)	Mn(2b)	62.53(10)
0(3)	Mn(1)	O(4)	95.8(4)
0(3)	Mn(1)	O(13)	98.0(3)
O(3)	Mn(1)	N(31)	180.0
O(4)	Mn(1)	O(4b)	168.4(7)
O(4)	Mn(1)	O(13)	89.8(4)
0(4)	Mn(1)	O(13b)	88.6(4)
O(4b)	Mn(1)	O(13b)	89.8(4)
O(4b)	Mn(1)	0(13)	88.6(4)
O(4)	Mn(1)	N(31)	84.2(4)
O(13)	Mn(l)	O(13b)	164.1(7)
0(13)	Mn(1)	N(31)	82.0(3)
Mn(1)	Mn(2)	Mn(2b)	58.73(5)
0(3)	Min(2)	U(6)	93.2(4)
0(3)	Mn(2)	0(15)	97.9(4)
0(3)	MB(2)	0(22)	92.6(4)
0(3)	Mn(2)	U(24)	94.9(4)
0(3)	Mn(2)	N(33)	178.4(3)
0(0)	Mn(2)	0(13)	07.9(4) 172.9(5)
0(6)	Mn(2)	0(24)	02 2(4)
0(6)	Mn(2)	N(35)	88 1(5)
0(15)	Mn(2)	0(22)	895(5)
0(15)	Mn(2)	0(24)	167.2(5)
0(15)	Mn(2)	N(35)	83.1(5)
0(22)	Mn(2)	Q(24)	89.2(4)
0(22)	Mn(2)	N(35)	86.1(5)
0(24)	Mn(2)	N(35)	84.2(5)
Mn(42)	Mn(41)	Mn(42)	61.73(11)
0(43)	Mn(41)	O(44)	96.4(3)
0(43)	Mn(41)	O(53)	95.3(3)
0(43)	Mn(41)	O(53)	95.3(3)
			(continued)

Table 2

Selected bond distances (Å) and angles (°) for  $[Mn_3O(O_2CPh)_6(py)_2]_2^-$ (4.4'-bpy) ·  $2Mn_3O(O_2CPh)_6(py)_3]$  · py ·  $14CH_3CN^*$ 

180.0 N(71) O(43) Mn(41) O(44) Mn(41) O(44) 167.1(6) O(53) O(44) Mn(41) 89.8(4) O(53) 89.0(4) O(44) Mn(41) 0(44) Mn(41) O(53) 89.8(4) O(44) Mn(41) N(71) 83.6(3) O(53) Mn(41) O(53) 169.4(6) Mn(41) N(71) 84.7(3) O(53) 0(43) Mn(42) O(46) 95.7(4) Mn(42) O(55) 93.5(4) O(43) O(43) Mn(42) O(62) 95.8(4) O(43) Mn(42) O(64) 92.4(4)O(43) Mn(42) N(75) 176.8(5) Mn(42) O(55) 89.0(5) O(46) O(46) Mn(42) O(62) 89.5(4) 171.2(5) O(46) Mn(42) O(64) N(75) O(46) Mn(42) 87.4(5) O(55) Mn(42) O(62) 170.7(5) O(64) O(55) Mn(42) 87.0(5) O(55) Mn(42) N(75) 85.6(5) O(62) Mn(42) 0(64) 93.2(4) O(62) Mn(42) N(75) 85.1(5) N(75) 84.5(5) O(64) Mn(42) Mn(1)0(3) Mn(2) 119.9(4) Mn(2) 0(3) Mn(2b) 120.2(7)Mn(42) Mn(41) O(43) 121.1(3) 0(43) Mn(42) Mn(42) 117.8(7)

\* Symmetry codes for 1 used in Tables and Figs.: a = 2.25 - x, 0.25 - y, z; b=x, 0.25-y, 0.25-z; c=2.25-x, y, 0.25-z; d=0.75-x, y, 1.75-z. Symmetry operations a, b and c are used in the 'dimer of triangles', and d is used in the single trinuclear species.

Each 'dimer' (Fig. 3) has a two-fold axis running through the 4,4'-bpy nitrogen atoms and one of the manganese atoms on each triangle. Another two-fold axis lies perpendicular to the first, relating the two triangular units. The asymmetric unit, therefore, contains a quarter of a 'dimer' and only two of the manganese atoms are unique. As in the analogous monomeric system [19], the unique manganese atom is assigned as Mn<sup>III</sup> and the Mn<sup>II</sup> and remaining Mn<sup>III</sup> are assigned as disordered among the two symmetry related sites. With the exception of the orientation of the bpy rings which are not perpendicular but parallel to the plane defined by the three manganese atoms, the linked triangles closely resemble the analogous monomeric trinuclear species.

#### 3.4. Description of structure of $[Mn_9O_7(O_2CC_6H_4$ p-OMe)<sub>13</sub>(4,4'-bpy)]<sub>2</sub>·20CH<sub>3</sub>CN(5·solv)

The octadecanuclear complex 5 has crystallographic twofold symmetry and the full molecule is shown in Fig. 4. The bond distances and angles for 5 solv are shown in Table 4 and the fractional coordinates are given in Table 5. A  $C_2$  axis is located between the two bridging 4,4'-bipyridine ligands. Atoms related by the two-fold axis are indicated by prime markings in the table of bond distances and angles. Each asymmetric unit also possesses virtual  $C_2$  symmetry within the Mn<sub>9</sub> unit itself. The packing of the molecules and solvents in the unit cell is shown in Fig. 5. The solvent molecules

Atom	x	у	Z	Biso
Mn(l)	9857(1)	1250*	1250*	28
Mn(2)	9160(1)	1499.8(4)	1318(2)	29
0(3)	9403(4)	1250*	1250*	35(3)
O(4)	9908(3)	1038(2)	1995(7)	48(3)
C(5)	9725(4)	902(3)	2266(9)	30(4)
0(6)	9438(3)	1631(2)	481(6)	33(2)
C(7)	9850(4)	787(2)	2879(9)	28(3)
C(8)	9651(5)	647(3)	3213(11)	52(5)
C(9)	9773(6)	550(3)	3825(14)	68(5)
C(10)	10080(6)	594(3)	4106(12)	66(6)
cin	10285(5)	726(3)	3764(12)	47(4)
C(12)	10163(5)	828(3)	3169(10)	43(4)
0(13)	9930(3)	1464(2)	2072(7)	44(3)
C(14)	9766(4)	1608(3)	2269(10)	33(4)
0(15)	9478(3)	1643(2)	2078(7)	43(3)
C(16)	9944(5)	1745(3)	2767(11)	49(5)
C(17)	10260(7)	1701(4)	2983(15)	81(7)
C(18)	10425(7)	1831(5)	3453(16)	101(8)
C(19)	10284(7)	1991(4)	3609(14)	76(6)
C(20)	9979(7)	2048(4)	3503(15)	94(8)
C(21)	9796(7)	1902(4)	2976(16)	94(8)
0(22)	8872(3)	1401(2)	2170(6)	39(3)
C(23)	8716(4)	1241(3)	2232(8)	31(3)
0(24)	8780(3)	1415(2)	585(6)	37(2)
C(25)	8426(3)	1241(3)	2747(8)	27(3)
C(26)	8379(6)	1399(4)	3191(14)	71(6)
C(27)	8120(6)	1398(4)	3696(15)	80(6)
C(28)	7893(5)	1248(3)	3700(12)	61(5)
C(29)	7937(5)	1090(3)	3257(11)	51(5)
C(30)	8208(5)	1095(3)	2776(10)	44(4)
N(31)	10368(4)	1250*	1250*	27(4)
C(32)	10545(4)	1243(3)	1865(9)	36(3)
C(33)	10887(4)	1247(3)	1894(8)	29(3)
C(34)	11062(5)	1250 ×	1250*	25(4)
N(35)	8876(4)	1774(2)	1401(8)	38(3)
C(36)	9035(5)	1941(3)	1444(11)	52(5)
C(37)	8868(7)	2109(4)	1574(13)	78(7)
C(38)	8522(9)	2103(5)	1683(17)	111(9)
C(39)	8363(8)	1924(5)	1644(16)	105(8)
C(40)	8553(6)	1763(4)	1518(12)	64(6)
Mn(41)	3750*	47.6(5)	8750*	28
Mn(42)	3705(1)	-369.1(4)	7831(1)	34
O(43)	3750*	-219(2)	8750*	33(3)
O(44)	3400(3)	83(2)	7896(6)	30(2)
C(45)	3232(4)	-33(3)	7510(9)	33(4)
O(46)	3290(3)	-218(2)	7458(6)	38(3)
C(47)	2956(4)	49(2)	7066(8)	25(3)
C(48)	2896(4)	245(3)	7037(10)	37(4)
C(49)	2635(5)	321(3)	6665(11)	47(5)
C(50)	2432(5)	203(3)	6287(12)	55(5)
C(51)	2478(6)	6(3)	6298(14)	69(5)
C(52)	2751(5)	-72(3)	6691(11)	52(5)
O(53)	3381(3)	75(2)	9488(6)	31(2)
C(54)	4154(4)	-21(3)	7430(9)	30(4)
0(55)	4013(3)	- 170(2)	7226(6)	38(3)
C(56)	4409(4)	67(2)	6891(9)	31(4)
C(57)	4441(5)	- 14(3)	6210(12)	52(4)
C(58)	4661(5)	71(3)	5705(12)	59(5)
C(59)	4848(5)	230(3)	5913(12)	56(5)

Table 3 Fractional coordinates and isotropic thermal parameters for {Mn<sub>3</sub>O-

14CH<sub>3</sub>CN

(O2CPh)6(py)2](4,4'-bpy)·2Mn3O(O2CPh)6(py)2]2(4,4'-bpy)·py·

(continued)

Table 3 (continued)

Atom	x	у	z	B <sub>iso</sub>
C(60)	4818(5)	318(3)	6583(12)	59(5)
C(61)	4593(5)	232(3)	7085(10)	42(4)
O(62)	3383(3)	- 594(2)	8274(6)	37(3)
C(63)	3251(4)	-606(2)	8882(9)	30(4)
0(64)	4137(3)	- 531(2)	8039(6)	44(3)
C(65)	2938(4)	-720(3)	8948(10)	41(4)
C(66)	2822(5)	- 830(3)	8405(11)	47(5)
C(67)	2516(6)	-939(4)	8464(14)	74(6)
C(68)	2361(6)	-927(4)	9089(16)	78(7)
C(69)	2456(7)	-821(4)	9634(16)	91(7)
C(70)	2756(6)	- 703(3)	9584(13)	68(6)
N(71)	3750*	355(3)	8750*	31(4)
C(72)	3745(5)	454(2)	8120(9)	37(4)
C(73)	3741(5)	658(3)	8109(10)	44(4)
C(74)	3750*	761(3)	8750*	38(5)
N(75)	3683(4)	-540(2)	6830(9)	48(4)
C(76)	3635(5)	-458(3)	6176(14)	62(5)
C(77)	3634(6)	560(4)	5546(13)	71(6)
C(78)	3681(6)	- 758(4)	5553(14)	80(7)
C(79)	3714(6)	- 851(3)	6222(15)	75(6)
C(80)	3713(6)	- 736(3)	6854(12)	60(5)
C(81)	3750*	- 1045(4)	8750*	54(6)
C(82)	3585(14)	-1152(9)	8174(30)	81(12)
C(83)	3597(12)	- 1147(8)	9301(25)	58(10)
N(84)	9277(5)	3749(4)	1330(14)	103(6)
C(85)	9400(5)	3720(4)	830(14)	72(6)
C(86)	9477(10)	3702(6)	51(25)	163(12)
C(87)	9473(6)	4303(4)	3663(14)	74(6)
C(88)	9134(10)	4274(6)	3809(24)	52(9)
C(89)	8880(8)	4230(5)	3900(20)	37(8)
C(90)	9375(10)	4465(7)	3936(23)	57(10)
C(91)	9307(13)	4626(8)	4288(29)	88(12)
C(92)	515(11)	2480(7)	259(24)	55(9)
C(93)	836(21)	2441(12)	46(44)	48(13)
C(94)	731(21)	2351(13)	448(46)	55(13)
C(95)	616(22)	2587(13)	- 113(48)	64(13)
C(96)	1129(21)	2460(12)	25(45)	61(13)
C(97)	1250*	3122(27)	1250*	118(9)
C(98)	1448(19)	3039(11)	1266(50)	57(13)

Fractional coordinates are  $\times 10^4$  for non-hydrogen atoms and  $\times 10^3$  for hydrogen atoms.  $B_{400}$  values are  $\times 10$ . Isotropic values for those atoms refined anisotropically are calculated using the formula given by Hamilton [29]. Parameters marked by an asterisk (\*) were not varied.

occupy large channels in the structure, and hence the packing of the unit cell facilitates loss of solvent of crystallization and the deterioration of the quality of the single crystals, making it quite difficult to obtain the X-ray structure. The very large unit cell of complex 5 solv has dimensions of 49.4 Å  $\times$  16.0 Å  $\times$  46.9 Å, and there are four of the dimers per unit cell.

There are several distinct Mn coordination environments in complex 5 as shown in Table 6 and Fig. 6. All bond lengths to the Mn ions are consistent with an 18 Mn<sup>III</sup> formulation for the complex. Mn(1) and Mn(3), the atoms that are coordinated to the 4,4'-bpy ligands that bridge the two halves of the molecule, have NO<sub>5</sub> coordination environments which are pseudo-octahedral with JT elongation along the 4,4'-bpy vector. Mn(1) and Mn(3) are also each bridged via two  $\mu_{3^-}$ oxides to the central Mn(2). The remainder of the coordination nation spheres of Mn(1) and Mn(3) is completed by  $\mu_{2^{-}}$  and  $\mu_{3}$ -methoxybenzoate ligands.

Four of the Mn atoms in the asymmetric unit (Mn(5), Mn(7), Mn(8) and Ma(9)) have O<sub>6</sub> coordination environments. Two  $\mu_3$ -oxide ligands bridge each of these Mn atoms to four other Mn atoms. Each of these Mn is also coordinated to one of the two *p*-methoxybenzoate ligands, as well as three  $\mu_2$ -methoxybenzoate ligands. Each of the four possesses a pseudo-octahedral geometry with the  $\mu_3$ -methoxybenzoate ligand located along the JT axis. Mn(4) and Mn(6) have a distorted O<sub>5</sub> environment, and are coordinated to two  $\mu_3$ oxides and three  $\mu_2$ -methoxybenzoate ligands. These atoms have an extremely long interaction with the oxygen of another methoxybenzoate ligand (~2.7 Å).

Mn(2) possesses a more unusual five-coordinate square pyramidal geometry, and is bridged to both Mn(1) and Mn(3) via two  $\mu_3$ -oxides. The bond between Mn(2) and O(14), the apical oxide of the square pyramid, is elongated (2.165 Å) relative to the other Mn-oxide bonds to Mn(2) (1.919 Å, av.). The base of the pyramid is not planar, and is instead bent with an Mn(1)-Mn(2)-Mn(3) angle of 145.50°.

The base of 5 consists of two  $Mn_4O_2$  'butterfly' units sharing the central five-coordinate Mn(2). The O(10)-Mn(1)-O(13)-Mn(2) unit is almost completely planar, with a dihedral angle of only 1.30° between the two halves, and the analogous O(11)-Mn(2)-O(12)-Mn(3) unit has a dihedral angle of 4.6° between the two halves. The other two five-coordinate Mn atoms (Mn(4) and Mn(6)) have distorted square-based pyramidal geometries with the Mn(4)-O(83) and Mn(6)-O(116) bonds located along the apical positions.

Most of the methoxybenzoate ligands in 5 bridge in the familiar syn,syn  $\mu_2$ -mode across two Mn atoms. However, four carboxylates bridge in the less common ( $\mu$ -O;O', $\mu_2$ -O) bridging mode. The shortest distance between Mn atoms on opposite halves of the molecule is 11.663(6) Å and is between Mn(1) and Mn(3) and their symmetry related equivalents. This distance is directly bridged by the 4,4'-bipyridine ligand. There is also a similar distance of 11.746(6) Å between Mn(1) and Mn(1'). The angle between the planes of the two 4,4'-bipyridine ligands are almost entirely encapsulated by the methoxybenzoate groups, as is clearly shown in Fig. 7.

There are several examples of  $Mn_9$  complexes in the literature, including two structures that are very similar to that of 5.  $[Na_2Mn_9O_7(O_2CPh)_{15}(CH_3CN)_2]$  (6) [21] was isolated from an attempted oxidation of ("Bu<sub>4</sub>N)- $[Mn_4O_2(O_2CPh)_9(H_2O)]$  (2) with dibenzoylperoxide (PhCO)\_2O\_2]. In addition,  $[Mn_9O_7(O_2CPh)_{13}(py)_2]$  (7) [26] was synthesized by treating  $[Mn_3O(O_2CPh)_6(py)_2-(H_2O)]$  with the oxygen transfer agent PhIO. Complex 7 is nearly identical to the benzoate derivative of the asymmetric unit of 5, with two pyridine ligands. A similar unpublished complex,  $[Mn_9O_7(O_2CPh)_{13}(H_2O)_2]$ , possessing two axially coordinated in the providence of the axially coordinated in the providence of the



Fig. 4. ORTEP representation of  $[Mn_0O_7(O_2CC_6H_4-p-OMe)_{13}(4,4'-bpy)]_2 \cdot 20CH_3CN (5 \cdot solv)$ . No hydrogen atoms or solvent molecules are shown and outer atoms are de-emphasized. Thermal ellipsoids are shown at the 50% probability level.

dinated H<sub>2</sub>O molecules instead of terminal N-donor ligands was isolated from the electrochemical oxidation of ("Bu<sub>4</sub>N)-[Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CPh)<sub>9</sub>(H<sub>2</sub>O)] upon slow evaporation of the CH<sub>3</sub>CN reaction solvent [27]. Another example of an Mn<sub>9</sub> aggregate which has a much different arrangement of atoms is [Mn<sub>9</sub>O<sub>4</sub>(O<sub>2</sub>CPh)<sub>8</sub>(sal)<sub>4</sub>(salH)<sub>2</sub>(py)<sub>4</sub>], where salH<sub>2</sub> is salicylic acid. This complex contains 8 Mn<sup>III</sup> and one Mn<sup>II</sup> ion arranged such that the eight-coordinate central Mn<sup>II</sup> is bridged by salicylate ligands to two Mn<sub>4</sub>O<sub>2</sub> butterfly units [28]. The largest number of Mn atoms in a discrete structurally characterized Mn oxide aggregate is 18. Complex 5 is only the second example of an Mn aggregate containing 18 metal atoms. The only other example, [Mn<sub>18</sub>K<sub>4</sub>O<sub>16</sub>- $(O_2CPh)_{22}(phth)_2(H_2O)_4]$ , has a very different, almost planar structure, and is coordinated by benzoate and phthalate ligands [23].

Bond distances and angles of 5 appear to be quite similar to those in the enneanuclear complex [Mn<sub>9</sub>O<sub>7</sub>(O<sub>2</sub>CPh)<sub>13</sub>-(py)<sub>2</sub>] (7). The average Mn-N distance in complex 5 to 4,4'-bpy, for example, is 2.329 Å, while in complex 7 the analogous bond to the axial pyridine molecules is 2.30 Å. The Mn-O-Mn angles in the base are almost identical in the two structures. On the other hand, [Na2Mn9O7(O2CPh)15- $(CH_3CN)_2$  (6) shows distortions in its structure relative to those of 5 and 7 as shown in Table 7. Compared with complex 6, complex 5 has a slightly more planar square pyramidal structure and the Mn-O-Mn angles between Mn(1) and Mn(3) and between Mn(1) and Mn(2) via the bridging oxides are slightly larger. The Mn-O-Mn angle between the apical and planar oxides is also reduced in complex 5 relative to complex 6. The Mn(1)-Mn(2)-Mn(3) angle is comparatively more obtuse (145.50°) than in [Na2Mn9O7-

Table 4 Selected bond lengths (Å) and angles (°) for  $[Mn_sO_7(O_2CC_6H_4\cdot p-OMe)_{13}$ (4.4'-bny)]. 20CH<sub>2</sub>CN (5 solv)

(4,4'-opy)]2·20CH30	JN (5.SOIV)		
Mn(1)Mn(2)	2.880(4)	Mn(1)Mn(4)	3.362(5)
Mn(1)Mn(7)	3.264(4)	Mn(2)…Mn(3)	2.872(4)
Mn(2)Mn(4)	3.293(4)	Mn(2)Mn(5)	3.310(4)
Mn(2)Mn(6)	3.324(4)	Mn(2)…Mn(7)	3.317(4)
Mn(2)…Mn(8)	3.416(6)	Mn(2)…Mn(9)	3.397(6)
Mn(3)…Mn(5)	3.256(4)	Mn(3)…Mn(6)	3.366(5)
Mn(4)…Mn(5)	3.407(4)	Mn(4)…Mn(9)	3.259(5)
Mn(5)…Mn(9)	3.029(5)	Mn(6)…Mn(7)	3.384(4)
Mn(6)…Mn(8)	3.252(5)	Mn(7)…Mn(8)	3.018(6)
Mn(8)…Mn(9)	3.322(4)	Mn(1)-O(10)	1.898(13)
Mn(1)-O(13)	1.868(13)	Mn(1)-O(17)	1.959(14)
Mn(1)-O(28)	1.958(13)	Mn(1)O(39)	2.190(12)
Mn(1)-N(160)	2.329(14)	Mn(2)-O(10)	1.907(13)
Mn(2)-O(11)	1.916(13)	Mn(2)-O(12)	1.897(12)
Mn(2)-O(13)	1.956(13)	Mn(2)O(14)	2.165(12)
Mn(3)-O(11)	1.851(13)	Mn(3)-O(12)	1.864(13)
Mn(3)-O(50)	1.943(12)	Mn(3)-O(61)	1.990(13)
Mn(3)-O(72)	2.181(13)	Mn(3)-N(166)	2.320(15)
Mn(4)-O(10)	1.846(12)	Mn(4)-O(16)	1.874(13)
Mn(4)-O(19)	1.943(14)	Mn(4)-O(83)	2.097(16)
Mn(4)0(94)	1.939(13)	Mn(5)-O(11)	1.901(13)
Mn(5)-O(16)	1.865(13)	Mn(5)-O(52)	1.977(13)
Mn(5)=0(74)	2.232(13)	Mn(5)-0(85)	2.115(15)
Mn(5) = O(105)	1.978(12)	Mn(6) = O(12)	1.8/3(13)
Mn(6) = O(15) Mn(6) = O(116)	1.001(13)	Mn(0) = O(03) Mn(6) = O(137)	1.929(13)
$M_{n}(0) = O(110)$ $M_{n}(7) = O(13)$	1.874(13)	$M_{\rm H}(0) = O(127)$ $M_{\rm H}(7) = O(15)$	1,936(14)
Mn(7)=O(13) Mn(7)=O(30)	1.874(13)	Mn(7)=O(41)	2 276(12)
$M_{\rm H}(7) = O(118)$	2.146(13)	$M_{n}(7) = O(138)$	1 975(12)
Mn(8)-O(14)	1.837(13)	Mn(8) = O(15)	1.885(12)
Mn(8)-O(41)	2.256(13)	Ma(8)-O(129)	2.195(14)
Mn(8)-O(140)	2.023(13)	Mn(8)-O(149)	1.926(13)
Mn(9)-O(14)	1.858(12)	Mn(9)-O(16)	1.892(12)
Mn(9)-O(74)	2.263(12)	Mn(9)-O(96)	2.172(16)
Mn(9)-O(107)	1.999(13)	Mn(9)-O(151)	1.957(15)
O(10) Ma(1) O(13)	83.2(5)	O(10) Mp(1) -O(17)	94 7(6)
O(10) - Min(1) - O(13)	1743(5)	O(10) - Mm(1) - O(17)	94.2(0)
O(10) = Mn(1) = O(20)	) 90.0(5)	O(13) - Mn(1) - O(17)	174 9(5)
O(13) = Mn(1) = O(28)	94.3(6)	O(13) = Mn(1) = O(39)	99 3(5)
O(13) = Mn(1) = O(16)	) 92.9(5)	O(17) - Mn(1) - O(28)	87.9(6)
O(17) - Mn(1) - O(39)	85.1(5)	O(17) - Mn(1) - N(160)	82.8(5)
O(28)-Mn(1)-O(39)	91.9(5)	O(28)-Mn(1)-N(160)	85.0(5)
O(39)-Mn(1)-N(160	)) 167.6(5)	Mn(1)-Mn(2)-Mn(3)	145.5(2)
O(10)-Mn(2)-O(11)	95.4(6)	O(10)-Mn(2)-O(12)	162.1(5)
O(10)-Mn(2)-O(13)	80.7(5)	O(10)-Mn(2)-O(14)	99.7(5)
O(11)-Mn(2)-O(12)	79.2(5)	O(11)-Mn(2)-O(13)	149.6(5)
O(11)-Mn(2)-O(14)	106.0(5)	O(12)-Mn(2)-O(13)	95.3(5)
O(12)-Mn(2)-O(14)	98.1(5)	O(13)-Mn(2)-O(14)	104.4(5)
O(11)-Mn(3)-O(12)	) 81.7(6)	O(11)-Mn(3)-O(50)	93.7(6)
O(11)-Mn(3)-O(61)	) 175.2(6)	O(11)-Mn(3)-O(72)	97.9(5)
O(11)-Mn(3)-N(166	5) 93.3(6)	O(12)-Mn(3)-O(50)	173.9(6)
O(12)-Mn(3)-O(61)	94.3(5)	O(12)-Mn(3)-O(72)	94.1(5)
O(12)-Mn(3)-N(160	5) 90.0(6)	O(50)-Mn(3)-O(61)	90,1(5)
U(50)-Mn(3)-O(72)	90.5(5)	U(50)-Mn(3)-N(166)	86,2(5)
U(01)-Mn(3)-O(72)	) 85.1(5)	U(01)-Mn(3)-N(166)	84.0(5)
O(12) - Mn(3) - N(16)	0) 108.0(5)	O(10) - Mn(4) - O(10) O(10) - Mn(4) - O(10)	88.7(0) 07.6(6)
O(10)-Ma(4)-O(19)	) 94.9(0) \ 159.4/4\	O(16) = Ma(4) = O(163) O(16) = Ma(4) = O(10)	97.0(0) 174.8(5)
O(16)-MB(4)-O(94)	(0)C.6CI ( 06.8(A)	O(16) = Mn(4) = O(19)	1/4.0(J) 07.7(6)
O(10)-Mn(4)-O(83)	, 50.0(0) \ <u>979/6</u> \	O(19) = Mn(4) = O(74)	92.7(U) 83 0/6)
O(83)-Mn(4)-O(94)	) 103.6(6)	O(11) - Mn(5) - O(16)	88.6(6)
~,00) mil(4)~0(34)	,	~()(.)(10)	00.0(0)

0(11) 14-(5) 0(5)	00.110	0/11/ 14-70- 0/04	~~~~
O(11) - Mn(5) - O(52)	95.1(5)	O(11) - Mn(5) - O(14)	90.6(3)
O(11)-Mn(5)-O(85)	90.7(0)	O(11)-MR(5)-O(105)	109.8(0)
U(16)-Mn(5)-U(52)	170.2(5)	O(10)-Mn(5)-O(74)	84.4(5)
O(16)-Mn(5)-O(52)	176.2(5)	O(16)-Mn(5)-O(74)	84.4(5)
O(16)-Mn(5)-O(85)	94.4(6)	O(16)-Mn(5)-O(105)	87.8(5)
O(52)-Mn(5)-O(74)	94.7(5)	O(52)-Mn(5)-O(85)	86.0(5)
O(52)-Mn(5)-O(105)	88.4(5)	O(74)-Mn(5)-O(85)	172.6(5)
O(74)-Mn(5)-O(105)	79.6(5)	O(85)-Mn(5)-O(105)	93.1(5)
O(12)-Mn(6)-O(15)	87.3(5)	O(12)-Ma(6)-O(63)	94.4(6)
O(12)-Mn(6)-O(116)	95.6(5)	O(12)-Mn(6)-O(127)	163.8(5)
O(15)-Mn(6)-O(63)	172.7(5)	O(15)-Mn(6)-O(116)	97.8(5)
O(15)-Mn(6)-O(127)	91.2(6)	O(63)-Mn(6)-O(116)	89.1(5)
O(63)-Mn(6)-O(127)	85.2(6)	O(116)-Mn(6)-O(127)	100.6(5)
O(13)-Mn(7)-O(15)	89.4(6)	O(13)-Mn(7)-O(30)	94.2(6)
O(13)-Mn(7)-O(41)	90.5(5)	O(13)-Mn(7)-O(118)	93.0(5)
O(13)-Mn(7)-O(138)	172.2(5)	O(15)-Mn(7)-O(30)	175.6(5)
O(15)-Mn(7)-O(41)	84.0(5)	O(15)-Mn(7)-O(118)	96.0(5)
O(15)-Mn(7)-O(138)	87.5(5)	O(30)-Mn(7)-O(41)	93.4(5)
O(30)-Mn(7)-O(118)	86.3(5)	O(30) - Mn(7) - O(138)	88.6(5)
O(41)-Mn(7)-O(118)	176.5(5)	O(41) - Mn(7) - O(138)	82.1(5)
O(118)Mn(7)-O(138)	94.4(5)	O(14)-Mn(8)-O(15)	90.6(5)
O(14)-Mn(8)-O(41)	89.1(5)	O(14) - Mn(8) - O(129)	103.1(6)
O(14)-Mn(8)-O(140)	169.8(5)	O(14)-Mn(8)-O(149)	97 2(6)
O(15)-Mn(8)-O(41)	83.4(5)	O(15)-Mn(8)-O(129)	84 3(5)
$O(15) - M_{\rm B}(8) - O(140)$	86 3(5)	O(15) - Mn(8) - O(149)	170.6(6)
O(41) - Mn(8) - O(170)	167 8(5)	$O(41) - M_0(8) - O(140)$	80.0(5)
O(41) - Mn(8) - O(123)	101 8(5)	$O(170) - M_{0}(2) = O(140)$	96 / (5)
O(47) = Min(3) = O(143)	00.0(5)	O(127) - Ma(0) - O(140) $O(140) M_{-}(9) O(140)$	00.4(3)
O(123) = min(3) = O(143) $O(14) = M_{\pi}(3) = O(16)$	01 0(5)	O(140) = Min(0) = O(147) O(14) = Min(0) = O(74)	90.0(5)
O(14) = Win(3) = O(10)	71.7(J) 00.0(6)	O(14) = Ma(3) = O(14)	160.4(5)
O(14) = Min(3) = O(30)	05 3(6)	$O(14) - M_{H}(0) - O(107)$	83.0(5)
O(14) - Min(3) - O(151)	93.2(0)	O(10) - Ma(9) - O(14)	04.7(J) 97.0(5)
O(10) - Will(9) - O(30)	07.1(0)	O(10) - Mil(9) - O(107)	67.U(J)
O(10) - Mn(9) - O(151)	1/2.0(0)	O(74)-MR(9)-O(90)	107.5(3)
O(74)-Mn(9)-O(107)	80.4(5)	O(74)-Mn(9)-O(151)	100,7(6)
O(96)-Mn(9)-O(107)	91.5(6)	O(96)-MB(9)-O(151)	88.3(0)
O(107)-Mn(9)-O(151)	86.7(6)	Mn(1)-O(10)-Mn(2)	98.4(6)
Mn(1)-O(10)-Mn(4)	127.8(7)	Mn(2)-O(10)-Mn(4)	122.7(7)
Mn(2)-O(11)-Mn(3)	99.4(6)	Mn(2)-O(11)-Mn(5)	120.3(6)
Mn(3)-O(11)-Mn(5)	120.4(7)	Mn(2) = O(12) = Mn(3)	99.6(6)
Mn(2)-O(12)-Mn(6)	123.6(6)	Mn(3)-O(12)-Mn(6)	128.4(7)
Mn(1)-O(13)-Mn(2)	97.7(6)	Mn(1)-O(13)-Mn(7)	121.4(7)
Mn(2)-O(13)-Mn(7)	120.0(7)	Mn(2)-O(14)-Mn(8)	116.9(6)
Mn(2)-O(14)-Mn(9)	115.0(6)	Mn(8)-O(14)-Mn(9)	128.0(6)
Mn(6)-O(15)-Mn(7)	131.3(7)	Mn(6)-O(15)-Mn(8)	119.4(7)
Mn(7)-O(15)-Mn(8)	108.5(6)	Ma(4)-O(16)-Ma(5)	131.3(7)
Mn(4)-O(16)-Mn(9)	119.9(7)	Mn(5)-O(16)-Mn(9)	107.5(6)
Mn(7)-O(41)-Mn(8)	83.5(4)	Mn(5)-O(74)-Mn(9)	84.7(4)

 $(O_2CPh)_{15}(CH_3CN)_2$  (6) (140.50°), because additional coordination of the central bridging oxides to the Na<sup>+</sup> ions in the latter heterobimetallic species results in more acute angles for the base.

# 3.5. Miscellaneous characterization of [Mn<sub>9</sub>O<sub>7</sub>(O<sub>2</sub>CCR)<sub>13</sub>(L-L)]<sub>2</sub> complexes

The proton NMR spectra of  $({}^{B}\text{U}_4\text{N}) [Mn_4O_2(O_2\text{CPh})_9-(H_2O)]$  (2) and its methoxybenzoate derivative (4) in CD<sub>2</sub>Cl<sub>2</sub> are quite broad, and individual proton resonances are difficult to distinguish. All of the resonances are in the 20 to 0 ppm range as might be expected for a paramagnetic complex ligated by only aromatic carboxylates, and it is not possible

(continued)

Table 5						
Fractional	coordinates	and	isotropic	thermal	parameters	fo
[Mn <sub>9</sub> O <sub>7</sub> (O <sub>2</sub>	CC6H4-p-OM	e) <sub>13</sub> (4,	4'-bpy)]2·2	20CH <sub>3</sub> CN	(5·solv)	

# Table 5 (continued)

Fractional [Mn <sub>9</sub> O <sub>7</sub> (O	coordinates 2CC <sub>6</sub> H <sub>4</sub> -p-OM	and isotropic e) <sub>13</sub> (4,4'-bpy)] <sub>2</sub> -2	thermal par 20CH <sub>3</sub> CN (5·so	ameters for lv)	Atom	x	у	z	B <sub>iso</sub>
Atom	x	у	z	Biso	O(61)	10238(3)	9370(8)	9049(3)	23(3)
					C(62)	10344(5)	8897(13)	9311(6)	27(4)
Mn(1)	8868(1)	7438(2)	7601(1)	22	O(63)	10170(3)	8348(8)	9336(3)	27(3)
Mn(2)	9214(1)	8460(2)	8219(1)	20	C(64)	10684(5)	8974(13)	9607(5)	26(4)
Mn(3)	9770(1)	9543(2)	8649(1)	20	C(65)	10891(6)	9568(16)	9614(6)	44(5)
Mn(4)	8476(1)	9163(2)	7596(1)	24	C(66)	11226(7)	9609(18)	9899(8)	58(6)
Mn(5)	9051(1)	10459(2)	8238(1)	21	C(6/)	11339(7)	90/2(18)	101/9(8)	56(6)
Mn(6)	9/88(1)	7692(2)	9001(1)	20	C(68)	11140(6)	8466(15)	10184(6)	41(5)
Mn(7)	9258(1)	6405(2)	8334(1)	20	C(69)	10/94(5)	8423(15)	9887(6)	37(3)
Min(8)	9018(1)	1300(2)	8703(1)	20	C(70)	11008(3)	9180(15)	10452(6)	(0)05
MR(9)	8083(1)	9230(2)	0373(1)	21	O(72)	0688(3)	0734(27)	10/06(11)	110(11)
0(10)	0225(3)	0615(8)	9264(3)	27(3)	C(72)	9000(3)	0001(12)	9044(3)	20(3)
0(11)	9555(3)	8428(8)	8630(3)	27(3)	0(74)	9430(3)	10017(8)	9023(3)	20(4)
O(12)	0223(3)	7326(8)	8068(3)	25(3)	C(75)	9439(4)	9677(12)	0344(5)	20(3)
0(13)	8951(3)	8334(8)	8459(3)	21(3)	C(76)	9735(5)	9357(12)	9636(5)	24(4)
0(14)	0300(3)	7109(8)	8701(3)	24(3)	C(77)	9744(5)	9103(14)	9030(5)	34(5)
0(15)	8709(3)	9677(8)	8035(3)	24(3)	C(78)	9459(5)	9178(14)	0915(6)	34(5)
0(17)	8517(3)	7636(9)	7108(4)	33(3)	C(79)	9166(5)	9533(15)	9639(6)	36(5)
C(18)	8262(5)	8036(13)	6986(5)	25(4)	C(80)	9155(5)	9788(13)	9338(6)	30(4)
0(19)	8211(3)	8578(9)	7153(4)	30(3)	0(81)	9434(4)	8945(11)	10191(5)	52(4)
C(20)	8006(7)	7920(18)	6619(8)	56(6)	C(82)	9732(7)	8555(19)	10493(8)	64(7)
C(21)	7682(7)	8263(18)	6455(8)	60(7)	O(83)	8552(4)	10103(10)	7337(4)	45(4)
C(22)	7427(8)	8142(21)	6101(9)	73(8)	C(84)	8758(8)	10642(22)	7466(9)	75(8)
C(23)	7488(18)	7633(43)	5914(19)	184(17)	O(85)	8915(3)	10975(9)	7757(4)	34(3)
C(24)	7825(15)	7339(35)	6055(16)	153(14)	C(86)	8914(9)	10843(25)	7227(11)	96(10)
C(25)	8073(10)	7438(28)	6423(12)	113(11)	C(87)	9283(9)	11262(25)	7494(11)	99(10)
O(26)	7216(10)	7603(28)	5540(13)	188(13)	C(88)	9328(11)	11450(31)	7195(14)	131(13)
C(27)	7306(24)	7238(64)	5309(26)	331(25)	C(89)	9121(12)	11130(28)	6825(13)	109(11)
O(28)	8931(3)	6334(9)	7466(4)	28(3)	C(90)	8838(12)	10759(30)	6651(12)	121(12)
C(29)	9049(5)	5713(14)	7650(6)	30(4)	C(91)	8714(10)	10539(27)	6869(12)	108(11)
O(30)	9101(3)	5603(8)	7955(3)	24(3)	O(92)	9279(10)	11359(27)	6647(12)	193(13)
C(31)	9173(6)	4996(16)	7550(7)	44(5)	C(93)	9068(16)	11146(42)	6228(19)	198(18)
C(32)	9359(7)	4372(20)	7789(8)	68(7)	O(94)	8050(3)	9445(9)	7503(4)	33(3)
C(33)	9524(9)	3740(24)	7714(10)	91(9)	C(95)	7988(5)	9104(14)	7708(6)	31(4)
C(34)	9410(11)	3835(30)	7341(12)	111(11)	O(96)	8207(4)	8717(10)	7984(4)	42(3)
C(35)	9235(7)	4378(20)	/112(8)	62(7)	C(97)	/658(5)	9140(14)	7628(6)	31(4)
C(36)	9109(6)	4980(16)	7217(6)	42(5)	C(98)	7588(6)	8815(17)	7848(7)	50(6)
O(37)	9618(8)	3198(22)	7323(9)	146(10)	C(99)	7258(7)	8834(18)	7753(8)	60(7)
C(38)	9611(11)	3289(29)	0980(12)	122(12)	C(100)	/006(6)	9146(16)	7425(7)	47(6)
C(39)	8409(3)	6700(12)	7034(3)	25(3)	C(101)	7070(6)	9473(16)	7205(7)	47(6)
O(40)	0401(3) 8743(3)	6656(8)	2105(3)	23(4)	O(102)	7401(0)	9450(15)	7304(0)	41(5)
C(42)	8160(5)	6731(13)	7865(5)	22(3)	C(103)	6431(7)	9139(12)	7303(3)	03(4) 66(7)
C(43)	7860(5)	6896(14)	7547(6)	31(4)	O(105)	8757(3)	11220(8)	9275(3)	23(3)
C(44)	7557(5)	6850(14)	7507(6)	35(5)	C(105)	8560(5)	11059(13)	8348(5)	23(3) 24(4)
C(45)	7569(5)	6620(13)	7803(6)	28(4)	O(107)	8474(3)	10319(8)	8380(3)	24(4)
C(46)	7869(5)	6432(13)	8126(6)	30(4)	C(108)	8411(5)	11745(12)	8423(5)	23(4)
C(47)	8158(5)	6506(13)	8154(5)	27(4)	C(109)	8128(5)	11656(14)	8427(6)	33(5)
O(48)	7289(4)	6557(9)	7802(4)	38(3)	C(110)	8006(5)	12328(15)	8506(6)	39(5)
C(49)	6963(6)	6601(16)	7453(7)	48(6)	COID	8172(6)	13101(16)	8574(6)	44(5)
O(50)	9868(3)	10701(8)	8614(3)	20(2)	C(112)	8443(5)	13225(15)	8582(6)	38(5)
C(51)	9693(4)	11342(12)	8562(5)	20(4)	C(113)	8557(5)	12550(15)	8481(6)	37(5)
O(52)	9395(3)	11337(8)	8458(3)	25(3)	O(114)	8027(4)	13735(12)	8656(5)	58(4)
C(53)	9865(5)	12165(13)	8617(5)	25(4)	C(115)	8231(7)	14519(19)	8812(8)	62(7)
C(54)	10189(5)	12174(13)	8730(5)	27(4)	O(116)	10091(3)	6961(8)	8920(3)	25(3)
C(55)	10358(5)	12919(13)	8789(6)	29(4)	C(117)	10012(4)	6485(12)	8665(5)	20(4)
C(56)	10189(5)	13648(13)	8756(5)	27(4)	O(118)	9747(3)	6104(8)	8484(4)	28(3)
C(57)	9861(5)	13682(14)	8649(6)	31(4)	C(119)	10262(5)	6388(12)	8592(5)	25(4)
C(58)	9698(5)	12912(13)	8582(5)	28(4)	C(120)	10570(6)	6768(16)	8809(6)	45(5)
C(59)	10693(6)	14433(10)	8833(4)	40(3)	C(121)	10817(7)	6680(18)	8742(7)	56(6)
L(00)	10082(5)	14467(15)	8907(0)	38(5)	C(122)	10731(7)	6230(18)	8452(8)	60(7)
				(continued)					(continued)

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Table 5 (continued)

Atom	x	у	z	<b>B</b> iso
C(123)	10=24(5)	5835(15)	8232(6)	38(5)
C(124)	10193(5)	5905(13)	8302(5)	25(4)
O(125)	10941(6)	6137(15)	8344(6)	88(6)
C(126)	11208(13)	6766(35)	8474(14)	152(14)
0(127)	9855(3)	7134(9)	9409(4)	30(3)
C(128)	9626(4)	7266(12)	9446(5)	1 <b>9(</b> 4)
0(129)	9387(3)	7736(9)	9246(4)	32(3)
C(130)	9635(5)	6819(13)	9728(5)	25(4)
C(131)	9902(5)	6301(14)	9949(6)	33(5)
C(132)	9896(5)	5811(14)	10200(6)	33(5)
C(133)	9642(5)	5906(14)	10229(6)	31(4)
C(134)	9368(6)	6400(15)	10005(6)	41(5)
C(135)	9372(5)	6884(14)	9759(6)	32(4)
O(136)	9612(4)	5435(10)	10463(4)	44(3)
C(137)	98/5(6)	4837(17)	106/8(7)	34(0) 20(2)
0(138)	9246(3)	5501(8)	8013(3)	20(2)
C(139)	9166(4)	5555(11)	8822(3)	10(3)
O(140)	9063(3)	0190(8)	0015(5)	19(2)
C(141)	9201(3)	4/04(12)	9013(3)	23(4)
C(142)	9283(3)	4022(13)	0112(6)	36(5)
C(143)	9320(3)	3325(13)	9370(5)	27(4)
C(144)	9275(5)	4052(14)	9471(6)	34(5)
C(145)	9158(5)	4798(13)	9288(6)	30(4)
O(140)	9797(4)	2631(11)	9563(4)	52(4)
C(148)	9369(7)	1843(20)	9463(8)	70(8)
O(149)	8677(3)	7540(9)	8778(4)	33(3)
C(150)	8568(6)	8144(16)	8833(7)	47(6)
0(151)	8597(3)	8860(10)	8731(4)	39(3)
C(152)	8402(5)	8120(15)	8994(6)	34(5)
C(153)	8379(7)	7353(19)	9119(8)	62(7)
C(154)	8225(10)	7241(28)	9303(11)	108(11)
C(155)	8126(12)	7983(36)	9359(13)	133(13)
C(156)	8133(11)	8820(31)	9248(12)	122(12)
C(157)	8284(8)	8850(22)	9054(9)	81(8)
O(158)	7933(9)	8077(26)	9501(10)	175(12)
C(159)	7867(15)	7159(45)	9595(17)	194(17)
N(160)	9205(3)	7917(10)	7436(4)	19(3)
C(161)	9395(6)	7409(17)	7409(7)	51(6)
C(162)	9564(7)	7673(21)	7262(8)	74(8)
C(163)	9543(5)	8485(13)	7158(5)	24(4)
C(164)	9351(6)	9016(17)	7199(7)	50(6)
C(165)	9190(6)	8699(16)	7343(6)	42(5)
N(166)	9967(4)	9224(10)	8310(4)	23(3)
C(167)	10045(7)	9765(18)	8103(7)	38(0) 50(7)
C(168)	10201(7)	9304(19)	8000(7)	39(7)
C(169)	10291(5)	8703(13)	8144(9)	27(4)
C(170)	10194(7)	8208(20)	8300(9)	79(8)
C(172)	10034(0)	15506(34)	6693(14)	53(12)
C(173)	12552(10)	15556(27)	6347(12)	28(8)
N(174)	12356(11)	15546(30)	6102(13)	62(11)
C(175)	8457(26)	3054(73)	6626(29)	184(26)
C(176)	8700(14)	3162(39)	6392(16)	65(13)
N(177)	8784(12)	3292(31)	6204(13)	72(12)
C(178)	13134(10)	10553(26)	6984(11)	28(8)
C(179)	12807(17)	10607(43)	6728(19)	78(15)
N(180)	12533(14)	10479(37)	6509(16)	89(14)
C(181)	14099(18)	8682(45)	10278(18)	83(16)
C(182)	13862(23)	8565(56)	10219(22)	108(19)
N(183)	13725(15)	8260(41)	10297(16)	98(15)
C(184)	8818(12)	12820(32)	7699(14)	47(11)
				{ continued

Table 5 (continued)					
Atom	X	у	z	B <sub>iso</sub>	
C(185)	8579(13)	12613(33)	7344(14)	47(11)	
N(186)	8339(14)	12573(38)	7076(16)	94(14)	
C(187)	13851(19)	13194(53)	10380(22)	105(18)	
C(188)	13849(19)	12916(53)	10159(21)	99(18)	
N(189)	13720(17)	11965(48)	10238(19)	128(17)	
C(190)	11588(26)	11860(74)	4423(29)	181(28)	
C(191)	8818(20)	8886(53)	6100(22)	109(19)	
N(192)	11258(19)	11219(53)	3718(22)	156(20)	
C(193)	12496(13)	12774(36)	8549(15)	61(13)	
C(194)	12293(27)	12571(76)	8752(30)	189(29)	
C(195)	11829(18)	4983(49)	8735(20)	99(17)	
C(196)	13039(19)	11263(53)	5513(21)	113(18)	
C(197)	8594(19)	15059(50)	9729(20)	103(17)	
C(198)	8381(29)	15003(79)	9802(31)	199(27)	
C(199)	11558(23)	14983(64)	9334(25)	150(23)	

Fractional coordinates are  $\times 10^4$  for non-hydrogen atoms and  $\times 10^3$  for hydrogen atoms.  $B_{uo}$  values are  $\times 10$ . Isotropic values for those atoms refined anisotropically are calculated using the formula given by Hamilton [29]. Parameters marked by an asterisk (\*) were not varied.

to easily assign the <sup>1</sup>H resonances of these complexes. However, the products of the reaction of 1 equiv. of 4,4'-bpy with both the benzoate and methoxybenzoate derivatives of the 'naked butterfly' led to the observation of new <sup>1</sup>H NMR spectra. Most prominent is the appearance in both cases of broad peaks at ~35 and 65 ppm which can be attributed to the protons in the 2- and 3-positions of the 4,4'-bipyridine group coordinated to paramagnetic Mn<sup>III</sup> centers. Proton NMR resonances due to <sup>n</sup>Bu<sub>4</sub>N<sup>+</sup> are also absent in the spectra of the new products.

The virtual symmetry of 5 suggests only two types of protons from the 4,4'-bpy ligand. Although this molecule contains only one  $C_2$  axis in the solid state, in solution it would have considerably more flexibility; the 4,4'-bpy ligands should be equivalent, and the two rings of a single 4,4'-bpy ligand should be equivalent as well. The 2-H, located ortho to the heteroatom of the ring would be expected to be broadened and shifted more significantly than the 3-H located meta to the metal coordination site. The peak at  $\sim$  35 ppm is thus assigned to the 3-H and the peak at ~65 ppm to the 2-H. Longitudinal relaxation times  $(T_1)$  were measured for the 4,4'-bpy resonances of [Mn<sub>9</sub>O<sub>7</sub>(O<sub>2</sub>CPh)<sub>13</sub>(4,4'-bpy)<sub>2</sub>]<sub>2</sub> in order to help to confirm the peak assignments.  $T_1$  values were measured using the inversion recovery  $(180^\circ - \tau - 90^\circ)$ method. The relaxation time of the 2-H (0.7 ms) is significantly shorter than that of the 3-H (2.8 ms), as would be expected for protons which are located closer to the metal coordination site. The proton NMR spectra, although not particularly informative, do suggest that 4.4'-bpy is still coordinated in CD<sub>2</sub>Cl<sub>2</sub> solution and that the dimer remains intact. From the virtual symmetry of the complexes in solution, the benzoate ligands might be expected to give ratios of 2:4:1:4:2 (2:2:1 for each type of benzoate) for 15 peaks total. The observed paramagnetic NMR spectra have approximately the correct number of peaks for the crystallographically charac-



Fig. 5. ORTEP representation of a unit cell of  $[Mn_9O_7(O_2CC_6H_4-p-OMe)_{13}(4,4'-bpy)]_2 \cdot 20CH_3CN$  (5 · solv). This view emphasizes the large solvent channels present in the lattice.

#### Table 6

Coordination environments of Mn atoms in the asymmetric unit of [Mn<sub>9</sub>O<sub>7</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-p-OMe)<sub>13</sub>(4,4'-bpy)]<sub>2</sub> (5)

Min atom	Geometry	Coordination	Oxide ligation
Mn(1), Mn(3)	pseudo-octahedral	NO <sub>5</sub>	$2 \mu_3$ -oxides
Mn(2)	square pyramidal	Os	5 $\mu_3$ -oxides
Mn(4), Mn(6)	distorted square pyramidal	O <sub>s</sub>	$2 \mu_3$ -oxides
Mn(5), Mn(7), Mn(8), Mn(9)	pseudo-octahedral	O <sub>6</sub>	2 $\mu_3$ -oxides



Fig. 6. ORTEP representation of one half of  $[Mn_9O_7(O_2CC_6H_4\cdot p-OMe)_{13}(4.4'-bpy)_2]_2^{-2}20CH_3CN (5 \cdot solv)$ . The view emphasizes the core of the molecule. Thermal ellipsoids are shown at the 50% level and hydrogen atoms and solvent molecules are not shown.



Fig. 7. Stereoview of a space-filling representation of 5, which shows the steric congestion between the two Mn<sub>9</sub>O<sub>7</sub> units.

#### Table 7

Comparison of bond distances (Å) and angles (°) in complexes containing  $[Mn_9O_7(O_2CR)_{13}]$  moieties:  $[Mn_9O_7(O_2CC_6H_4-p-OMe)_{13}(4.4'-bpy)]_2$  (5) and  $[Na_2Mn_9O_7(O_2CPh)_{15}(CH_3CN)_2]$  (6)

Parameter	5	6
Mn(1)Mn(2)	2.880	2.886
Mn(2)…Mn(3)	2.872	2.871
Mn(2)-O <sub>b</sub> *	1.919	1.920
Mn(1), Mn(3)-N(O) b	2.329	2.177
Mn(2)-O(14)	2.165(12)	2.111(4)
O(10)-Mn(2)-O(13)	80.7(5)	80.9(2)
O(11)-Mn(2)-O(12)	79.2(5)	81.3(2)
O(10)-Mn(1)-O(13)	83.2(5)	82.4(2)
O(11)-Mn(3)-O(12)	81.7(6)	82.8(2)
Mn(1)-Mn(2)-Mn(3)	145.5(1)	140.5
Sum of angles at O(10), O(12)	350.3	343.1
Sum of angles at O(11), O(13)	339.6	340.8
Sum of angles in plane Mn(2)	350.6	346.2
O(10)-Mn(2)-O(11)	95.4(6)	92.6(2)
O(12)-Mn(2)-O(13)	95.3(5)	91.4(2)
$O_{h}-Min(2)-O_{an}^{a}$	102.0	104.3
Mn(1)-O(10)-Mn(2)	98.4(6)	98.0(2)
Mn(2)-O(12)-Mn(3)	99.6(6)	97.4(2)
Mn(2)-O(11)-Mn(3)	99.4(6)	98.5(2)
Mn(2)-O(13)-Mn(1)	97.6(6)	98.8(2)

<sup>a</sup>  $O_b = oxygen in the base of the molecule, <math>O_{ap} = apical O of square pyramid.$ <sup>b</sup> Value is an average.

terized compound, although the 0-15 ppm region is quite broad with many overlapping peaks.

Conductivity measurements confirmed the neutral character of  $[Mn_9O_7(O_2CC_6H_4-p-OMe)_{13}(4,4'-bpy)]_2$  (5) and its benzoate derivative in CH<sub>2</sub>Cl<sub>2</sub> solution.  $[Na_2Mn_9O_7-(O_2CPh)_{15}(CH_3CN)_2]$  (6) shows rich albeit irreversible electrochemistry, so the electrochemical behavior of  $[Mn_9O_7-(O_2CC_6H_4-p-OMe)_{13}(4,4'-bpy)]_2$  (5) was of great interest. Unfortunately, complex 5 showed only broad, irreversible processes in solution.

#### 3.6. Magnetochemistry

## 3.6.1. [Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(py)<sub>2</sub>]<sub>2</sub>(4,4'-bpy)

The magnetic properties of mixed-valence trinuclear Mn<sub>3</sub>O species have been previously characterized and these compounds have been generally found to possess S = 1/2 or S=3/2 ground states depending on the particular system [20] due to the spin frustration in the triangular system. The effective magnetic moment of [Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(py)<sub>2</sub>]<sub>2</sub>-(4,4'-bpy) decreases from 11.6  $\mu_B/Mn_3$  at 320 K to 4.74  $\mu_B$ at 5.01 K. At low temperature the effective moment per Mn<sub>3</sub> unit approaches that of [Mn<sub>3</sub>O(O<sub>2</sub>CMe)<sub>6</sub>(py)<sub>3</sub>(py)], which was previously characterized as having an S=3/2 ground state spin, rather than the S = 1/2 ground state seen for the asymmetrically ligated species [Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(py)<sub>2</sub>-(H<sub>2</sub>O)] · 1/2CH<sub>3</sub>CN. Reduced magnetization versus field studies performed using 5-50 kG applied field also support the formulation of this new 'dimer of triangles' as an S =3/2 unit with only weak interactions between the two halves of the molecule.

### 3.6.2. $[Mn_9O_7(O_2CC_6H_4-p-OMe)_{13}(4,4'-bpy)]_2$

The magnetic properties of  $[Mn_9O_7(O_2CC_6H_4-p-OMe)_{13}-(4,4'-bpy)]_2$  (5) were investigated via d.c. and a.c. magnetic susceptibility measurements and by reduced magnetization versus field measurements. Because the 4,4'-bpy ligand is twisted, it might be expected to transmit only very weak

magnetic interactions through the bridge, resulting in negligible interactions between the halves of the molecule. A variable temperature magnetic susceptibility study of  $[Mn_9O_7-(O_2CC_6H_4-p-OMe)_{13}(4,4'-bpy)]_2$  (5) was performed in an applied field of 10 kG in the temperature range 2–300 K. At 300 K, the magnetic moment is 11.68  $\mu_B$  per Mn<sub>9</sub> unit, as compared to a spin only value of 16.70  $\mu_B$  for une noninteracting Mn<sup>III</sup> ions, indicating the presence of significant intra-unit antiferromagnetic interactions. Values of  $\chi_{\rm MT}$  per Mn<sub>9</sub> drop from 17.50 cm<sup>3</sup> K mol<sup>-1</sup> at 300 K to 5.28 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K.

A simplified Hamiltonian based on the identity of the bridging groups, including only coupling interactions within the Mn<sub>9</sub> asymmetric units and considering only nearest neighbor metal atoms, is given by Eq. (2). A total of  $(2S + 1)^n$  magnetic states exist for a complex of *n* ions of spin *S*, so that for a complex containing nine  $S = 2 \text{ Mn}^{\text{III}}$  ions, there would be 5<sup>9</sup> states (i.e. a matrix of dimensions (1953125 × 1953125)). Like many other high nuclearity aggregates, the symmetry is such that simplification of the Hamiltonian via the Kambe method is not possible, and thus pairwise coupling constants, *J*, could not be determined. As a result, reduced magnetization versus field data were collected at low temperatures in order to determine the ground state for complex 5.

$$\begin{aligned} \hat{H} &= -2J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3) - 2J_2(\hat{S}_2 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_5 + \hat{S}_2 \cdot \hat{S}_6 \\ &+ \hat{S}_2 \cdot \hat{S}_7) - 2J_3(\hat{S}_2 \cdot \hat{S}_8 + \hat{S}_2 \cdot \hat{S}_9) - 2J_4(\hat{S}_5 \cdot \hat{S}_9 + \hat{S}_7 \cdot \hat{S}_8) \\ &- 2J_5(\hat{S}_1 \cdot \hat{S}_4 + S_3 \cdot \hat{S}_6 + \hat{S}_4 \cdot \hat{S}_5 + \hat{S}_4 \cdot \hat{S}_9 \\ &+ \hat{S}_6 \cdot \hat{S}_7 + \hat{S}_6 \cdot \hat{S}_8 + \hat{S}_8 \cdot \hat{S}_9) - 2J_6(\hat{S}_1 \cdot \hat{S}_7 + \hat{S}_1 \cdot \hat{S}_5) \end{aligned}$$
(2)

Reduced magnetization measurements were made in applied field strengths of 0.5 to 20 kG. Only low temperature data (2-4 K) were used in the fitting of the data because at higher temperatures low lying excited states were populated, and the inclusion of this higher temperature data resulted in lower quality fit of the data. The best fitting parameters for the ground state were found to be S = 2, g = 1.94, and  $D_z = -1.36$  cm<sup>-1</sup>. The least-squares fit of the data is shown in Fig. 8.

The a.c. magnetic susceptibility  $(\chi'_{M})$  of  $[Mn_9O_7-(O_2CC_6H_4-p-OMe)_{13}(4,4'-bpy)]_2$  (4) was measured in a magnetic field oscillating at 250 Hz to provide another probe of the ground state spin of the complex. A plot of  $\chi'_{M}T$  versus T is shown in Fig. 9. No out-of-phase component  $(\chi''_{M})$  of the magnetic susceptibility is seen, indicating no magnetic phase transition or slow relaxation behavior. At 0 K,  $\chi'_{M}T$  extrapolates to 1-1.5 cm<sup>3</sup> K mol<sup>-1</sup>, indicating a ground state of S = 1 or 2, which is consistent with the reduced magnetizzation fit. The continuous decrease in  $\chi'_{M}T$  at low temperature supports the supposition that the ground state is not well-isolated.

The analogous complex,  $[Na_2Mn_yO_7(O_2CPh)_{15}(CH_3CN)_2]$ (6), was previously found to possess an S = 4 ground state. The d.c. magnetic susceptibility data of 5 and 6 are similar at high temperatures, but at low temperature the  $\chi'_MT$  data for



Fig. 8. Plot of the reduced magnetization,  $M/N\beta$  vs. HT for  $[Mn_0O_T - (O_2CC_8H_4-P-OME)]_3(4,4'-bpy)]_2$  (5). Data were collected in the 2.0-4.0 K range in applied magnetic fields of 0.5 ( $\oplus$ ), 1 ( $\bigcirc$ ), 2 ( $\lor$ ), 3 ( $\Box$ ), 5 ( $\blacktriangle$ ), 10 ( $\bigcirc$ ), 20 ( $\lor$ ) kG.



Fig. 9. Plot of  $\chi'_M T$  vs. T for a polycrystalline sample of  $[Mn_0O_7-(O_2CPhOMe)_{13}(4.4'-bpy)]_2(5)$ .  $\chi'_M$  is the in-phase component of the a.c. magnetic susceptibility measured in zero d.c. field and in the presence of a 1 G a.c. field oscillating at 250 Hz.

5 drop more precipitously. The ground state of complex 6 was rationalized using the description of two wing-tip fused  $[Mn_4O_2]^{8+}$  units which share a body Mn atom as shown in Fig. 10, which gives an S = 6 ground state for the  $Mn_7O_4$  unit. Antiferromagnetic coupling of the two additional manganese ions to the  $Mn_7O_4$  base can result in the S = 2 ground state seen for complex 5. It is possible that the small geometric changes in 5 relative to 6 could result in the change from the S = 4 ground state that is found for complex 6. Unfortunately no detailed magnetic studies of  $[Mn_9O_7(O_2CPh)_{13}(py)_2]$  have been performed for comparison. Additional studies of similar complexes might be useful in elucidating the com-



Fig. 10. Coupling scheme for the  $Mn_7O_4$  base of one-half of  $[Mn_9O_7 (O_2CC_6H_4$ -*p*-OMe)<sub>13</sub>(4,4'-bpy)]<sub>2</sub>(5).

peting magnetic interactions in this class of enneanuclear aggregates.

#### 4. Conclusions

The complexes  $[Mn_3O(O_2CPh)_6(py)_2]_2(4,4'-bpy)$  (1) and  $[Mn_9O_7(O_2CC_6H_4-p-OMe)_{13}(4,4'-bpy)]_2$  (5) represent new examples of larger multinuclear complexes linked into a 'dimer of aggregates' via the bifunctional linker, 4,4'bipyridine. The complex  $[Mn_3O(O_2CPh)_6(py)_2](4,4'$ bpy) represents the first structurally characterized example of linked trinuclear  $Mn_3O$  species and is unusual because of its cocrystallization with monomeric trinuclear species. It appears to have an S = 1/2 ground state similar to that of  $[Mn_3O(O_2CMe)_6(py)_3] \cdot py.$ 

The linking of two Mn<sub>p</sub> complexes is an unusual example of a one-pot aggregation (Mn<sub>4</sub> to Mn<sub>9</sub>) and dimerization reaction. Such reactions which perform molecular engineering of aggregates of aggregates will become more important as inorganic chemists seek to design new increasingly complex supramolecular materials. The new Mn<sub>9</sub>O<sub>7</sub> complex is structurally quite similar to two previously characterized complexes containing the Mn<sub>9</sub>O<sub>7</sub> core, but the two Mn<sub>9</sub> units are now linked by two bifunctional 4,4'-bipyridine ligands. Crystal packing shows that large channels containing solvent exist in the solid. Magnetic studies of 5 show data consistent with two non-interacting  $Mn_9O_7$  units, each having an S=2ground state. The magnetic properties of this new complex are somewhat intriguing when compared with the structurally similar  $[Na_2Mn_9O_7(O_2CPh)_{15}(CH_3CN)_2]$  (5) (S=4). It appears that relatively slight changes in the structural parameters of these complexes result in variation in the magnetic ground state in this class of complexes.

#### 5. Supplementary material

Complete tables of bond distances and angles, anisotropic thermal parameters of the non-hydrogen atoms and fractional coordinates of the hydrogen atoms are available from the authors.

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