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Synthesis, Magnetic Property, and Crystal Structure of Imidazolate-Bridged Manganese(III)-Copper(II) Dinuclear Complex

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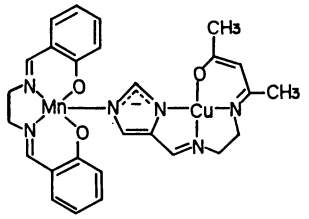
The synthesis, crystal structure, and magnetic property of an imidazolate-bridged manganese(III)-copper(II) dinuclear complex [Mn(salen)Cu(A)]BPh_4 are described, where [H_2salen]=*N*,*N*′-disalicylideneethylenediamine, [H_2A]=4-(6-methyl-8-oxo-2,5-diazanonane-1,5,7-trienyl)imidazole, and BPh_4=tetraphenylborate. The X-ray analysis confirmed an imidazolate-bridged manganese(III)-copper(II) dinuclear structure, in which the coordination geometries of the manganese(III) and copper(II) ions are square pyramid and square planar, respectively. The apical position of the manganese(III) ion is occupied by an imidazolate nitrogen N(3) of the [Cu(A)] moiety with the bond distance of Mn-N(3) 2.165(5) Å. As the temperature is lowered, the effective magnetic moment per molecule decreases gradually from 5.17 B.M. at 300.2 K, reaches the minimum value 4.44 B.M. at 24.9 K, and then increases to 4.73 B.M. at 4.2 K, indicating that antiferro- and ferro-magnetic interactions are co-operative in the complex.

The molecular design of hetero-metal polynuclear complexes has been an attractive subject to mimic some biological metal enzymes[1,2] and to develop ferromagnets and ferrimagnets.[3] Imidazolate-bridged hetero-metal dinuclear structure has been found in the active site of bovine erythrocyte superoxide dismutase (BESOD)[1] and has been one of the candidate structures of the active site of the resting form of cytochrome c oxidase.[2] In order to develop structural model compounds of BESOD, Lippard's group[4-8] and other groups[9-14] have synthesized and characterized a number of imidazolate-bridged di- and polynuclear copper(II) complexes. However, only a few examples of imidazolate-bridged hetero-metal complexes have been reported so far.[15-18] Recently we have shown an effective synthetic route to prepare imidazolate-bridged hetero-metal dinuclear complexes with various combinations of metal ions.[19-23] The complexes thus obtained may provide not only structural model compounds of the metal enzymes but also a novel family of hetero-metal complexes which makes it possible to investigate systematically magnetic interaction between magnetic centers with the different electronic configurations. This paper describes the synthesis, magnetic property, and crystal structure of an imidazolate-bridged manganese(III)-copper(II) complex [Mn(salen)Cu(A)]BPh_4, where [H_2salen]=*N*,*N*′-disalicylideneethylenediamine, [H_2A]=4-(6-methyl-8-oxo-2,5-diazanonane-1,5,7-trienyl)imidazole, and BPh_4=tetraphenylborate. The schematic structure of the complex is shown in the drawing.



Experimental

Syntheses. Component Compounds. The component compounds [Mn(salen)]BPh_4[24] and [Cu(A)]0.5$CHCl_3$[20] were prepared according to the methods reported earlier.

[Mn(salen)Cu(A)]BPh_4. To a solution of [Mn(salen)]-BPh_4 (500 mg, 1 mmol) in 50 cm^3 of methanol was added a solution of [Cu(A)]0.5$CHCl_3$ (342 mg, 1 mmol) in 50 cm^3 of methanol. The mixture was stirred for 10 min on a hot plate and then filtered. The filtrate was left to stand at room temperature overnight. Red-brown crystals precipitated were collected by suction filtration and dried in air (yield ca. 45%). Attempts for recrystallization were unsuccessful, leading to decomposition of the complex. Calcd for $C_{51}H_{48}N_6BO_3MnCu$: C, 66.42; H, 5.25; N, 9.11; Mn, 5.95; Cu, 6.89%. Found: C, 66.96; H, 5.30; N, 9.05; Mn, 6.06; Cu, 6.92%. Λ_M 83 S mol^{-1} cm^2 (acetonitrile).

Physical Measurements. Elemental analyses (C, H, and N) were performed at the Elemental Analysis Center of Kyushu University. Elemental analyses for Mn and Cu were carried out on a Nippon Jarrel Ash AA 781 atomic absorption and flame emission spectrophotometer. Electrical conductivity was measured on a Denki Kagaku Keiki AOL-10 conductivity meter in ca. 10^{-3} mol dm^{-3} acetonitrile solution. Magnetic susceptibilities were obtained at 4.2—100 K by use of a HOXAN HSM-2000 SQUID magnetometer under the magnetic field of 0.5 T and at 80—300 K by the Faraday balance designed in our laboratory. Data were corrected for magnetization of the sample holder and for the diamagnetism of the component atoms by the use of Pascal's constants. The molar effective magnetic moments were calculated by the equation $\mu_{eff}=2.828(\chi_M T)^{1/2}$.

X-Ray Crystallography. Reflection data were measured on a Rigaku Denki AFC-5 automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation at room temperature. Three standard reflections were monitored every 100 reflections and showed no systematic decrease in the intensity. The reflection data were corrected for Lorentz and polarization factors and used in the structure determination. Corrections for absorption and extinction effects were not made. Unit cell parameters were determined by 25 reflections ($20°<2\theta<30°$).

Crystal Data: [Mn(salen)Cu(A)]BPh_4, Formula=$MnCuO_3N_6C_{51}BH_{48}$, F.W.=922.2, triclinic, space group=$P\bar{1}$, crystal dimension 0.2×0.3×0.2 mm, a=14.215(3) Å, b=15.745(3) Å, c=13.944(3) Å, α=121.20(2)°, β=114.28(2)°, γ=58.49(2)°, V=2233.5(1.2) Å^3, μ(Mo$K\alpha$)=7.72 cm^{-1}, d_{calcd}=1.371 g cm^{-3} (Z=2), d_{obsd}=1.36 g cm^{-3} (by floatation method in aqueous KI solution), scan mode θ-2θ, scan speed 6 deg min^{-1}, scan range 2.5°<2θ<45°, scan width (1.2+0.35tanθ)°, octant measured +h, ±k, ±l, no. independent reflections 4698, R=7.32%, R_w=7.29%. the largest residue in the final D-Fourier synthesis 0.8 e Å^{-3}.

The structure was solved by the standard heavy-atom method and refined by the block-diagonal least-squares method, where the function minimized is $\sum w(|F_o|-|F_c|)^2$ and equal weight for all reflections was adopted. The contribution of hydrogen atoms bound to carbon were introduced in the calculated positions. These hydrogen atoms were included in the structure factor calculation but not refined. The atomic scattering factors were taken from literature.[25] All computations were performed on a FACOM M 780 computer at the Computer Center of Kyushu University using the UNICS III program system.[26] The final atomic prameters are given in Table 1. Tables of observed and calculated structure factors, listings of atomic positional and anisotropic thermal parameters, and complete lists of bond lengths and angles with their estimated standard deviations have been deposited as Document No. 8903 at the Office of the Editor of Bull. Chem. Soc. Jpn.

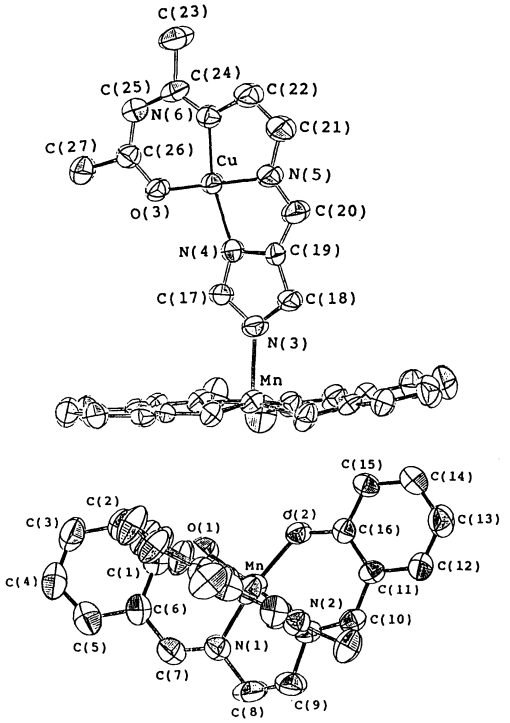


Fig. 1. Molecular structure of the cation [Mn(salen)-Cu(A)]$^+$ with the atom numbering scheme: (1) view projected on the plane of [Cu(A)] part; (2) view projected on the plane of salen ligands.

Table 1. Positional Parameters (×10^4) for [Mn(salen)Cu(A)]BPh_4

Atom	x	y	z	B_{eqv}/Å^2	Atom	x	y	z	B_{eqv}/Å^2
Mn	5995(1)	4008(1)	5644(1)	3.6	C(22)	12415(7)	−924(8)	7474(9)	5.7
O(1)	6439(5)	4354(4)	4839(4)	4.6	C(23)	12607(8)	−2086(8)	8587(9)	6.7
O(2)	5493(4)	3007(4)	4314(4)	3.5	C(24)	11489(7)	−1276(6)	8249(7)	4.6
N(1)	6114(5)	5306(5)	7030(5)	4.0	C(25)	10542(7)	−1135(7)	8525(7)	4.7
N(2)	5209(5)	4020(4)	6544(5)	3.5	C(26)	9465(6)	−393(6)	8360(6)	4.0
C(1)	7142(6)	4837(6)	5275(6)	3.8	C(27)	8557(8)	−402(8)	8644(8)	5.5
C(2)	7715(7)	4691(7)	4564(8)	5.1	B	3024(7)	3025(7)	8250(7)	3.3
C(3)	8428(8)	5189(9)	4961(9)	6.2	C(28)	2267(6)	4345(6)	8745(7)	4.1
C(4)	8600(8)	5875(9)	6098(10)	7.0	C(29)	2087(7)	4958(7)	8184(8)	5.1
C(5)	8040(8)	6040(8)	6828(8)	5.8	C(30)	1447(8)	6060(7)	8508(9)	6.1
C(6)	7322(7)	5527(6)	6446(7)	4.4	C(31)	1017(9)	6583(8)	9482(11)	7.4
C(7)	6726(7)	5774(7)	7237(7)	4.6	C(32)	1174(10)	6055(8)	10106(10)	8.0
C(8)	5409(9)	5700(8)	7823(8)	6.3	C(33)	1797(8)	4920(7)	9705(8)	5.9
C(9)	5313(8)	4789(7)	7739(7)	5.3	C(34)	2474(6)	2430(6)	6924(6)	3.6
C(10)	4683(6)	3421(6)	6193(6)	3.6	C(35)	1522(8)	2934(8)	6254(7)	5.3
C(11)	4590(6)	2607(6)	5065(6)	3.4	C(36)	1134(10)	2354(12)	5101(9)	8.6
C(12)	4048(7)	1979(7)	4848(7)	4.6	C(37)	1741(11)	1251(12)	4630(9)	9.0
C(13)	3946(8)	1165(7)	3792(8)	5.3	C(38)	2624(10)	730(9)	5240(9)	7.4
C(14)	4375(7)	974(7)	2936(7)	4.7	C(39)	2997(7)	1288(7)	6376(7)	4.9
C(15)	4882(6)	1595(6)	3119(6)	3.7	C(40)	3071(7)	2461(6)	8990(6)	3.7
C(16)	5001(6)	2432(6)	4189(6)	3.3	C(41)	2074(8)	2528(8)	9041(8)	5.3
Cu	10047(1)	355(1)	7321(1)	3.5	C(42)	2070(9)	2057(9)	9648(9)	6.9
O(3)	9136(4)	322(4)	7963(4)	4.0	C(43)	3063(9)	1491(8)	10205(8)	6.5
N(3)	7613(5)	2874(5)	6168(5)	4.1	C(44)	4044(9)	1403(7)	10149(7)	5.8
N(4)	8901(5)	1537(5)	6747(5)	3.7	C(45)	4055(7)	1881(6)	9555(7)	4.5
N(5)	11013(5)	416(5)	6719(6)	4.8	C(46)	4308(6)	2848(6)	8352(6)	3.3
N(6)	11418(5)	−746(5)	7727(6)	4.0	C(47)	4759(6)	3597(6)	9267(6)	3.5
C(17)	7826(6)	2199(6)	6625(7)	4.0	C(48)	5866(7)	3456(6)	9452(7)	4.1
C(18)	8623(6)	2620(7)	6001(8)	4.8	C(49)	6581(7)	2559(6)	8737(7)	4.1
C(19)	9415(6)	1786(6)	6347(7)	4.2	C(50)	6165(7)	1813(7)	7821(7)	4.3
C(20)	10584(7)	1160(7)	6349(8)	5.4	C(51)	5062(6)	1949(6)	7630(6)	3.9
C(21)	12184(7)	−362(8)	6791(10)	6.7					

Results and Discussion

The component complex [Cu(A)] plays a key role in producing imidazolate-bridged hetero-metal complexes, because [Cu(A)] functions like a monodentate ligand at the imidazolate nitrogen, coordinating to another metal ion to form an imidazolate-bridged complex. The mixed-metal complex was readily prepared by mixing [Mn(salen)]BPh_4 and [Cu(A)] in methanol. The elemental analysis (C, H, N, Cu, and Mn) was consistent with the formula of [Mn(salen)-Cu(A)]BPh_4. Molar electrical conductance in acetonitrile was 83 S mol^{-1} cm^2 which is consistent with 1:1 electrollyte.

Structural Description. The molecular structure of $[Mn(salen)Cu(A)]^+$ with the atom numbering scheme is shown in Fig. 1. Selected bond distances and bond angles are given in Table 2. The X-ray analysis has confirmed that the complex assumes an imidazolate-bridged manganese(III)-copper(II) dinuclear structure. The coordination geometries of the manganese(III) and copper(II) ions are square pyramid and square planar, respectively. In the square pyramid of the manganese(III) ion, the basal coordination plane is occupied by the N_2O_2 donor set of the salen ligand with the bond distances 1.869(4)—1.985(5) Å and the apical position is occupied by the imidazolate nitrogen atom N(3) of the [Cu(A)] moiety with the bond distance of Mn-N(3) 2.125(5) Å. The bond distance of Mn-N(3) 2.125(5) Å is shorter than those of Mn(III)-apical imidazole nitrogen atom of $[Mn(HIm)(salen)]ClO_4$ (2.231(4) Å) and $[Mn(biim)(salen)]ClO_4$ (2.278(5), 2.283(4) Å), where HIm=imidazole and biim=1,4-di(1-imidazolyl)butane.[24] The manganese(III) ion deviates by 0.23 Å toward the apical position from the basal coordination plane. The [Cu(A)] plane is nearly perpendicular to the [Mn(salen)] plane and intersects it approximately at the Mn-O(2) and Mn-N(1) bonds, where the dihedral angle between the mean planes of these moieties is 86.8°.

Figure 2 shows a packing view of two crystallographically unique units related by the inversion center. As often seen in the metal complexes with salen, two manganese(III) ions are bridged by two phenoxo oxygen atoms O(1) and O(1)* ($-x$, $-y$, $-z$) of the salen in the out-of-plane fashion, where the distance of Mn-O(1)* is 3.103(5) Å. The bond distance is substan-

Table 2. Bond Distance (Å) and Angles (deg) for $[Mn(salen)Cu(A)]BPh_4$

Bond distances (Å)				N(1)-Mn-N(3)	95.5(2)	N(2)-Mn-N(3)	94.2(3)
				Mn-O(1)-C(1)	126.2(5)	O(1)-C(1)-C(2)	119.4(6)
(a) Manganese site				O(1)-C(1)-C(6)	122.7(10)	C(2)-C(1)-C(6)	117.7(9)
Mn-Mn*	3.658(2)	Mn-O(1)	1.878(9)	C(1)-C(2)-C(3)	121.9(8)	C(2)-C(3)-C(4)	120.9(14)
Mn-O(1)	3.103(5)	Mn-O(2)	1.869(4)	C(3)-C(4)-C(5)	118.6(13)	C(4)-C(5)-C(6)	121.5(8)
Mn-N(1)	1.985(5)	Mn-N(2)	1.982(9)	C(5)-C(6)-C(1)	119.2(11)	C(5)-C(6)-C(7)	118.6(7)
Mn-N(3)	2.165(5)	O(1)-C(1)	1.327(13)	C(1)-C(6)-C(7)	121.9(10)	C(6)-C(7)-N(1)	125.1(7)
C(1)-C(2)	1.388(18)	C(2)-C(3)	1.367(19)	Mn-N(1)-C(7)	124.9(6)	Mn-N(1)-C(8)	113.0(7)
C(3)-C(4)	1.386(13)	C(4)-C(5)	1.382(22)	C(7)-N(1)-C(8)	121.9(7)	N(1)-C(8)-C(9)	109.1(7)
C(5)-C(6)	1.395(17)	C(6)-C(7)	1.437(17)	C(8)-C(9)-N(2)	110.1(9)	Mn-N(2)-C(9)	112.8(7)
N(1)-C(7)	1.273(16)	N(1)-C(8)	1.471(16)	Mn-N(2)-C(10)	126.8(5)	C(9)-N(2)-C(10)	120.2(9)
C(8)-C(9)	1.453(20)	N(2)-C(9)	1.469(9)	N(2)-C(10)-C(11)	124.5(10)	C(10)-C(11)-C(12)	116.9(9)
N(2)-C(10)	1.281(13)	C(10)-C(11)	1.432(8)	C(10)-C(11)-C(16)	123.1(9)	C(12)-C(11)-C(16)	119.9(6)
C(11)-C(12)	1.400(17)	C(11)-C(16)	1.406(14)	C(11)-C(12)-C(13)	120.3(11)	C(12)-C(13)-C(14)	119.7(12)
C(12)-C(13)	1.376(10)	C(13)-C(14)	1.387(18)	C(14)-C(15)-C(16)	120.7(9)	C(15)-C(16)-O(2)	118.0(9)
C(14)-C(15)	1.366(17)	C(15)-C(16)	1.406(8)	C(15)-C(16)-C(11)	118.2(9)	O(2)-C(16)-C(11)	123.6(6)
O(2)-C(16)	1.317(13)			Mn-O(2)-C(16)	129.5(5)		
(b) Copper site				(b) Copper site			
Cu-O(3)	1.884(8)	Cu-N(4)	2.014(7)	O(3)-Cu-N(4)	99.5(3)	O(3)-Cu-N(6)	96.3(3)
Cu-N(5)	1.941(11)	Cu-N(6)	1.924(5)	N(4)-Cu-N(5)	81.0(3)	N(5)-Cu-N(6)	82.9(3)
N(3)-C(17)	1.355(15)	N(3)-C(18)	1.362(13)	N-N(3)-C(18)	126.4(8)	Mn-N(3)-C(17)	127.7(6)
N(4)-C(17)	1.325(8)	N(4)-C(19)	1.364(16)	C(17)-N(3)-C(18)	105.5(7)	N(4)-C(17)-N(3)	112.2(10)
C(19)-C(18)	1.374(13)	C(19)-C(20)	1.420(10)	C(17)-N(4)-C(19)	105.8(8)	Cu-N(4)-C(17)	144.3(9)
N(5)-C(20)	1.276(16)	N(5)-C(21)	1.463(9)	Cu-N(4)-C(19)	109.7(4)	N(4)-C(19)-C(20)	109.7(4)
C(21)-C(22)	1.450(22)	N(6)-C(22)	1.451(15)	N(4)-C(19)-C(18)	108.5(8)	C(18)-C(19)-C(20)	134.3(13)
N(6)-C(24)	1.309(16)	C(24)-C(23)	1.504(11)	N(3)-C(18)-C(19)	107.8(11)	C(19)-C(20)-N(5)	114.4(12)
C(24)-C(25)	1.426(17)	C(25)-C(26)	1.371(9)	Cu-N(5)-C(20)	117.2(6)	Cu-N(5)-C(21)	116.4(9)
C(26)-C(27)	1.505(19)	O(3)-C(26)	1.293(13)	C(20)-N(5)-C(21)	126.2(11)	N(5)-C(21)-C(22)	110.2(11)
				C(21)-C(22)-N(6)	114.0(7)	Cu-N(6)-C(22)	115.3(7)
Bond angles (deg)				Cu-N(6)-C(24)	120.6(7)	C(22)-N(6)-C(24)	120.6(7)
				N(6)-C(24)-C(23)	120.3(10)	N(6)-C(24)-C(25)	123.3(7)
(a) Manganese site				C(23)-C(24)-C(25)	116.3(7)	C(24)-C(25)-C(26)	125.6(7)
O(1)-Mn-O(2)	93.1(2)	O(1)-Mn-N(1)	90.1(3)	C(25)-C(26)-C(27)	118.2(11)	C(25)-C(26)-O(3)	115.5(6)
O(2)-Mn-N(2)	91.3(2)	N(1)-Mn-N(2)	82.2(3)	C(27)-C(26)-O(3)	126.2(11)	Cu-O(3)-C(26)	123.8(5)
O(1)-Mn-N(3)	99.1(3)	O(2)-Mn-N(3)	97.9(2)				

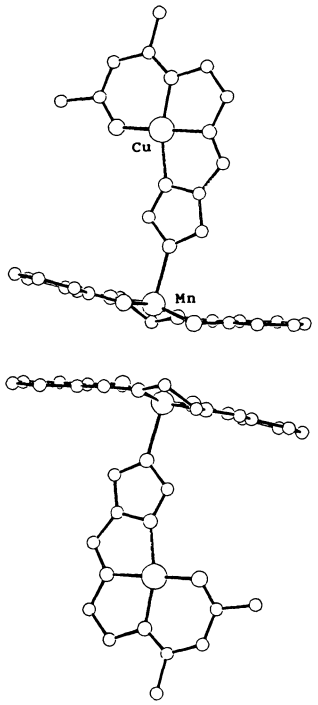


Fig. 2. Arrangement of two cations related by a center of symmetry, showing weak interactions between Mn and O(3)* with out-of-plane fashion.

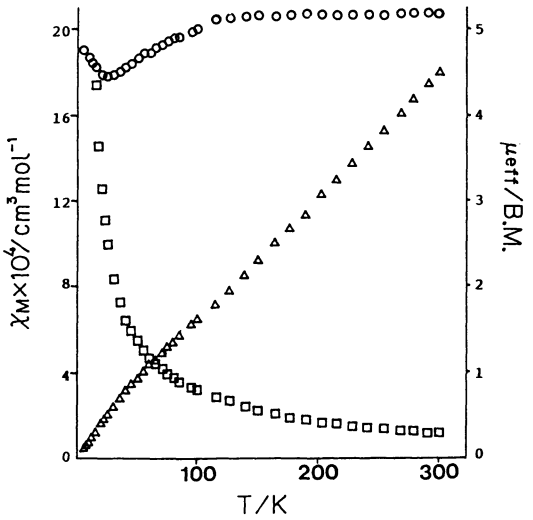


Fig. 3. Temperature dependence of the magnetic susceptibility per molecule (□), the reciprocal magnetic susceptibility per molecule (△), and the effective magnetic moment (○).

cially longer than the corresponding Mn-O bonds of the related manganese(III) complexes [Mn(HIm)(salen)]ClO_4 (2.635(3) Å)[24] and [Mn(hapacen)H_2O]ClO_4(2.305(2) Å),[27] where hapacen denotes the condensation product of acetylacetone, ethylenediamine, and *o*-hydroxyacetophenone with the mole ratio 1 : 1 : 1.

Magnetic Property. The magnetic behavior of the complex is shown in Fig. 3 in the form of the χ_M vs. T, $1/\chi_M$ vs. T, and μ_{eff} vs. T plots, where χ_M denotes the magnetic susceptibility per molecule, μ_{eff} the effective magnetic moment per molecule, and T the absolute temperature. The numerical values of the observed magnetic data are given in the supplementary material.

The effective magnetic moment per molecule at room temperature, 5.17 B.M., is nearly equal to the spin-only value of dinuclear system (5.20 B.M.) assuming no magnetic interaction between high-spin manganese(III) (S_1=2) and copper(II) (S_2=1/2) ions. As the temperature is lowered, the moment decreases gradually from 5.17 B.M. at 300.2 K, reaches the minimum value 4.43 B.M. at 24.9 K, and then increases to 4.73 B.M. at 4.2 K, indicating antiferromagnetic behavior at the higher temperature region and ferromagnetic behavior at the lower temperature region. There are two magnetic interactions which could mainly contribute to this result, i.e., intradinuclear Mn-Cu and interdinuclear Mn-Mn interactions.

First, the magnetic interaction between manganese(III) and copper(II) ions through an imidazolate group is compared with that of the analogous imidazolate-bridged manganese(III)-copper(II) complex [Mn(L)Cu(A)]BPh_4,[22] in which no intermolecular Mn-Mn interaction is feasible because of the completion of six-coordination, where H_2L denotes a quinquedentate ligand 4-methyl-*N*,*N*′-disalicylidene-4-azaheptane-1,7-diamine. The magnetic moment decreases gradually from 5.11 B.M. at 299 K to 3.31 B.M. at 4.3 K through an inflection point 3.86 B.M. at 20 K. In this case the magnetic behavior can be explained by antiferromagnetic coupling between high-spin manganese(III) and copper(II) ions and the zero-field splitting of the spin ground state.

Magnetic interaction between two manganese(III) ions through phenoxo-oxygen atoms similar to the present system[27] can be seen in [Mn(hapacen)H_2O]ClO_4.[28] Its magnetic moment decreases gradually from 4.84 B.M. at 298 K to 1.70 B.M. at 4.4 K and can be well reproduced by the spin-Hamiltonian $H=-2JS_1S_2$ (S_1=S_2=2) with the parameters of J=−1.68 cm^{-1} and g=2.01.

On the basis of the above facts one could only expect antiferromagnetic interaction for the present complex. At present, we could not yet elucidate the origin of ferromagnetic behavior of the complex and more structural and magnetic data of more complexes are needed to settle the problem.

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