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Synthesis, Characterization, and Crystal Structure of Two Manganese Metallacrowns: 30-Metallacrown-10 and 18-Metallacrown-6 with Ligands Derived from 3-Hydroxy-2-naphthalenecarbohydrazide

Jianmin Dou,*[a] Mingli Liu,[a] Dacheng Li,[a] and Daqi Wang[a]

Keywords: Metallacrowns / Manganese / Crystal structure / Supramolecular chemistry / Crown compounds

Two manganese metallacrowns $[Mn_{10}(pnhz)_{10}(DMF)_4(H_2O)_6]\cdot 10.5H_2O\cdot MeOH\cdot DMF$ (**1**) and $[Mn_6(anhz)_6(DMF)_2(H_2O)_4]\cdot 6DMF$ (**2**), (H_3pnhz = 3-hydroxy-*N*-phenyl-2-naphthalenecarbohydrazide, H_3anhz = *N*-acyl-3-hydroxy-2-naphthalenecarbohydrazide) have been prepared by the reactions of two pentadentate ligands, H_3anhz and H_3pnhz, with the corresponding manganese(II) salt, respectively, and characterized by elemental analysis, IR spectra, and X-ray single-crystal diffraction analysis. Complex **1** has an $[Mn–N–N]_{10}$ skeleton with two kinds of Mn^{III} centers in an ···AABAB··· alignment, and the metallic centers exhibit a ···ΔΛΔΛ··· chiral configuration alignment. Adjacent molecules are linked by four intermolecular H bonds to form a 1D infinite chain structure. This is the first 1D supramolecular sample of a metallacrown formed by weak interactions. Complex **2** shows an $[Mn–N–N]_6$ skeleton with two kinds of Mn^{III} centers in a ···BAA··· alignment. The successive manganese centers possess a ···ΔΛΔΛ··· chiral configuration alignment.

Introduction

Since the first metallacrown (MC) [9-MC-3] was synthesized and confirmed by Pecoraro and coworkers[1] in 1989, this kind of metallic macrocyclic complex has received considerable attention in supramolecular chemistry, self-assembly, host–guest chemistry, and molecular recognition. Interest in the metallacrowns stems not only from their high symmetry and aesthetic molecular frameworks, but also from their magnetic properties and selective recognitions to cations and anions, along with the potential applications in chemically modified electrodes and liquid-crystal precursors.[2–10] At present, the groups of metallacrowns mainly include: (1) metallacrowns with a $[M–N–O]_n$ repeating linkage. This type of metallacrown can be synthesized by multidentate ligands such as hydroxamic,[11] ketonoxime,[11a,12] and aminohydroxamic acids[13] and their cyclic size has been enlarged from 9-MC-3 to 24-MC-8,[1,14–18] including several inverse metallacrowns.[2,19–21] (2) Metallacrowns with the $[M–N–N]_n$ repeating linkage, for example, azametallacrown, which can be synthesized by multidentate ligands such as *N*-substituted salicylhydrazide, salicylhydrazone, or 2-pyridinecarbaldehyde hydrazone. Their cyclic size has been developed from 18-MC-6 to 36-MC-12.[22–24] During the studies of the design of azametallacrowns, *N*-acyl-substituted salicylhydrazide ligands have often been used. In the last two years, the factors that control the ring size and nuclearity of azametallacrowns[25–26] have been investigated; the result shows that the nature of the *N*-acyl substituent group can influence the size and nuclearity of the macrocycle complex. Two- and three-dimensional networks can be constructed[27] if an *exo*-bidentate ligand is employed in the synthesis of azametallacrowns. To the best of our knowledge, only one azametallacrown prepared from a hydrazide that was derived from 3-hydroxy-2-naphthoic acid has been reported.[28] In this current work, we have synthesized two kinds of ligands that contain the 3-hydroxy-2-naphthyl, the *N*-acetyl-3-hydroxy-2-naphthalenecarbohydrazide, and the 3-hydroxy-*N*-phenyl-2-naphthalenecarbohydrazide groups and two azametallacrowns $[Mn_{10}(pnhz)_{10}(DMF)_4(H_2O)_6]\cdot 10.5H_2O\cdot MeOH\cdot DMF$ (**1**) and $[Mn_6(anhz)_6(DMF)_2(H_2O)_4]\cdot 6DMF$ (**2**) with the use of these two ligands, respectively.

Results and Discussion

Complex 1

Complex **1** was obtained by the reaction of manganese acetate tetrahydrate in methanol with H_3pnhz in DMF in a 1:1 molar ratio.[29] The crystallographic data is summarized in Table 1. The structure of complex **1** is illustrated in Figure 1. X-ray structural analysis shows that complex **1** has a planar decanuclear thirty-membered ring core. In the man-

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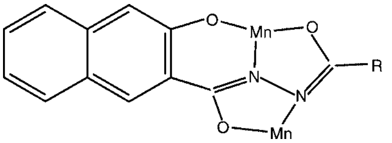
[a] Department of Chemistry, Liaocheng University,
Liaocheng 252059, P. R. China
Fax: +86-635-8239121
E-mail: jmdou@lctu.edu.cn

Table 1. Crystallographic data for the structure of complexes **1** and **2**.

Empirical formula	$C_{195}H_{178}Mn_{10}N_{25}O_{50.50}$	$C_{102}H_{118}Mn_6N_{20}O_{30}$
Formula weight	4229.03	2433.88
T [K]	298(2)	298(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	15.616(11)	12.755(16)
b [Å]	20.340(14)	15.278(19)
c [Å]	21.510(15)	17.50(2)
α [°]	99.599(12)	69.12(2)
β [°]	106.661(12)	71.75(2)
γ [°]	101.254(13)	76.55(3)
Volume [Å^3]	6237(7)	2998(6)
Z	1	1
$D_{calcd.}$ [g/cm^3]	1.126	1.348
μ(Mo-K_α) [mm^{-1}]	3.892	2.058
F(000)	15246	1260
Crystal size [mm]	0.38 × 0.31 × 0.12	0.33 × 0.30 × 0.26
θ range for data collection [°]	1.85 to 25.01	1.92 to 25.01
Limiting indices	$-17 \le h \le 18$, $-24 \le k \le 18$, $-25 \le l \le 25$	$-10 \le h \le 15$, $-18 \le k \le 17$, $-20 \le l \le 18$
Reflections collected/unique	32431/21451 [R(int) = 0.0847]	14763/10167 [R(int) = 0.1876]
Completeness to θ = 25.0 [%]	97.5	96.2
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.6523 and 0.3194	0.6167 and 0.5499
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	21451/487/1330	10167/360/770
Goodness-of-fit on F^2	0.943	0.873
R_1, wR_2 [$I > 2\sigma(I)$]	0.1066, 0.2550	0.1193, 0.2242
R_1, wR_2 (all data)	0.2614, 0.3757	0.3573, 0.3354
Largest diff. peak and hole [e·Å^{-3}]	1.012 and –0.594	0.790 and –0.541

ganese complex, a crystallographic centrosymmetric [-Mn–N–N-]$_{10}$ unit is exhibited with 5.001 Å, 4.934 Å, 4.886 Å, 4.937 Å, and 4.907 Å for the neighboring Mn···Mn distances which are consistent with 4.906(1)–4.986(2) Å for the corresponding distances in $[Mn(C_{14}H_9N_2O_3)(CH_3OH)]_{10}\cdot 5CH_2Cl_2\cdot 16CH_3OH\cdot H_2O$.[6] The average angle of the successive manganese ions is 136.91° and it is comparable to the interior angle of 144° in an n-decagon. The size or dimension and even the depth of the cavity of the 30-MC-10 in this communication exceeds those of the previous 30-MC-10 in ref.[6] The size of the cavity in the metallacrown is measured between the opposite carbon atoms: 13.206 Å for C5···C5#1, 8.987 Å for C77···C77#1, 12.335 Å for C23···C23#1, 9.830 Å for C41···C41#1, and 12.014 Å for C59···C59#1. The approximate dimensions of the oval-shaped cavity are about 7.948 Å in diameter at the entrance, approximately 16.4 Å at its largest diameter at the center of the cavity, and around 7.3703 Å in depth, which is large enough to capture some neutral molecules. So the solvent hydrate molecule (O25) is drawn in the cavity at a depth of 0.9061 Å during the self-assembly.

All manganese centers have a N_2O_4 geometry but in two different environments. The trivalent anionic nphz^{3-} acts as a pentadentate ligand chelate for two adjacent manganese atoms in a back-to-back mode by five atoms. One phenolate oxygen atom, one carbonyl oxygen atom (phenyl end), and one hydrazide nitrogen atom bind to one manganese ion; the residual carbonyl oxygen atom (naphthyl end) and the hydrazide nitrogen atom coordinate to the neighboring metal ions as illustrated in Scheme 1. Therefore, the ligands around the Mn^{III} ion are forced into a propeller configuration owing to the meridional coordination of the adjacent ligand to this metal ion. The other vertex position of each octahedral geometry is occupied by either a H_2O molecule or a DMF molecule, which forms two kinds of Mn centers and the geometric environments of them are named A and B, respectively. In each octahedral geometry around Mn^{III}, the mean axial distance of Mn–O/N is approximately 0.38 Å longer than the mean value of the basal distances. The typical Jahn–Teller elongation along the z axis of Mn^{III} ions that possess the high-spin d^4 orbit was also found in several Mn^{III} complexes.[7,26] Finally, the successive Mn^{III} centers show an environment with the ···AABAB··· alignment and with an alternating ···ΔΛΔΛ··· chiral configuration.[32]



Scheme 1.

Metallocrown 30-MC-10 forms a 1D chain structure through hydrogen bond interactions that are formed by a noncovalent force. Each coordinated O8 interacts with two DMF molecules through H bonds, and the O atoms in the DMF molecules further interact with O8#1 in an adjacent molecule also through H bonds. Therefore, the adjacent metallacrown molecules are linked together by two DMF molecules by four such H bonds to form a 1D chain struc-

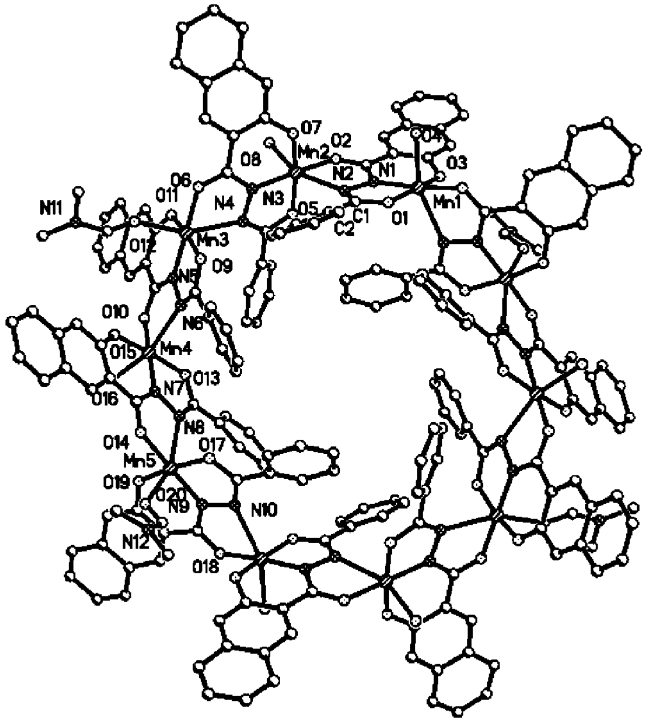


Figure 1. Molecular structure of complex **1**. All the solvent molecules have been omitted for clarity. Selected bond lengths [Å]: Mn1–O3 1.819(8) Mn1–O1 1.888(7), Mn1–N1 1.947(8), Mn1–O18#1 1.975(6), Mn1–O4 2.174(9), Mn1–N10#1 2.338(9), Mn2–O7 1.854(7), Mn2–O5 1.887(7), Mn2–O2 1.922(7), Mn2–N3 1.922(8), Mn2–O8 2.242(8), Mn2–N2 2.400(8), Mn3–O11 1.830(7), Mn3–O9 1.902(7), Mn3–N5 1.935(8), Mn3–O6 1.988(7), Mn3–O12 2.233(10), Mn3–N4 2.327(9), Mn4–O15 1.808(8), Mn4–O13 1.888(7), Mn4–N7 1.917(8), Mn4–O10 1.960(7), Mn4–O16 2.250(9), Mn4–N6 2.300(9), Mn5–O19 1.846(8), Mn5–O17 1.886(8), Mn5–N9 1.915(9), Mn5–O14 1.934(7), Mn5–O20 2.241(10), Mn5–N8 2.377(8). Selected bond angles [°]: O4–Mn1–N10#1 155.4(3), N1–Mn1–O18#1 170.6(3), O3–Mn1–O1 169.1(3), O7–Mn2–O5 170.5(3), O2–Mn2–N3 170.5(3), O8–Mn2–N2 155.1(3), O12–Mn3–N4 154.8(4), N5–Mn3–O6 173.5(3), O11–Mn3–O9 170.7(3), N7–Mn4–O10 172.0(3), O16–Mn4–N6 155.9(3), O15–Mn4–O13 171.5(3), O19–Mn5–O17 170.8(3), O20–Mn5–N8 156.1(3), N9–Mn5–O14 171.6(3).

ture as illustrated in Figure 2. The H bond lengths are 2.785(18) Å and 3.026(18) Å for O8···O21#2 and O8···O21#3, respectively. Among all of the azametallacrowns reported, no supramolecule has been formed by H bonds.

Complex 2

The reaction of manganese 2,4-pentanedionate in methanol with H_3anhz in DMF gives rise to the single-crystal of complex **2**; its crystallographic data is listed in Table 1. The X-ray structural analysis shown in Figure 3 reveals that complex **2** is a hexanuclear manganese azametallacrown with a $[Mn–N–N]_6$ unit. Different from previous analogues which either possess pseudo C_{3i}[23] or crystallographic C_{3i} symmetry,[22] this 18-MC-6 is a crystallographic C_{2i} symmetric molecule.

The two kinds of Mn^{III} centers both reside in the octahedral geometries of the complex that is composed of N_2O_4: five atoms from two dianionic anhz^{3-} and one O atom occupy one axial site from either H_2O (A-environment for the Mn^{III} center) or DMF (B-environment for the Mn^{III} center). The mean axial distances [mean value 2.183 Å for Mn(A)–O and 2.221 Å for Mn(A)–N; 2.177(10) Å for Mn(B)–O and 2.247(12) Å for Mn(B)–N] are all about 0.30 Å longer than the average basal bond lengths for each Mn^{III} center, which indicates that the elongation of the octahedrons takes place in the axial direction due to the Jahn–Teller distortion of the high-spin d^4 Mn^{III} ion. The pentadentate ligands anhz^{3-} not only bridge the adjacent manganese ions by -N–N-, but also forces the stereochemistry of the metal ions into a propeller configuration because of the meridional coordination of the neighboring ligands. As a result, the complex exhibits a combination of the ···BAA··· environment with the ···ΔΛΔΛ··· chiral configuration. The Mn···Mn distances fall in the range of 4.843–4.856 Å and Mn···Mn···Mn angles of 113.4–115.81°. Metallacrown **2** measures about 1.95 nm in diameter and 1.3 nm in thick-

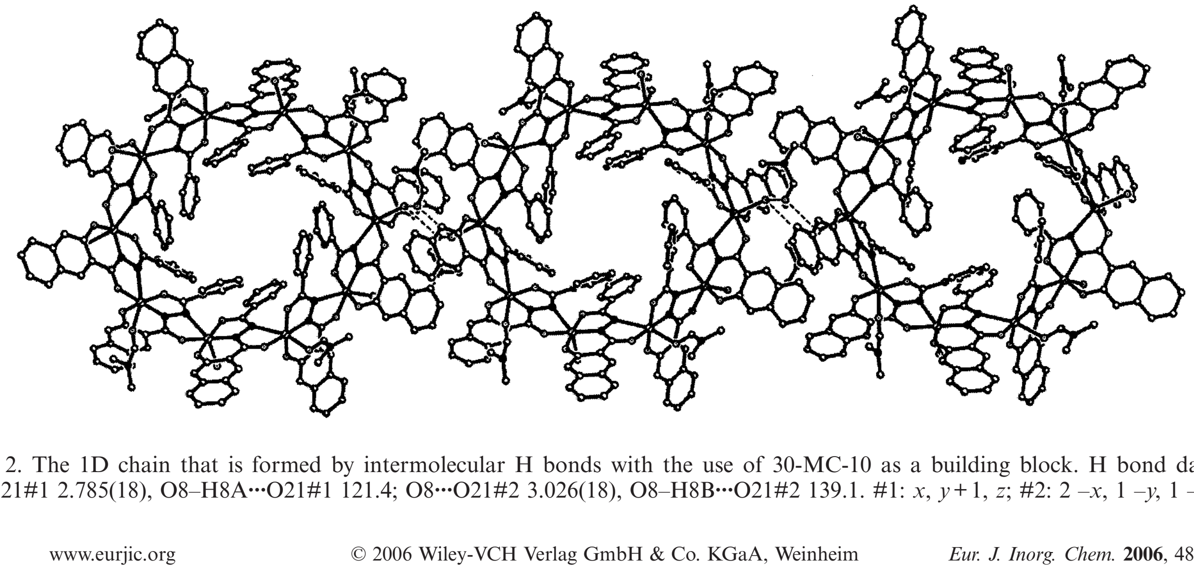


Figure 2. The 1D chain that is formed by intermolecular H bonds with the use of 30-MC-10 as a building block. H bond data [Å]: O8···O21#1 2.785(18), O8–H8A···O21#1 121.4; O8···O21#2 3.026(18), O8–H8B···O21#2 139.1. #1: *x*, *y* + 1, *z*; #2: 2 –*x*, 1 –*y*, 1 –*z*.

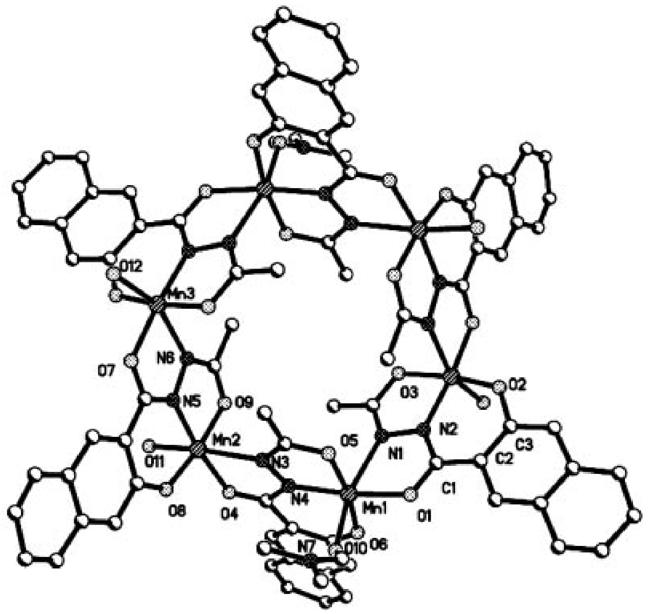


Figure 3. The molecular structure of complex **2**; all of the noncoordinated solvent molecules are removed for clarity. Selected bond lengths [Å]: Mn1–O6 1.818(10), Mn1–O5 1.919(11), Mn1–N4 1.934(12), Mn1–O1 1.953(10), Mn1–O10 2.177(10), Mn1–N1 2.247(12), Mn2–O8 1.838(11), Mn2–O9 1.887(10), Mn2–N5 1.933(12), Mn2–O4 1.941(10), Mn2–O11 2.157(12), Mn2–N3 2.249(14), Mn3–O2#1 1.821(11), Mn3–O3#1 1.910(10), Mn3–N2#1 1.91 6(11), Mn3–O7 1.960(9), Mn3–N6 2.194(13), Mn3–O12 2.209(12). Selected bond angles [°]: O6–Mn1–O5 170.3(5), N4–Mn1–O1 173.0(5), O10–Mn1–N1 160.0(5), N5–Mn2–O4 172.1(5), O11–Mn2–N3 164.0(5), O8–Mn2–O9 171.0(4), N6–Mn3–O12 155.1(5), N2#1–Mn3–O7 172.3(5), O2#1–Mn3–O3#1 170.6(5).

ness. Complex **2** possesses an empty cavity in the center of the metallacrown. Although the geometry and the chirality of the metallic center is similar to some reported 18-MC-6.[22] However, complex **2** possesses a larger cavity due to the heavier head of the 3-hydroxy-2-naphthyl groups and the paddle configuration. The size of the cavity, measured between the opposite carbon atoms, is 6.982 Å (C13···C13#1), 6.399 Å (C26···C26#1), and 6.370 Å (C39···C39#1). For the oval-shaped cavity, the minimum diameter is approximately 4.66 Å at the entrance and the maximum diameter is about 9.612 Å at the center of the cavity.

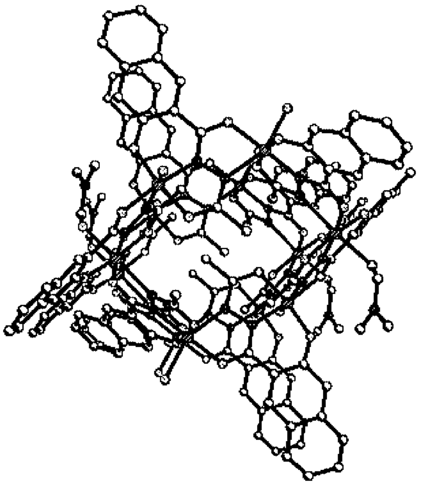


Figure 4. Crystal packing structure of complex **2**.

The crystal packing structure of complex **2** shows that the hexanuclear cluster is aligned approximately along the crystallographic *c* axis. The cavities of the clusters in the crystal structure are also aligned and one-dimensional channels are formed which is shown in Figure 4.

Magnetism Properties

Temperature-dependent magnetic susceptibility measurements on polycrystalline samples of the title complex indicate that the complex exhibits significant antiferromagnetic coupling between manganese centers. At 300 K, the molar effective magnetic moment (μ_{eff}) is equal to 4.26 μ_B, which is slightly smaller than the expected value for one isolated high-spin $\mathrm{Mn^{III}}$ center with $S = 2$ ($\mu_{\mathrm{eff}} = 4.90\ \mu_B$). If the sample is cooled, the value decreases gradually until the temperature is about 50 K, and then the value of μ_{eff} falls rapidly. The antiferromagnetic coupling is further confirmed by a negative Weiss constant –14.85 K, which is calculated with the use of the data within $T > 50$ K and with the use of the Curie–Weiss law $\chi_m^{-1}(T) = C/(T-\theta)$. Only the coupling of the neighboring (J_1) and near-neighboring centers (J_2) are considered and interactions between the paramagnetic centers in other positions are omitted because of the long distances (Figure 5).

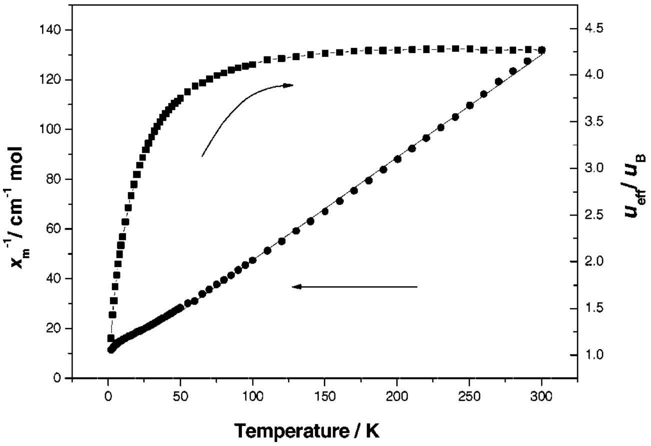


Figure 5. Plots of the effective magnetic moment (μ_{eff}) and the inverse susceptibility χ_m^{-1} versus temperature for complex **1**. The square and round points represent μ_{eff} and χ_m^{-1} data and the line through the round points represents the fitting curve according to the Curie–Weiss law.

Conclusions

Two azametallacrowns, 18-MC-6 and 30-MC-10, that contain the naphthalene group have been synthesized by introducing H_3anhz and H_3anhz as the supporting ligands.

Both crown compounds are found to possess larger cavities than those found in the corresponding metallacrowns reported previously, which indicates the higher probability that complex **1** can be used as a host to accept some ions or neutral molecules. This probability is realized by 30-MC-10 in which one cavity was able to capture a hydrate molecule. Because of the existence of free DMF in the system, a 1D chain of 30-MC-10 was assembled successfully, which is the first example of an azametallacrown supramolecule that is formed by noncovalent force.

Experimental Section

Materials and General Methods: The ligands H_3pnhz and H_3anhz were prepared as described in ref.[29] All other chemicals were commercially purchased and used without further purification. Elemental analyses (C, H, and N) were performed with a Perkin–Elmer 2400II analyzer. FTIR spectra of the complex were measured with a Nicolet-460 FTIR spectrometer in the range of 4000–400 cm^{-1}.

Synthesis of Complex 1: A solution of H_3pnhz (0.15 mmol, 0.046 g) in DMF (20 mL) was added to a solution of manganese acetate tetrahydrate (0.15 mmol, 0.030 g) in methanol (20 mL) at room temperature. The reaction mixture was then stirred for 3 h. The resultant dark red solution was left open to air to generate a dark red block crystal after about twenty days. Yield 0.12 g, 18.9%. M.p. $>$300 °C (dec.). $C_{195}H_{178}Mn_{10}N_{25}O_{50.50}$ (4229.03): calcd. C 55.60, H 4.18; found C 55.81, H 4.20. FTIR (KBr): 2929(w), 1654(vs), 1626(s), 1592(s), 1515(s), 1454(m), 1360(m), 1341(w), 1262(w), 1145(w), 1103(w), 918(w), 874(m), 801(m), 705(m) cm^{-1}.

Synthesis of Complex 2: A solution of H_3anhz (0.25 mmol, 0.062 g) in DMF (15 mL) was added to a solution of diacetylacetone manganese (0.25 mmol, 0.064 g) in a mixture of MeOH/$CHCl_3$ (1:1; 20 mL), and the reaction mixture was then stirred for two hours. The red–brown clear solution obtained after filtration was left open to air to afford a kind of dark red column crystal after one day. Yield 0.08 g. M.p. $>$300 °C (dec.) $C_{102}H_{118}Mn_6N_{20}O_{30}$ (2433.88): calcd. C 50.29, H 4.85; found C 50.11, H 5.07. FTIR (KBr): 2924(w), 1652(vs), 1627(vs), 1594(s), 1518(vs), 1454(m), 1381(vs), 1337(s), 1264(m), 1229(m), 800(m), 751(m), 659(m) cm^{-1}.

X-ray Crystallography: Data was collected with a Bruker SMART 1000 CCD diffractometer with the use of Mo-K_α radiation. Empirical absorption corrections were applied following the procedure of Sadabs.[30] The structures were solved by direct method and expanded with the use of difference Fourier techniques with the SHELXL-97 program[31] and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 with the use of the SHELXTL program package. Hydrogen atoms were placed geometrically and with U_{iso} constrained to be 1.2 (1.5 for methyl groups and hydroxy) times U_{eq} of the carrier atom. CCDC-279967 and -282855 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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