The First Structurally Characterized Trinuclear Dipicolinato Manganese Complex and its Conversion into a Mononuclear Species by Ligand Substitution

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The novel complex $[Mn_3(pdc)_3(bpy)_3(H_2O)_2]$ (**1**) (H_2pdc = 2,6-pyridinedicarboxylic acid, also known as 2,6-dipicolinic acid; bpy = 2,2′-bipyridine), has been obtained from the reaction of polymeric $[MnK_2(pdc)_2(H_2O)_7]_n$ (**2**) with bpy, and is the first example of a structurally characterized, trinuclear Mn complex incorporating dipicolinato ligands. All the Mn^{II} centers are seven-coordinate in severely distorted pentagonal-bipyramidal geometries. The conversion of **1** to mononuclear $[Mn(pdc)(bpy)(Him)_2]$ (**3**) (Him = imidazole), which is the first seven-coordinate Mn complex with a Him ligand, has also been achieved by substitution of the labile ligand in **1** by Him.

Introduction

Much attention has been paid to the design and synthesis of transition metal complexes incorporating 2,6-dipicolinic acid due to the versatile bidentate, tridentate, or bridging coordination modes of the ligand,[1] its diverse biological activity and its capacity to stabilize unusual oxidation states,[2] as well as its application to diverse areas of technology.[3] Up to now, the control of product architecture has been elusive and remains a major challenge of modern chemistry.[4] Only one example of a trinuclear 2,6-dipicolinate complex is known in the literature,[5] although many examples of mononuclear and dinuclear dipicolinates, as well as complexes with chain structures, have been reported.[6] Manganese complexes of 2,6-dipicolinates are nevertheless rare.[7] Recently, we obtained a Mn/K polymer, $[MnK_2(pdc)_2(H_2O)_7]_n$, from a reaction system containing Mn^{2+}, H_2pdc, and alkali metal hydrate as a member of the family $[MnK_2(pdc)_2(H_2O)_7]_n$ (M = Mn, Co, Zn etc.).[8] Here we report the reaction of the Mn/K polymer with bpy, from which the first example of a dipicolinato, trinuclear Mn complex, $[Mn_3(pdc)_3(bpy)_3(H_2O)_2]$ (**1**), was obtained. Further study of the reaction leads to the mononuclear complex $[Mn(pdc)(bpy)(Him)_2]$ (**3**) with three different ligands within the coordination sphere.

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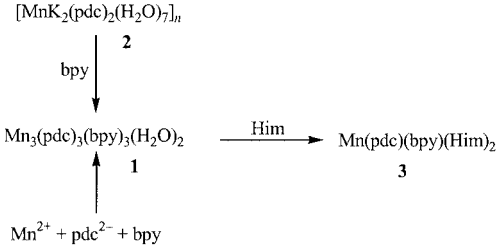
Results and Discussion

Dipicolinates commonly ligate to transition metals by either carboxylate bridges between metal centers, to form polymeric complexes, or tridentate (O,N,O′) chelation to one metal ion.[9] With the intention of preparing pdc-coordinated oligomers as model compounds for Mn-containing enzymes,[10] the bpy ligand, which strongly favours bidentate coordination, was used to cleave the carboxylate bridges of **2**, and a trinuclear cluster (**1**·9H_2O) was successfully isolated as single crystals. Complex **1** can also be obtained directly from a reaction mixture containing Mn^{2+}, pdc^{2-}, and bpy. However, the excess pdc^{2-} used in this direct synthesis gives rise to the formation of impurities and does not allow the formation of good quality single crystals. Upon reaction of **1** with an excess of imidazole (Him) in DMF/H_2O, substitution of H_2O by Him occurs and the trinuclear **1** decomposes, resulting in mononuclear **3**. Related reactions are compiled in Scheme 1.

Single-crystal X-ray analysis revealed **1** to be a discrete trimanganese cluster. As shown in Figure 1, all Mn atoms



Scheme 1. Preparation of **1** and its decomposition to produce **3**

are seven-coordinate, although two types of inequivalent Mn atoms are observed. Both bpy and pdc^{2-} ligands chelate to each Mn center in bi- and tridentate mode (N,N′ and O,N,O′) respectively, while one additional terminal water molecule binds to Mn1 and Mn2, giving the same coordination sphere for the Mn1 and Mn2 sites. In addition to bpy and pdc^{2-} chelation, Mn3 is bidentately coordinated by a carboxylate group of the pdc^{2-} ligand bound to the central Mn2 atom. Interestingly, the three pdc^{2-} ligands exhibit diverse coordination modes. The pdc^{2-} bridges between the Mn ions are also different from each other: double μ-O bridges occur between Mn1 and Mn2 and both carboxylate (μ-OCO) and μ-O bridges exist between Mn2 and Mn3. Consequently, each of the three metals possesses a highly asymmetrical coordination environment, forming a pentagonal bipyramidal geometry around each Mn^{II} center. The intracluster Mn···Mn separations were found to be 3.739(2) Å for Mn1···Mn2, and 4.607(2) Å for Mn2···Mn3; the difference of 0.86 Å in Mn···Mn separation in a single structure is rather rare.[11] Complex **1** is the first dipicolinato trimanganese complex, although a similar triiron dipicolinate [{Fe(pdc)(Hpdc)}$_2$Fe(H$_2$O)$_4$] has been reported.[5] High spin d^5 compounds can be expected to adopt geometries dictated by electrostatic effects, and many seven-coordinate Fe^{III} compounds are known.[12] Seven-coordinate Mn^{II} complexes are often observed with a quinquedentate ligand such as 15-crown-5,[13] which serves to define a pentagonal plane on the equator and leaves two axial positions open for further coordination to give a regular pentagonal bipyramid. However, the coordination sphere in **1** is severely distorted (Table 1) because the two planar ligands (bpy and pdc^{2-}) do not coexist in the equatorial plane and, therefore, large steric strain results between the ligands. On the other hand, linear connection between the metal centers and ligand distortion offer the possibility of further reaction with certain reagents, such as imidazole, to give mononuclear,

Table 1. Selected bond lengths [Å] and angles [°] with estimated standard deviations for **1**

Mn1−O13	2.168(5)	Mn2−O6	2.315(4)
Mn1−N1	2.260(5)	Mn2−N7	2.330(6)
Mn1−N5	2.293(6)	Mn2−O7	2.422(5)
Mn1−O2	2.310(5)	Mn3−N3	2.226(5)
Mn1−O6	2.315(4)	Mn3−N9	2.267(6)
Mn1−N4	2.323(6)	Mn3−O11	2.271(5)
Mn1−O4	2.401(4)	Mn3−N8	2.289(6)
Mn2−O14	2.183(5)	Mn3−O8	2.317(5)
Mn2−O4	2.236(4)	Mn3−O10	2.351(5)
Mn2−N6	2.276(5)	Mn3−O7	2.368(4)
Mn2−N2	2.288(5)		
O13−Mn1−N5	166.3(2)	N9−Mn3−O8	165.0(2)
O13−Mn1−O2	83.2(2)	N9−Mn3−O11	98.8(2)
O13−Mn1−O6	80.23(18)	N9−Mn3−N8	71.7(2)
O13−Mn1−N1	94.72(19)	N9−Mn3−N3	96.0(2)
O13−Mn1−N4	96.0(2)	N9−Mn3−O10	88.39(19)
O13−Mn1−O4	109.36(18)	N9−Mn3−O7	111.32(19)
N5−Mn1−N1	95.03(19)	O8−Mn3−N3	98.78(19)
N5−Mn1−O6	100.91(18)	O8−Mn3−O11	88.54(19)
N5−Mn1−O2	91.1(2)	O8−Mn3−N8	96.8(2)
N5−Mn1−N4	70.9(2)	O8−Mn3−O7	55.78(16)
N5−Mn1−O4	83.29(18)	O8−Mn3−O10	94.30(18)
O4−Mn2−O7	153.40(16)	O14−Mn2−O7	76.24(17)
O4−Mn2−N6	109.70(18)	N6−Mn2−O7	84.34(18)
O4−Mn2−N2	131.59(17)	N2−Mn2−O7	67.88(17)
O4−Mn2−O6	69.08(16)	O6−Mn2−O7	135.86(16)
O4−Mn2−O14	83.96(17)	N7−Mn2−O7	79.77(18)
O4−Mn2−N7	83.82(19)		

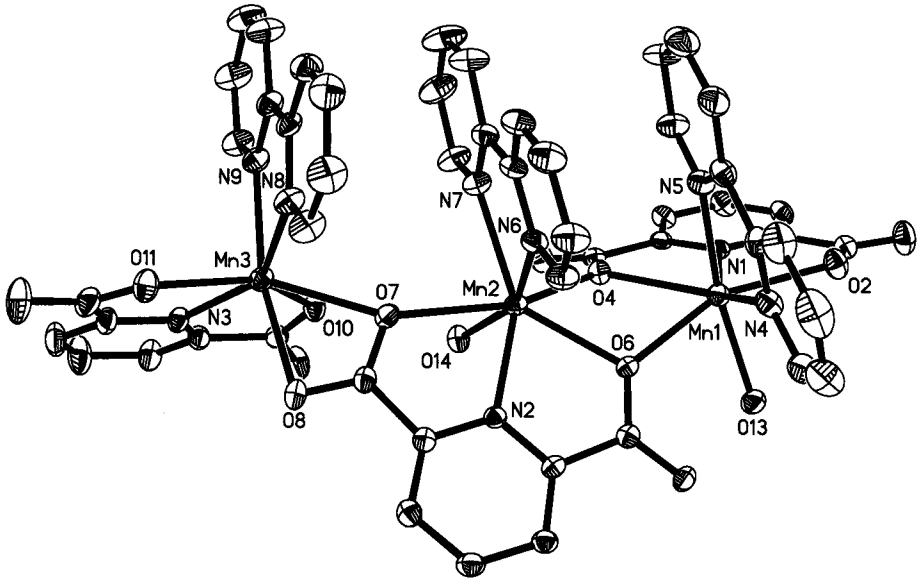


Figure 1. ORTEP drawing of **1** with independent atom-labeling showing thermal ellipsoids at 30% probability

seven-coordinate **3** containing three different ligands (pdc, bpy and Him). To the best of our knowledge, **3** is the first seven-coordinate Mn complex containing imidazole. A single-crystal X-ray analysis confirmed that the sphere around the seven-coordinate Mn^{II} center in **3** has a slightly

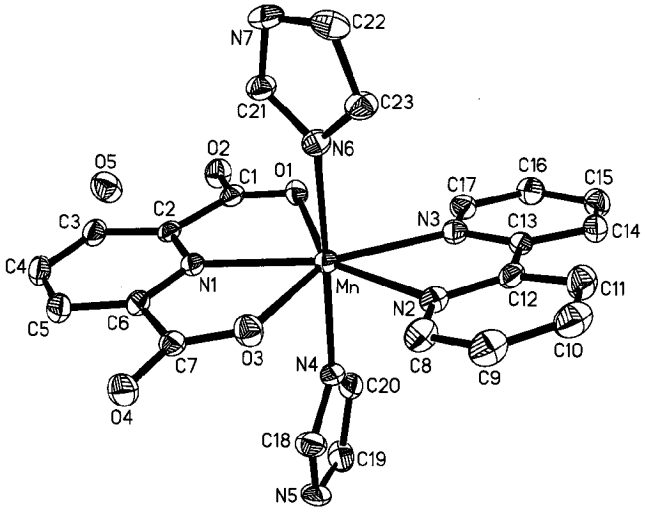


Figure 2. ORTEP drawing of $3{\cdot}H_2O$ with independent atom-labeling showing thermal ellipsoids at 30% probability

distorted pentagonal bipyramidal geometry (Figure 2). Three arene N atoms and two carboxylate O atoms from tridentate pdc^{2-} and bidentate bpy chelate to the Mn^{II} center and form the equatorial plane [a maximum deviation of 0.1494(2) Å from the plane occurs for N3], and two Him N atoms occupy the axial sites. The axial bond angle of 177.45(2)° for N4−Mn−N6 gives a more or less regular pentagonal bipyramid (Table 2). This arrangement of the

Table 2. Selected bond lengths [Å] and angles [°] with estimated standard deviations for **3**

Mn−N6	2.248(5)	Mn−O1	2.372(4)
Mn−N4	2.250(5)	Mn−N2	2.393(5)
Mn−N1	2.324(5)	Mn−N3	2.423(5)
Mn−O3	2.349(4)		
N6−Mn−N4	177.43(18)	N4−Mn−N2	93.30(17)
N6−Mn−N1	93.59(17)	N1−Mn−N2	146.13(18)
N4−Mn−N1	85.51(17)	O3−Mn−N2	78.11(17)
N6−Mn−O3	90.12(17)	O1−Mn−N2	145.91(17)
N4−Mn−O3	87.31(17)	N6−Mn−N3	93.38(17)
N1−Mn−O3	68.02(16)	N4−Mn−N3	88.72(17)
N6−Mn−O1	88.21(17)	N1−Mn−N3	145.32(18)
N4−Mn−O1	93.67(17)	O3−Mn−N3	145.85(17)
N1−Mn−O1	67.75(16)	O1−Mn−N3	78.57(16)
O3−Mn−O1	135.53(16)	N2−Mn−N3	68.27(18)
N6−Mn−N2	86.09(17)		

three ligands is evidently favorable to stabilize the structure and promotes the conversion of trinuclear **1** into mononuclear **3**.

The room-temperature magnetic moment measured for **3** (μ_{eff} = 10.3 B.M.) is close to that expected for the spin-only value of 10.24 B.M. for three uncoupled S = 5/2 sites. The effective magnetic moment remains essentially constant with decreasing temperature, but μ_{eff} decreases rapidly below 40 K, exhibiting a characteristic antiferromagnetic interaction between the neighboring Mn^{II} ions. A model containing a linear Mn_3 system was used for fitting the experimental magnetic data by invoking an exchange pathway through the carboxylate bridges, in which the magnetic exchange constant (J) between Mn2 and Mn1 (or Mn3) is assumed to be equal, for simplification, and the interaction between Mn1 and Mn3 is omitted. The spin-spin coupling

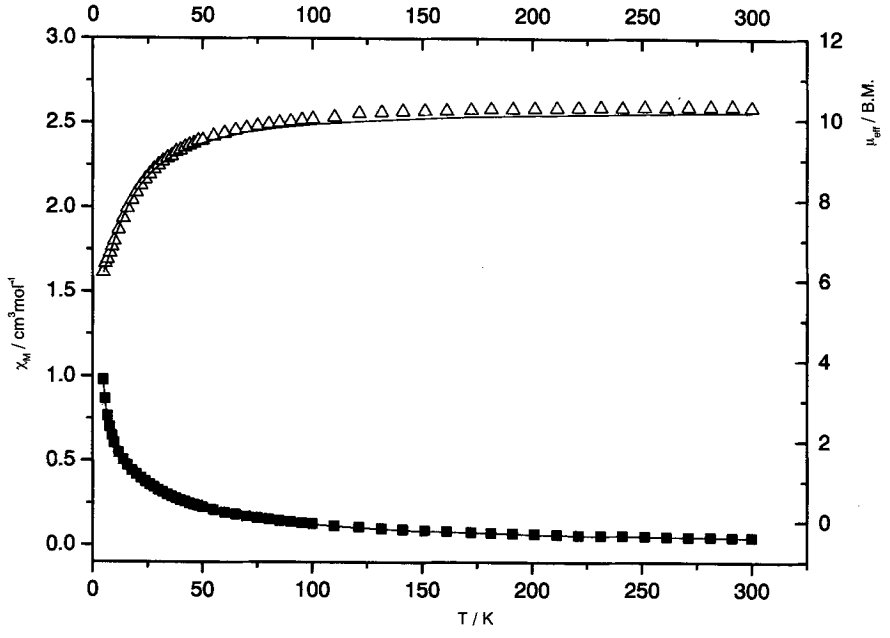


Figure 3. Experimental susceptibilities (χ_M, marked as square) and effective magnetic moment (μ_{eff}, marked as triangle) as functions of temperature for **1**; the solid lines represent the calculated values

Hamiltonian appropriate for describing the magnetic exchange interaction of the model is presented in Equation (1).

$$\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3)$$

$$\chi_M = \frac{Ng^2\beta^2}{3kT}\left[\frac{A}{B}\right]$$

$$A = 2040e^{-32x} + 1860e^{-17x} + 858e^{-4x} + 495e^{7x} + 252e^{16x} + 105e^{23x} + 1365e^{-27x} + 858e^{-14x} + 495e^{-3x} + 252e^{6x} + 105e^{13x} + 30e^{18x} + 858e^{-22x} + 492e^{-11x} + 252e^{-2x} + 105e^{5x} + 30e^{10x} + 3e^{13x} + 252e^{-8x} + 105e^{-x} + 30e^{4x} + 252e^{-12x} + 105e^{-5x} + 30 + 105e^{-7x}$$

$$B = 32e^{-32x} + 48e^{-17x} + 24e^{-4x} + 24e^{7x} + 16e^{16x} + 12e^{23x} + 28e^{-27x} + 24e^{-14x} + 20e^{-3x} + 16e^{6x} + 12e^{13x} + 8e^{18x} + 24e^{-22x} + 20e^{-11x} + 16e^{-2x} + 12e^{5x} + 8e^{10x} + 4e^{13x} + 16e^{-8x} + 12e^{-x} + 8e^{4x} + 16e^{-12x} + 12e^{-5x} + 8 + 12e^{-7x}$$

$$x = \frac{-J}{kT} \qquad (1)$$

The best fitting curves are depicted in Figure 3 for **1**. The best fitting parameters are $J = -0.81$ cm^{-1}, $g = 2.02$, and $R = [(\chi_M)_{obsd.} - (\chi_M)_{calcd.}]^2/(\chi_M)^2_{obsd.}] = 1.84 \times 10^{-4}$, showing weak antiferromagnetic exchange interactions between the metal atoms.

Conclusion

This work has described the synthesis and structure of a novel trinuclear Mn complex **1** derived from a polymeric Mn/K precursor **2**, as well as the conversion of **1** into a mononuclear species, **3**, which represents a preliminary result in the control of product nuclearity by ligand exchange or substitution. The control of product architecture is yet to be explored.

Experimental Section

General: All manipulations were performed under aerobic conditions with materials as received. Polymeric $[MnK_2(pdc)_2(H_2O)_7]_n$ was prepared from the reaction of dipicolinic acid and KOH with $Mn(OAc)_2{\cdot}4H_2O$.[8] The IR spectra were recorded on a Bio-Rad FTS-40 Model spectrophotometer. The variable-temperature susceptibilities were measured on a Model CF-1 superconducting extraction sample magnetometer with a crystalline sample kept in a capsule between 5 and 300 K. Diamagnetic corrections were made with Pascal's constants. Elemental analyses were performed by a Vario EL Elemental Analyzer.

$[Mn_3(pdc)_3(bpy)_3(H_2O)_2]{\cdot}9H_2O$ ($1{\cdot}9H_2O$): 2,2′-Bipyridine (0.32 g, 2 mmol) in 10 mL of EtOH was added to a solution of $[MnK_2(pdc)_2(H_2O)_7]_n$ (1.18 g, 2 mmol) in 5 mL of H_2O with continuous stirring. The mixture was refluxed for six days, producing large plate-like crystals of $1{\cdot}9H_2O$. Yield: 0.39 g (44%). $C_{51}H_{55}Mn_3N_9O_{23}$ (1326.86): calcd. C 46.17, H 4.18, N 9.50, Mn 12.42; found C 46.11, H 4.15, N 9.54, Mn 12.47. IR (KBr pellet): $\tilde{\nu}$ = 3396 (br. s), 1645 (m), 1616 (s), 1603 (s), 1579 (s), 1566 (s), 1493 (w), 1475 (m), 1439 (s), 1375 (s), 1363 (s), 1317 (w), 1277 (m), 1246 (w), 1186 (m), 1161 (w), 1119 (w), 1076 (m), 1063 (w), 1043 (w), 1016 (s), 962 (w), 916 (m), 862 (w), 837 (w), 773 (s), 762 (s), 737 (m), 698 (m), 661 (m), 625 (w), 530 (w), 432 (m), 413 cm^{-1} (w).

$[Mn(pdc)(bpy)(Him)_2]{\cdot}H_2O$ ($3{\cdot}H_2O$): Imidazole (0.68 g, 10 mmol) was added to a solution of $1{\cdot}9H_2O$ (1.33 g, 1 mmol) dissolved in 20 mL of H_2O/DMF (1:4, v/v). The mixture was refluxed for two hours and was then filtered. The filtrate was left in a desiccator with $CaCl_2$ for six days to produce yellow crystals of $3{\cdot}H_2O$. Yield: 0.86 g (54%). $C_{23}H_{21}MnN_7O_5$ (530.41): calcd. C 52.08, H 3.99, N 18.49, Mn 10.36; found C 52.02, H 3.97, N 18.44, Mn 10.42. IR (KBr pellet): $\tilde{\nu}$ = 3492 (s), 3379 (br. s), 3107 (m), 3045 (w), 2846 (m), 2611 (w), 1622 (s), 1587 (m), 1531 (m), 1437 (s), 1377 (s), 1327 (w), 1279 (m), 1244 (w), 1184 (m), 1159 (w), 1136 (m), 1101 (m), 1065 (s), 1011 (m), 935 (m), 904 (w), 843 (m), 804 (w), 768 (s), 725 (s), 698 (m), 661 (s), 642 (w), 623 (m), 521 (w), 415 cm^{-1} (w).

X-ray Crystallography: Data were collected at 293 K on a Siemens SMART CCD diffractometer for $1{\cdot}9H_2O$ and $3{\cdot}H_2O$ with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) using the ω-scan mode, and were corrected with the SADABS program. Structure solutions were made with the SHELXTL program.[14] The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically with three exceptions: O20, O21 and O22 of the solvate water molecules in $1{\cdot}9H_2O$ are disordered over two positions with occupancies of 0.5 each.

Crystal Data for $1{\cdot}9H_2O$: $C_{51}H_{55}Mn_3N_9O_{23}$, M_r = 1326.86, monoclinic, space group $P2_1/n$, a = 21.2089(3), b = 10.0559(2), c = 28.1400(1) Å, β = 108.017(1)°, V = 5707.26(1) Å^3, Z = 4, $D_{calcd.}$ = 1.544 g/cm^3, $F(000)$ = 2732, μ = 0.743 mm^{-1}. R = 0.0754 and Rw = 0.1683 for 5979 observed reflections with $I > 2\sigma(I)$.

Crystal Data for $3{\cdot}H_2O$: $C_{23}H_{21}MnN_7O_5$, M_r = 530.41, monoclinic, space group $P2_1/n$, a = 8.1309(1), b = 16.9103(5), c = 17.3252(5) Å, β = 102.017(2)°, V = 2329.94(1) Å^3, Z = 4, D_c = 1.512 g/cm^3, $F(000)$ = 1092, μ = 0.618 mm^{-1}. R = 0.0698 and Rw = 0.1956 for 2766 observed reflections with $I > 2\sigma(I)$.

CCDC-188829 (**$1{\cdot}9H_2O$**) and -188830 (**$3{\cdot}H_2O$**) contain the supplementary crystallographic data for $1{\cdot}9H_2O$ and $3{\cdot}H_2O$. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat. +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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