Preparation and Magnetic Properties of a Neutral Octadecanuclear Manganese Complex $[Mn^{II}_4Mn^{III}_{14}(O)_{14}(O_2CMe)_{18}(hmp)_4(hmpH)_2(H_2O)_2]$

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Received January 15, 2004

Key Words : Manganese complex, Metal cluster, Magnetic properties

The synthesis of a magnetic molecule having unusually large spin value and large negative anisotropy value is an area of intensive current research, because it is the prerequisite for developing the emerging class of single-molecule magnets (SMMs). SMMs, nanometer-size single-domain magnetic clusters, have been found to display intramolecular magnetic hysteresis loop due to very slow magnetic relaxation below their blocking temperature as well as steps in the hysteresis loop assigned to the presence of quantum tunneling of the magnetization.[1] Since the dodecanulear manganese cluster with the composition $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ (Mn12ac) had been discovered as an single-molecule magnet,[2,3] many efforts have been made to achieve larger cluster compounds showing SMM behaviors.[4] Especially, manganese carboxylate cluster chemistry has proved to be a rich source of a variety of polynuclear species.[5,6] Specific examples of SMMs except Mn12ac include the tetranuclear cubane $[Mn^{IV}Mn^{III}_3O_3X]^{6+}$ core[7] and $[Fe_4(sae)_4(MeOH)_4]$ (sae = 2-salicylidene-amino-1-ethanol),[8] the octanuclear Fe(III) cluster $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$ (tacn = tetraazacyclononane),[9] and the tetranuclear butterfly complex $[V_4O_2(O_2CR)_7(L)_2]n+$ (L=bipyridine or picolinate).[10] Recently, a new family of manganese-based SMMs, such as $[Mn_7(OH)_3Cl_3(hmp)_9]^{2+}$ and $[Mn_{12}O_8X_4(O_2CPh)_8L_8]$, has been designed by using of hmp-bridging ligand (hmpH = 2-hydroxymethylpyridine).[11,12] On the other hand, oxidation of Mn(II) by MnO_4^- in CH_2Cl_2 leads to $Mn^{II}_2Mn^{III}_2$ chain complex instead of Mn12 cluster.[13] Thus we have been trying new oxidation reaction of Mn(II) by MnO_4^- in a presence of hmpH and obtained a new octadecanuclear mixed-valent Mn cluster of formula $[Mn_{18}O_{14}(O_2CMe)_{18}(hmp)_4(hmpH)_2(H_2O)_2]$ (**1**).

The synthesis of **1** was achieved by reaction of an aqueous slurry of one equivalent of $Mn(O_2CCH_3)_2{\cdot}4H_2O$ in methylene chloride, 2.5 equivalents of hmpH, 0.5 equivalents of $NBu^n_4MnO_4$ in a presence of carboxylic acid. $NBu^n_4MnO_4$ oxidizes Mn^{II} to Mn^{III} in presence of water and carboxylic acid.

An ORTEP diagram of **1** with atom labeling scheme is displayed in Figure 1. The centrosymmetric complex **1** consists of $[Mn_{18}(\mu_3\text{-}O)_{10}(\mu_4\text{-}O)_4]$ core with peripheral chelation provided by eighteen acetate ligands and six hmp^- ligands, and two terminal water molecules. On the basis of Jahn-Teller distortions and bond valence sum calculations, the seven manganese atoms (Mn1-Mn7) in a crystallographically asymmetric unit were assigned to Mn^{III} and Mn8 and Mn9 to Mn^{II}. The elongated axial Mn^{III}-O distances (2.144(4)-2.456(4) Å) are significantly longer than the other bonds (1.854(3)-1.977(4) Å). The Mn^{II}-O bond distances are in a range from 2.104(4) Å to 2.267(3) Å. As shown in the side view, ten manganese atoms from Mn1 to Mn5 and their

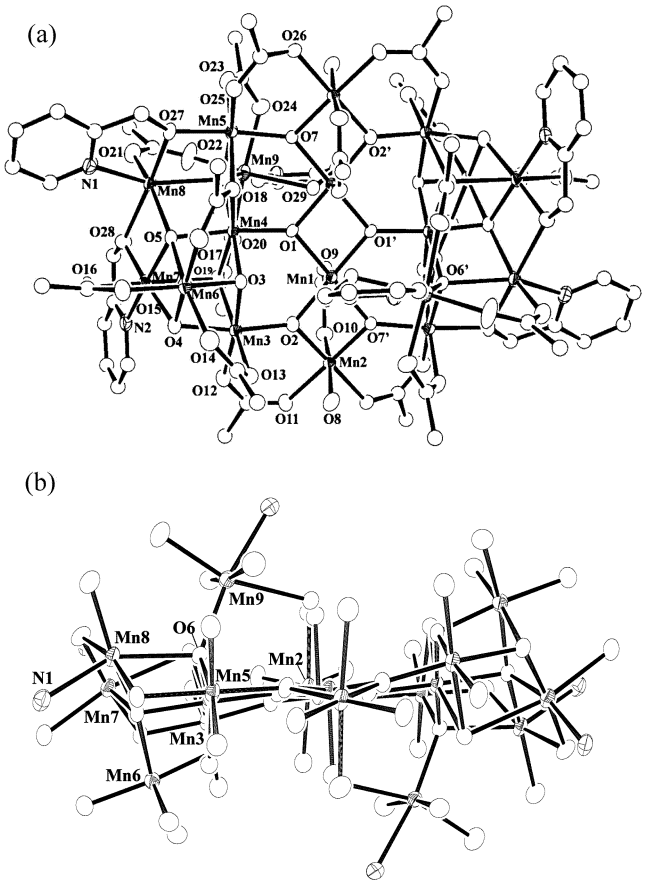

Figure 1. (a) ORTEP diagram of **1** with atom numbering scheme. (b) A side view emphasizing the planarity of $[Mn_{10}O_6]$ unit.

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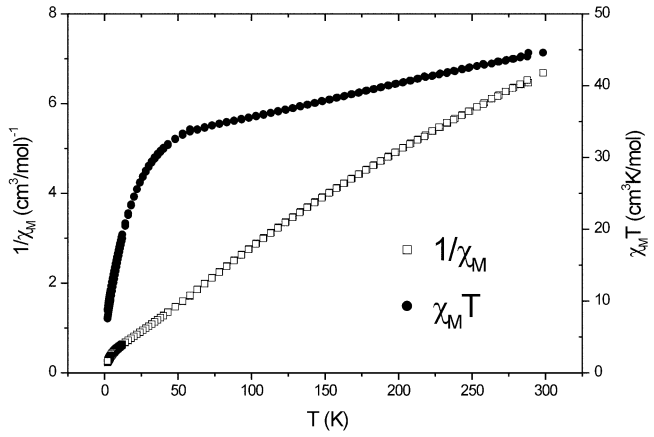

Figure 2. Temperature dependence of the $\chi_M T$ (●) and $1/\chi_M$ (□) for **1** at 1000 Oe.

symmetry related partners are almost co-planar and comprise a central planar $[Mn_{10}(m_3\text{-}O)_6]$ unit. This planar $[Mn_{10}(m_3\text{-}O)_6]$ unit was also observed in the other Mn_{18} cluster $[Mn_{18}O_{16}(O_2CPh)_{22}(phthalate)_2(H_2O)_4]^{4-}$.[14] Two Mn^{III} ions (Mn6, Mn7) are located above and below the $[Mn_{10}(m_3\text{-}O)_6]$ plane and bridged by oxygen atoms to form a distorted cubane $[Mn_4(O_{oxide})_3(O_{carboxylate})]$ unit (Mn3, Mn4, Mn6, Mn7). The distance (3.610(1) Å) between two Mn^{II} ions is quite longer than the other Mn-Mn distances (2.810(1)-3.211(1) Å). The octahedral geometry around Mn(8) is severely distorted such that the trans N1-Mn-O6 angle becomes 142.3(1)°. Charge considerations require protonation of two of oxygen donating ligands. Careful examination of structural parameters reveals that O29 is protonated and quite close to O9 (2.622 Å) due to hydrogen bonds.

Magnetic susceptibility experiments were carried out on a powder sample **1** dried under air. TGA experiment indicates *ca.* three CH_2Cl_2 molecules exist even in a air-dried sample. The magnetic susceptibility data as a function of temperature, measured with an applied filed of 1 KG by using a SQUID magnetometer are displayed in Figure 2. $\chi_M T$ decreases almost linearly from 44.6 emuK/mol at 298 K to 33.6 emuK/mol at 58 K. It is clear that there are strong intramolecular antiferromagnetic exchange interactions within complex **1** since $\chi_M T$ = 59.5 emuK/mol is expected for an aggregate of noninteracting four S = 5/2 and fourteen S = 2. Below ~50 K, $\chi_M T$ drops faster down to 2.0 K (7.6 emuK/mol) indicating the existence of antiferromagnetic intermolecular interactions and/or zero-field splitting effects.[15] Magnetization data were collected in the ranges 40-50 kG and 2.0-10.0 K and the reduce magnetization M/N_B is plotted as a function of H/T in Figure 3. The split of isofield lines shows that the zero-field splitting exists in the complex **1**.

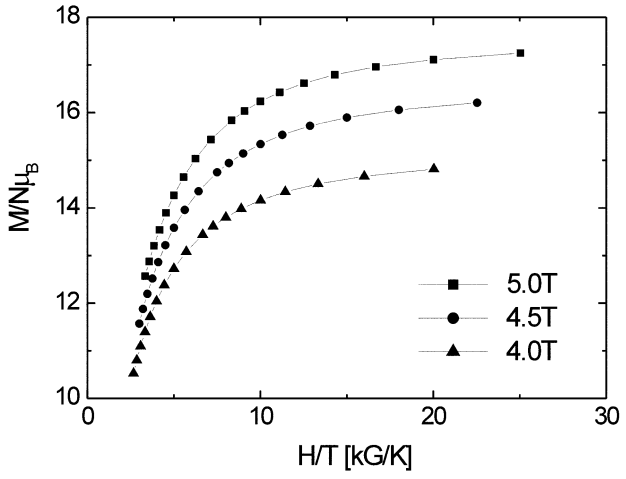

Figure 3. Plot of $M/N\mu_B$ *vs* H/T for **1**.

Also carried out were ac susceptibility measurements for the powder sample **1** in a 5.0 G ac field oscillating at 250-1000 Hz in the temperature range of 2.0-10 K. Preliminary results showed no out-of-phase (χ_M'') signals within the temperature range. However, G. Christou and his co-workers reported a new $[Mn_{18}]^{2+}$ single-molecule magnet which has the same structure with our Mn_{18} complex but two Mn^{II} ions are further oxidized to Mn^{III} compared to our Mn_{18} compound.[16] The $[Mn_{18}]^{2+}$ complex shows characteristics of single-molecule magnet such as temperature dependency of ac susceptibility in the 0.99-1.44 K region and magnetic hysteresis loop in the 0.04-1.0 K. The total ground spin value was estimated as S = 13 which is unusually large spin for a molecular species. Furthermore, such SMM behaviors were observed in the smaller Mn_{12} cage which is also mixed-valent and consists of oxide and hmp^- bridging ligand.[12] Based on these recent results, we expect our Mn_{18} cluster may exhibit single-molecule magnetic behavior below 2.0 K.

Experimental Section

General. Tetrabutylammonium permanganate was prepared by the previously reported methods.[17,18] All other reagents were purchased from Aldrich Chemical Co. and Sigma Chemical Co. and were used as received.

Elemental analyses (C, H and N) were performed by Fisons EA 1110 analyzer. IR spectra were recorded as compressed KBr discs on a Perkin Elmer Model 983 spectrophotometer in 4000-400 cm^{-1} range. Dc and ac Magnetic susceptibility measurements were carried out using a Quantum design MPMS*XL* susceptometer well equipped with a 5 T magnet and operating in the range 2.0 to 300 K.

Synthesis. To an aqueous slurry of $Mn(acetate)_2{\cdot}4H_2O$ (0.34 g, 1.63 mmol) in 1 mL water, a solution of hmpH (0.4 mL, 4 mmol) in 20 mL of CH_2Cl_2 was added and followed by addition of 2 mL of acetic acid. The colorless reaction mixture was continuously stirred and treated with $NBu^n_4MnO_4$ (0.29 g, 0.815 mmol) portionwise within an interval of 10 min. The color of solution changes to dark brown. After 1 h, the solvent was removed *in vacuo* and the oily residue was dissolved in CH_2Cl_2. Addition of equivolume of hexane and slow evaporation at room temperature for two weeks yielded crystals of **1** suitable for X-ray crystallography. Elemental analyses have been done with samples dried overnight in *vacuo*. Compound **1**: FTIR (KBr,

Table 1. Crystallographic data for complex **1**

Empirical formula	$C_{78}H_{108}Cl_{12}Mn_{18}N_6O_{58}$
Molecular weight	3472.02
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	14.411(1)
b (Å)	15.177(1)
c (Å)	15.729(1)
α (°)	70.328(2)
β (°)	78.407(2)
γ (°)	81.046(2)
V (Å^3)	3159.0(5)
Z	1
ρ_{calc} (mg m ^{3})	1.825
F(000)	1736
μ (mm^{-1})	2.072
Temperature (K)	173(2)
$2\theta_{max}$ (°)	56.64
Transmission factor	0.4911-0.8196
Reflections collected	17933
Independent reflections	13817 [R_{int} = 0.0424]
Observed reflections [$I > 2\sigma(I)$]	8549
No. of parameters	815
R_1, wR_2, GOF	0.0585, 0.1349, 1.006

Table 2. Selected Bond Distances (Å) and Angles (°) for **1**

distances

Mn1	-	O1	1.948(3)	Mn1	-	O2	1.910(4)				
Mn1	-	O1	1.920(3)	Mn1	-	O1'	1.889(4)				
Mn1	-	O2	1.919(4)	Mn1	-	O7'	1.934(3)				
Mn1	-	O9	2.222(4)	Mn1	-	O29'	2.455(4)				
Mn2	-	O2	1.858(4)	Mn2	-	O7'	1.865(4)				
Mn2	-	O8	2.328(4)	Mn2	-	O10	2.244(4)				
Mn2	-	O11	1.977(4)	Mn2	-	O26'	1.959(4)				
Mn3	-	O2	1.886(4)	Mn3	-	O3	1.876(4)				
Mn3	-	O4	1.932(4)	Mn3	-	O12	1.958(4)				
Mn3	-	O13	2.187(4)	Mn3	-	O19	2.371(4)				
Mn4	-	O1	1.876(3)	Mn4	-	O3	1.920(4)				
Mn4	-	O5	1.947(3)	Mn4	-	O6	1.910(4)				
Mn4	-	O18	2.237(4)	Mn4	-	O19	2.291(4)				
Mn5	-	O6	1.903(3)	Mn5	-	O7	1.891(3)				
Mn5	-	O18	2.422(4)	Mn5	-	O23	2.144(4)				
Mn5	-	O25	1.959(4)	Mn5	-	O27	1.908(4)				
Mn6	-	O3	1.880(4)	Mn6	-	O4	1.942(4)				
Mn6	-	O5	2.226(4)	Mn6	-	O14	2.180(4)				
Mn6	-	O15	1.966(4)	Mn6	-	O17	1.964(4)				
Mn7	-	O4	1.915(4)	Mn7	-	O5	1.854(3)				
Mn7	-	O16	2.174(4)	Mn7	-	O19	2.456(4)				
Mn7	-	O28	1.889(4)	Mn7	-	N2	2.043(5)				
Mn8	-	O5	2.197(4)	Mn8	-	O6	2.267(3)				
Mn8	-	O21	2.104(4)	Mn8	-	O27	2.136(4)				
Mn8	-	O28	2.216(4)	Mn8	-	N1	2.244(5)				
Mn9	-	O6	2.109(4)	Mn9	-	O20	2.207(4)				
Mn9	-	O22	2.128(4)	Mn9	-	O24	2.190(4)				
Mn9	-	O29	2.332(4)	Mn9	-	N3	2.286(5)				
Mn1	⋯	Mn1'	2.893(2)	Mn1	⋯	Mn2	2.810(1)				
Mn3	⋯	Mn4	3.082(1)	Mn3	⋯	Mn6	2.818(1)				
Mn3	⋯	Mn7	3.210(1)	Mn4	⋯	Mn5	3.059(1)				
Mn4	⋯	Mn6	2.940(1)	Mn4	⋯	Mn7	3.211(1)				
Mn4	⋯	Mn8	3.119(1)	Mn5	⋯	Mn8	3.203(1)				
Mn6	⋯	Mn7	2.840(1)	Mn7	⋯	Mn8	3.116(1)				

Table 2. continued

angles

O1	-	Mn1	-	O1'	81.15(15)	O1	-	Mn1	-	O2	99.36(15)
O1	-	Mn1	-	O7'	179.30(15)	O1	-	Mn1	-	O9	89.07(14)
O1	-	Mn1	-	O29'	90.75(13)	O1	-	Mn1	-	O7'	99.08(15)
O1	-	Mn1	-	O9	91.99(15)	O1	-	Mn1	-	O29'	77.56(14)
O2	-	Mn1	-	O1'	176.62(16)	O2	-	Mn1	-	O7'	80.45(15)
O2	-	Mn1	-	O9	91.36(15)	O2	-	Mn1	-	O29'	99.08(14)
O7	-	Mn1	-	O9	90.26(14)	O7	-	Mn1	-	O29'	89.95(13)
O9	-	Mn1	-	O29'	169.44(14)	O2	-	Mn2	-	O7'	83.89(15)
O2	-	Mn2	-	O8	88.49(15)	O2	-	Mn2	-	O10	94.77(15)
O2	-	Mn2	-	O11	94.72(16)	O2	-	Mn2	-	O26'	178.73(17)
O7	-	Mn2	-	O8	95.18(16)	O7	-	Mn2	-	O10	91.49(15)
O7	-	Mn2	-	O11	178.60(16)	O7	-	Mn2	-	O26'	96.94(16)
O8	-	Mn2	-	O10	172.86(15)	O8	-	Mn2	-	O11	84.75(17)
O8	-	Mn2	-	O26'	92.38(16)	O10	-	Mn2	-	O11	88.64(16)
O10	-	Mn2	-	O26'	84.26(16)	O11	-	Mn2	-	O26'	84.45(16)
O2	-	Mn3	-	O3	90.76(15)	O2	-	Mn3	-	O4	168.99(17)
O2	-	Mn3	-	O12	95.37(16)	O2	-	Mn3	-	O13	95.55(15)
O2	-	Mn3	-	O19	87.74(15)	O3	-	Mn3	-	O4	82.81(15)
O3	-	Mn3	-	O12	173.33(15)	O3	-	Mn3	-	O13	91.27(15)
O3	-	Mn3	-	O19	83.52(14)	O4	-	Mn3	-	O12	90.72(16)
O4	-	Mn3	-	O13	93.52(16)	O4	-	Mn3	-	O19	82.68(14)
O12	-	Mn3	-	O13	90.73(17)	O12	-	Mn3	-	O19	94.09(16)
O13	-	Mn3	-	O19	173.89(14)	O1	-	Mn4	-	O3	88.29(15)
O1	-	Mn4	-	O5	173.71(16)	O1	-	Mn4	-	O6	95.27(15)
O1	-	Mn4	-	O18	97.77(14)	O1	-	Mn4	-	O19	95.88(13)
O3	-	Mn4	-	O5	86.31(15)	O3	-	Mn4	-	O6	174.45(15)
O3	-	Mn4	-	O18	88.14(14)	O3	-	Mn4	-	O19	84.78(14)
O5	-	Mn4	-	O6	90.36(15)	O5	-	Mn4	-	O18	85.28(14)
O5	-	Mn4	-	O19	80.42(13)	O6	-	Mn4	-	O18	87.17(14)
O6	-	Mn4	-	O19	99.05(14)	O18	-	Mn4	-	O19	164.41(14)
O6	-	Mn5	-	O7	91.49(15)	O6	-	Mn5	-	O18	82.14(14)
O6	-	Mn5	-	O23	100.58(16)	O6	-	Mn5	-	O25	167.23(17)
O6	-	Mn5	-	O27	84.40(15)	O7	-	Mn5	-	O18	89.58(14)
O7	-	Mn5	-	O23	93.98(16)	O7	-	Mn5	-	O25	95.02(15)
O7	-	Mn5	-	O27	175.06(17)	O18	-	Mn5	-	O23	175.44(14)
O18	-	Mn5	-	O25	86.93(15)	O18	-	Mn5	-	O27	87.14(15)
O23	-	Mn5	-	O25	89.93(16)	O23	-	Mn5	-	O27	89.48(16)
O25	-	Mn5	-	O27	88.50(15)	O3	-	Mn6	-	O4	82.43(15)
O3	-	Mn6	-	O5	79.73(14)	O3	-	Mn6	-	O14	90.20(16)
O3	-	Mn6	-	O15	174.99(16)	O3	-	Mn6	-	O17	92.40(16)
O4	-	Mn6	-	O5	80.14(14)	O4	-	Mn6	-	O14	93.14(16)
O4	-	Mn6	-	O15	94.23(16)	O4	-	Mn6	-	O17	171.80(17)
O5	-	Mn6	-	O14	168.50(14)	O5	-	Mn6	-	O15	96.06(15)
O5	-	Mn6	-	O17	92.72(15)	O14	-	Mn6	-	O15	93.72(17)
O14	-	Mn6	-	O17	93.24(17)	O15	-	Mn6	-	O17	90.49(17)
O4	-	Mn7	-	O5	91.15(16)	O4	-	Mn7	-	O16	89.41(16)
O4	-	Mn7	-	O28	174.52(17)	O4	-	Mn7	-	N2	97.32(18)
O5	-	Mn7	-	O16	94.51(15)	O4	-	Mn7	-	O19	80.74(14)
O5	-	Mn7	-	O19	77.88(14)	O5	-	Mn7	-	O28	88.64(16)
O5	-	Mn7	-	N2	165.52(18)	O16	-	Mn7	-	O28	96.06(17)
O16	-	Mn7	-	O19	167.35(14)	O16	-	Mn7	-	N2	97.28(17)
O19	-	Mn7	-	O28	93.86(15)	O19	-	Mn7	-	N2	91.87(15)
O28	-	Mn7	-	N2	81.80(18)	O5	-	Mn8	-	O6	75.57(13)
O5	-	Mn8	-	O21	156.52(15)	O5	-	Mn8	-	O27	97.70(14)
O5	-	Mn8	-	O28	72.67(13)	O5	-	Mn8	-	N1	96.47(16)
O6	-	Mn8	-	O21	103.73(15)	O6	-	Mn8	-	O27	71.02(13)
O6	-	Mn8	-	O28	115.22(14)	O6	-	Mn8	-	N1	142.40(15)
O21	-	Mn8	-	O27	104.27(16)	O21	-	Mn8	-	O28	87.07(16)
O21	-	Mn8	-	N1	97.47(17)	O27	-	Mn8	-	O28	165.72(15)
O27	-	Mn8	-	N1	73.86(16)	O28	-	Mn8	-	N1	96.36(16)
O6	-	Mn9	-	O20	91.62(15)	O6	-	Mn9	-	O22	102.09(16)
O6	-	Mn9	-	O24	99.78(15)	O6	-	Mn9	-	O29	97.44(13)
O6	-	Mn9	-	N3	167.47(16)	O20	-	Mn9	-	O22	90.68(19)
O20	-	Mn9	-	O24	168.49(15)	O20	-	Mn9	-	O29	89.57(14)
O20	-	Mn9	-	N3	83.04(17)	O22	-	Mn9	-	O24	88.54(19)
O22	-	Mn9	-	O29	160.45(16)	O22	-	Mn9	-	N3	89.35(17)
O24	-	Mn9	-	N3	85.46(17)	O24	-	Mn9	-	O29	87.34(15)
O29	-	Mn9	-	N3	71.28(15)						

symmetry codes: ' –x+1, –y+1, –z

cm^{-1}): 1609 (vs), 1576 (vs), 1541 (vs), 1419 (vs) 1341 (w), 718 (m), 668 (s), 617 (s), 554 (m). Anal. Calcd for $C_{72}H_{96}Mn_{18}N_6O_{58}$: C, 29.19; H, 3.27; N, 2.83%. Found: C, 29.45; H, 3.33; N, 3.01.

Crystal Structure Determination. Reflection data were collected on an Bruker SMART CCD diffractometer using monochromated Mo Kα (λ = 0.71073 Å) radiation. The data were integrated and scaled using SAINT software package.[19] Collected data were corrected for absorbance using SADABS[14] based upon the Laue symmetry using equivalent reflections. Structure was solved by direct method and refined by least-squares calculations with the SHELXL-PLUS 5.05 software package.[20] The non-hydrogen atoms were refined anisotropically and the geometrically restrainted hydrogen atoms were treated using appropriate riding model. A summary of the crystallographic parameters and data is given in Table 1.

Acknowlegement. This work was supported by the NRL program of the Ministry of Science and Technology, Korea. One of the authors (S.Y.) acknowledges the support by KOSEF via Electron Spin Science Center at POSTECH.

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