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Syntheses, Crystal Structures, and Magnetic Properties of μ-O/μ-Cl Bridged Dinuclear Manganese(II) and Copper(II) Complexes with Schiff base Ligand HL [HL = 2-(benzothiazol-2-yl-hydrazonomethyl)-6-methoxyphenol]

Yajie Gao,[a] Yufei Ji,[a] Shuai Ding,[a] Zhiliang Liu,*[a] and Jinkui Tang*[b]

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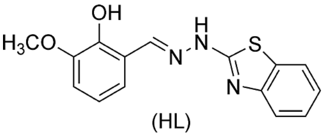
Abstract. A novel versatile multidentate ligand 2-(benzothiazol-2-yl-hydrazonomethyl)-6-methoxyphenol (HL), was obtained from a condensation reaction between 2-hydrazino benzothiazole and *o*-vanillin. The reactions of HL with $CuCl_2{\cdot}2H_2O/Mn(ClO_4)_2{\cdot}6H_2O$ generated two novel dinuclear compounds $Cu_2L(\mu\text{-}Cl)Cl_2(CH_3OH)_2$ (**1**) and $Mn_2L_3(ClO_4)(CH_3CH_2OH)_3$ (**2**). The crystal structures of **1** and **2** were determined by X-ray diffraction studies. The two copper atoms in complex **1** are connected by a L^- anion and a single chloro bridge with a Cu···Cu separation of 3.2729(4) Å. In complex **2**, the two manganese atoms are held together by two L^- anion bridges and the Mn···Mn separation amounts to 3.3433(7) Å. As expected, variable-temperature magnetic susceptibility measurements of complex **1** showed strong antiferromagnetic intramolecular coupling between the copper(II) atoms with $J = -102.2\ cm^{-1}$, and evidenced for complex **2** weak antiferromagnetic coupling with $J = -1.68\ cm^{-1}$.

Introduction

Intra- and intermolecular coupling of transition metal complexes is an important aspect of molecule-based magnets.[1] Structural features, which correlate with strength and sign of such interactions, constitute a necessary step. In the case of dinuclear transition metal complexes, the nature of the two metal ions, bridging ligands, and the distance between them are the key elements in assembling exchange interaction species.[2]

Schiff-base ligands are ubiquitous in coordination chemistry, where they are used in synthesis of a large variety of transition metal complexes with a range of structural architectures. These ligands are often obtained in good yields and high purity, through a straight forward synthetic pathway. All these reasons justify their high popularity in coordination chemistry.[3] Many Schiff-base-containing coordination compounds have shown attractive properties. For example, Schiff-base coordination compounds exhibit interesting magnetic properties.[4–9] Many Schiff-base complexes have also found interesting applications in nonlinear optical,[10–16] fluorescence properties,[17] catalysis,[18–22] DNA-hydrolytic characters,[23–25] and antibacterial behavior.[26,27]

In this work, we have successfully synthesized a new dinuclear cooper(II) complex and a dinuclear manganese(II) complex containing Schiff-base bridging ligands. Our strategy is the using of polydentate Schiff-base ligands to control nuclear number of the complexes. Herein, 2-(benzothiazol-2-yl-hydrazonomethyl)-6-methoxyphenol (HL, see Scheme 1) was used as bridging ligands to construct the dinuclear complexes. We report the synthesis, crystal structures, and magnetic properties of the dinuclear copper(II) complex $Cu_2L(\mu\text{-}Cl)Cl_2(CH_3OH)_2$ (**1**) and the dinuclear manganese(II) complex $Mn_2L_3(ClO_4)(CH_3CH_2OH)_3$ (**2**).



Scheme 1. The structure of the ligand (HL).

Results and Discussion

Crystal Structures

*$[Cu_2L(\mu\text{-}Cl)Cl(CH_3OH)_2]Cl$ (**1**)*

Structural analysis shows that complex **1** crystallizes in the monoclinic space group $P2_1/c$ and each of the unit cells comprises of four dinuclear units. The structure of **1** consists of cationic entities $[Cu_2L(\mu\text{-}Cl)Cl(CH_3OH)_2]^+$, an uncoordinated chlorate anion for charge balance. A perspective view of the

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* Prof. Dr. Z. Liu
Fax: +86-471-4992147
E-Mail: cezlliu@imu.edu.cn
* Dr. J. Tang
Fax: +86-431-85262054
E-Mail: tang@ciac.jl.cn
[a] College of Chemistry and Chemical Engineering
Inner Mongolia University
Hohhot, 010021, P. R. China
[b] State Key Laboratory of Rare Earth Resource Utilization
Changchun Institute of Applied Chemistry
Chinese Academy of Sciences
Changchun 130022, P. R. China

metal atoms of the dinuclear core of **1** is depicted in Figure 1, well-isolated dinuclear units, in which copper(II) ions are bridged by a μ_2-phenoxido oxygen atom from the L^- ligand and a μ-chloride anion. The coordination spheres of two Cu^{II} ions observed in complex **1** are very different. The Cu(1) ion is located in a CuN_2OCl distorted rectangular coordination environment, which is formed by two nitrogen atoms and one bridging phenoxido oxygen atom belonging to L^- ligand, and one μ-chloride atom. The coordination plane suffers distortion as indicated by a Cu(1) ion deviation from the average plane of 0.0846 Å, whereas the coordination polyhedron around Cu(2) ion is a distorted CuO_4Cl_2 octahedron. One bridging phenoxido oxygen atom and one oxygen atom from the methoxy group belonging to L^- ligand, together with one μ-chloride atom and another chloride anion occupy the equatorial positions. The axial coordination sites are occupied by methoxy oxygen atoms. The octahedral coordination sphere around the Cu(2) ion suffers distortion, which is indicated by a much longer Cu(2)–Cl(2) bond length [Cu(2)–Cl(2) = 2.6329(6) Å]. Moreover, the relevant atoms making up the equatorial coordination plane of the CuO_2Cl_2 chromophore deviate 0.0584 Å from the average plane. The central Cu_2(μ-O)(μ-Cl) ring is distorted from rectangular arrangement with Cu–O–Cu and Cu–Cl–Cu bond angles of 110.68(7)° and 84.101(19)°, respectively. The two copper(II) atoms are separated by 3.2729(4) Å. All N–Cu^{II} and O–Cu^{II} bond lengths are within the normal range observed in other copper(II) complexes.[28–30] The larger Cu–Cl distance values are similar to those found in other pentacoordinate copper(II) complexes that contain bridging phenoxy oxygen atoms.[31,32] Selected bond lengths and angles are listed in Table 1.

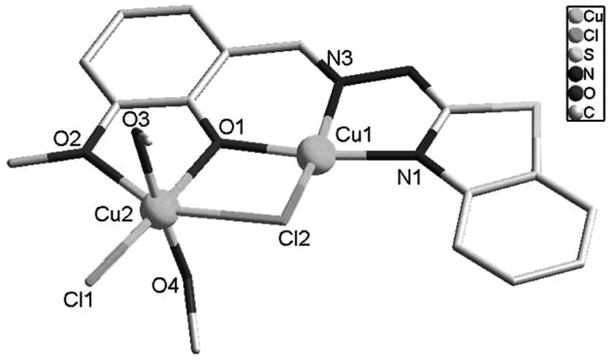

Figure 1. Perspective view of the structure of the $[Cu_2L(\mu\text{-}Cl)Cl(CH_3OH)_2]^+$ cation. Hydrogen atoms are omitted for clarity.

$[Mn_2L_3](ClO_4)(CH_3CH_2OH)_3$ (**2**)

Complex **2** crystallizes in the monoclinic space group $P2_1/c$. The crystal structure consists of cationic entities $[Mn_2L_3]^+$, an uncoordinated perchlorate anion for charge balance, and three ethanol molecules of crystallization. A perspective view of the dinuclear cation with atom numbering scheme is depicted in Figure 2a, and some selected bond lengths and angles are presented in Table 2. The metal atoms of the dinuclear core are linked by two μ_2-phenoxido oxygen atoms from two L^- ligands to form a rectangular arrangement of the metal ions and oxygen atoms. The central $Mn_2(\mu\text{-}O)_2$ ring is quite distorted from rectangular, showing Mn(1)–O(3)–Mn(2) 104.43(9)° and Mn(1)–O(5)–Mn(2) 99.79(8)° bond angles. The distance of these two Mn^{II} ions is 3.3433(7) Å. The two ligands bridging the Mn(1) and Mn(2) atoms are almost planar and the two planes are in an intersectant fashion a dihedral angle of 71.155(24)° (see Figure 2b).

The coordination spheres of the Mn^{II} ions are completed by the Schiff-base ligand to create a six-coordinate environment. The coordination polyhedron around Mn(1) and Mn(2) atoms can be described as MnN_2O_4 and MnN_4O_2 chromophore with an trigonal antiprismatic arrangement, respectively. This type of coordination structure is much rarer but nonetheless important in six-coordinate complexes. The chelating ligands such as L^-, which is somewhat inflexible and has too short a "bite" (the distance between the two atoms bonded to the metal atoms) can sometimes form the structural motif with trigonal antiprismatic arrangement.[33]

Magnetic Properties

The magnetization properties of the two compounds were studied to evaluate the magnetic interactions between the two paramagnetic centers in **1** and **2**. Variable temperature magnetic susceptibility measurements in the 1.8–300 K tempera-

Table 1. Selected bond lengths /Å and angles /° for **1**.

Cu(1)–O(1)	1.9542(15)	Cu(2)–O(1)	2.0244(14)
Cu(1)–N(3)	1.9634(18)	Cu(2)–O(3)	2.0287(16)
Cu(1)–N(1)	1.9872(18)	Cu(2)–Cl(1)	2.2030(6)
Cu(1)–Cl(2)	2.2334(6)	Cu(2)–O(2)	2.3008(16)
Cu(2)–O(4)	1.9942(15)	Cu(2)–Cl(2)	2.6329(6)
O(1)–Cu(1)–N(3)	90.01(7)	O(3)–Cu(2)–Cl(1)	92.30(5)
O(1)–Cu(1)–N(1)	171.78(7)	Cl(1)–Cu(2)–O(2)	101.11(4)
N(3)–Cu(1)–N(1)	81.89(7)	O(4)–Cu(2)–Cl(2)	89.17(5)
O(1)–Cu(1)–Cl(2)	87.68(4)	O(1)–Cu(2)–Cl(2)	76.01(4)
N(3)–Cu(1)–Cl(2)	168.72(6)	O(3)–Cu(2)–Cl(2)	90.54(5)
N(1)–Cu(1)–Cl(2)	100.01(6)	Cl(1)–Cu(2)–Cl(2)	108.94(2)
O(4)–Cu(2)–Cl(1)	93.40(5)	O(2)–Cu(2)–Cl(2)	149.65(4)
O(1)–Cu(2)–Cl(1)	174.63(5)	Cu(1)–Cl(2)–Cu(2)	84.101(19)
		Cu(1)–O(1)–Cu(2)	110.68(7)

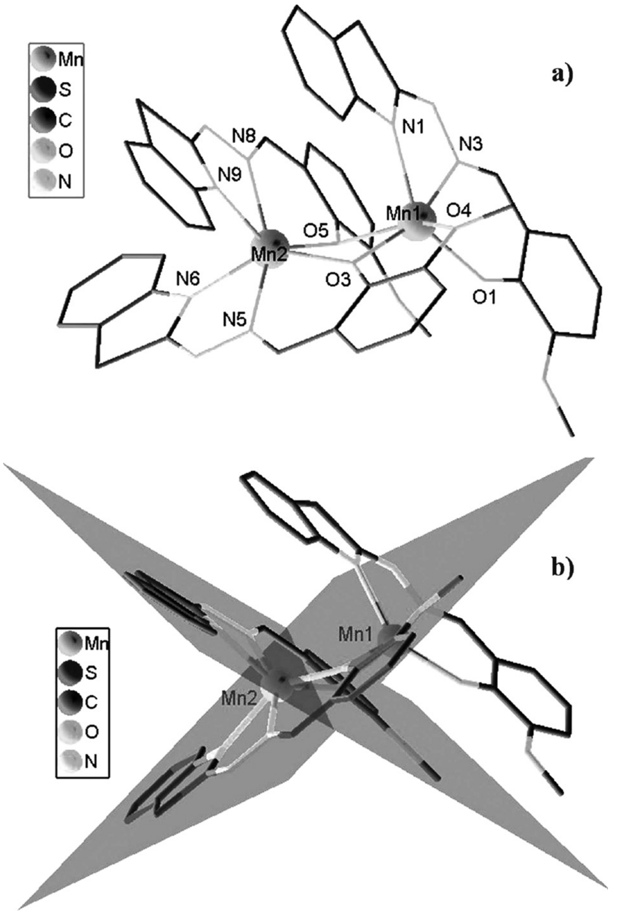

Figure 2. (a) Perspective view of the structure of the $[Mn_2L_3]^+$ cation. Hydrogen atoms are omitted for clarity. (b) Representation of intersectant fashion of the two planes, which are formed by the bridging ligands L^-.

ture range, under a constant magnetic field of 1 kOe were carried out.

The magnetic properties of complex **1** as χ_M and $\chi_M T$ against T plots (χ_M is the magnetic susceptibility per Cu^{II} dimer) are shown in Figure 3. Data were corrected for gelatine capsule sample holder as well as for diamagnetic and temperature independent paramagnetism contributions. As shown in Figure 3, the room-temperature value of $\chi_M T$ (0.69 $cm^3 \cdot K \cdot mol^{-1}$) is lower than that expected for two uncorrelated spins with $S = 1/2$ ($\chi_M T = 0.75$ $cm^3 \cdot K \cdot mol^{-1}$ assuming $g = 2$), and $\chi_M T$ decreases fast upon lowering of the temperature. This result indicates that there exists antiferromagnetic coupling interaction in complex **1**.

For the theoretical analysis of the magnetic behavior of compound **1**, the analytical expression based upon the Hamil-

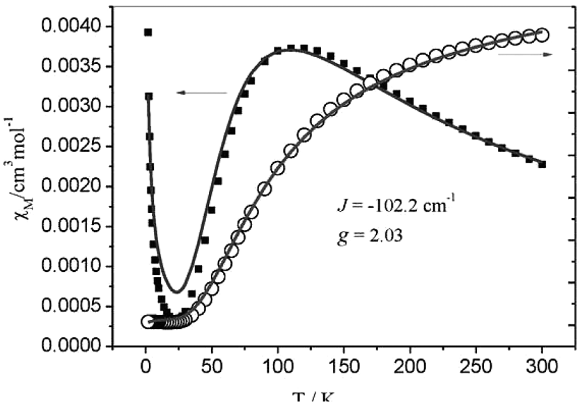

Figure 3. Plots of χ_M and $\chi_M T$ versus T for the complex **1**; the solid line represents the best fitting with $J = -102.2$ cm^{-1} and $g = 2.03$.

Table 2. Selected bond lengths /Å and angles /° for **2**.

Mn(1)–O(1)	2.070(2)	Mn(2)–O(3)	2.110(2)
Mn(1)–O(3)	2.120(2)	Mn(2)–O(5)	2.165(2)
Mn(1)–O(5)	2.206(2)	Mn(2)–N(6)	2.258(3)
Mn(1)–N(3)	2.239(3)	Mn(2)–N(8)	2.274(3)
Mn(1)–N(1)	2.259(3)	Mn(2)–N(5)	2.296(2)
Mn(1)–O(4)	2.326(2)	Mn(2)–N(9)	2.346(2)
O(1)–Mn(1)–O(3)	113.43(8)	O(3)–Mn(2)–O(5)	73.83(8)
O(1)–Mn(1)–O(5)	104.63(8)	O(3)–Mn(2)–N(6)	142.78(9)
O(3)–Mn(1)–O(5)	72.82(8)	O(5)–Mn(2)–N(6)	107.85(8)
O(1)–Mn(1)–N(3)	81.84(9)	O(3)–Mn(2)–N(8)	122.00(9)
O(3)–Mn(1)–N(3)	161.37(9)	O(5)–Mn(2)–N(8)	77.48(8)
O(5)–Mn(1)–N(3)	93.54(9)	N(6)–Mn(2)–N(8)	93.74(9)
O(1)–Mn(1)–N(1)	146.17(9)	O(3)–Mn(2)–N(5)	77.26(8)
O(3)–Mn(1)–N(1)	96.93(8)	O(5)–Mn(2)–N(5)	126.20(8)
O(5)–Mn(1)–N(1)	98.13(9)	N(6)–Mn(2)–N(5)	72.34(9)
N(3)–Mn(1)–N(1)	71.97(9)	N(8)–Mn(2)–N(5)	154.90(9)
O(1)–Mn(1)–O(4)	89.10(8)	O(3)–Mn(2)–N(9)	103.66(9)
O(3)–Mn(1)–O(4)	70.60(8)	O(5)–Mn(2)–N(9)	141.14(8)
O(5)–Mn(1)–O(4)	143.41(7)	N(6)–Mn(2)–N(9)	96.99(9)
N(3)–Mn(1)–O(4)	122.25(9)	N(8)–Mn(2)–N(9)	71.38(9)
N(1)–Mn(1)–O(4)	87.21(9)	N(5)–Mn(2)–N(9)	89.27(9)
Mn(1)–O(3)–Mn(2)	104.43(9)	Mn(1)–O(5)–Mn(2)	99.79(8)

tonian ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$) was used. Accordingly, the molar magnetic susceptibility for this dicopper(II) complex is expressed as Equation (1) and the temperature dependence of the magnetic susceptibility of compound **1** was fitted.

$$\chi_M = \frac{2N\beta^2 g^2}{kT}[3 + \exp(-\frac{2J}{kT})]^{-1}(1 - \rho)\,\frac{N\beta^2 g^2}{2kT}\,\rho + N_\alpha \tag{1}$$

J is the interaction parameter between two spin carriers, ρ is the proportion of the paramagnetic impurity [presumably non-coupled monomeric copper(II) complex], N_α is the temperature-independent paramagnetism (120×10^{-6} $cm^3 \cdot mol^{-1}$) and the other symbols have their usual meaning. The simulation of the experimental data of **1** leads to $J = -102.2$ cm^{-1}, $g = 2.03$ and $\rho = 0.009$. The agreement factor R defined as $\Sigma[(\chi_M)_{obs}-(\chi_M)_{calc}]^2/\Sigma[(\chi_M)_{obs}]^2$ is 1.17×10^{-3}. Studies have shown that short Cu–O bonds and large Cu–O–Cu angles in phenolate-bridged copper dimers result in strong overlap of $d_{x^2-y^2}$ orbitals and thus produce strong antiferromagnetic couplings.[31,34,35] Copper(II) dimers with both halide and phenolate bridges are shown to exhibit strong antiferromagnetic coupling constants around -100 cm^{-1}.[36] The short Cu–O bonds (1.9542 and 2.0244 Å) and the large Cu–O–Cu angle (110.68°) of the phenolate bridge in **1**, relative to the long Cu–Cl bonds (2.2334 and 2.6329 Å), points at a dominant coupling through the phenolate bridge. The coordination sphere around one of the two copper ions is distorted rectangle, whereas the other has a distorted octahedron environment. In the both case, the unpaired electron of copper(II) occupies the $d_{x^2-y^2}$ orbital, which would points along the Cu–O(phenolate) bond. Short Cu–O bonds and large Cu–O–Cu angles in phenolate-bridged copper dimers result in a strong overlap of $d_{x^2-y^2}$ orbitals and thus produces strong antiferromagnetic couplings.[36,37] On the other hand, if one of the copper ions in such dimers has a trigonal-bipyramidal environment, weaker overlap is expected, and even weak ferromagnetic coupling was observed.[38,39]

The magnetic properties of complex **2** as χ_M and $\chi_M T$ against T plots (χ_M is the magnetic susceptibility per Mn^{II} dimer) are shown in Figure 4. Data were corrected for gelatine capsule sample holder as well as for diamagnetic contributions. As shown in Figure 4, the room-temperature value of $\chi_M T$ (8.71 $cm^3 \cdot K \cdot mol^{-1}$) is lower than that expected for two uncorrelated spins with $S = 5/2$ ($\chi_M T = 8.75$ $cm^3 \cdot K \cdot mol^{-1}$ assuming $g = 2$), and $\chi_M T$ decreases slowly upon lowering of the temperature. This result indicates that there exists weak antiferromagnetic coupling interaction in complex **2**. Above 25 K, the variation of χ_M with temperature follows the Curie–Weiss law. The corresponding Curie constant (C) and Weiss constant (θ) are found to be 8.70 $cm^3 \cdot K \cdot mol^{-1}$ and -0.26 K, respectively. At lower temperature, the single-ion zero-field splitting causes depopulation into a low-spin ground state, which accounts for the sharp decreasing of $\chi_M T$ values.

For the theoretical analysis of the magnetic behavior of compound **2**, the analytical expression based upon the Hamiltonian ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$) was used. Accordingly, the molar magnetic susceptibility for this dimanganese(II) complex is expressed as Equation (2) and the temperature dependence of the magnetic susceptibility of compound **2** was fitted. The simulation of the experimental data of **2** leads to $J = -1.68$ cm^{-1}, and $g = 2.0$. The agreement factor R defined as $\Sigma\,[(\chi_M)_{obs}-(\chi_M)_{calc}]^2/\Sigma[(\chi_M)_{obs}]^2$ is 3.50×10^{-4} and the fitting result is presented in Figure 4.

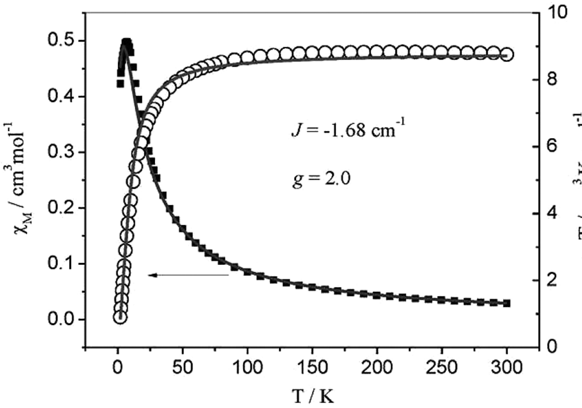

Figure 4. χ_M versus T and $\chi_M T$ versus T plots for complexes **2**.

$$\chi_M = \frac{2N\beta^2 g^2}{kT} \cdot \frac{A}{B} \tag{2}$$

$A = 55 + \exp(-10J/kT) + 14\exp(18J/kT) + 5\exp(-24J/kT) + \exp(-28J/kT)$

$B = 11 + 9\exp(-10J/kT) + 7\exp(18J/kT) + 5\exp(-24J/kT) + 3\exp(-28J/kT) + \exp(-30J/kT)$

Taking into consideration the μ-O bridged dinuclear manganese(II) compounds in the literatures.[40–43] the magnetic interaction in these compounds show weak ferro- or antiferromagnetic behavior, with J values between +1.2 cm^{-1} and -4.5 cm^{-1}. For complex **2**, the fitting result indicates that there exists weak antiferromagnetic coupling in the $[Mn_2(\mu\text{-}O)_2]$ core with $J = -1.68$ cm^{-1}. This result is within the normal range observed in other dinuclear Mn^{II} complexes with monatomic oxo bridging ligands, such as alkoxo/phenoxo, carboxylate, *N*-oxide and phosphonate.

Conclusions

Two novel dinuclear complexes of the Schiff-base ligand 2-(benzothiazol-2-yl-hydrazonomethyl)-6-methoxyphenol (HL) were synthesized and characterized. The L^- ligand acts as a versatile tri- or tetradentate donor and allows formation of interesting complexes. For complex **1**, the coordination spheres of the two Cu^{II} ions are very different. The Cu(1) ion is located in a distorted rectangular coordination environment and the Cu(2) ion is located in a distorted octahedral coordination mode. For complex **2**, the coordination polyhedra around the atoms Mn(1) and Mn(2) can be described as MnN_2O_4 and MnN_4O_2 chromophores with an trigonal antiprismatic arrangement, respectively. This type of coordination is less frequent but nonetheless important in six-coordinate Mn^{II} complexes. Both complexes **1** and **2** presented antiferromagnetic interactions.

Experimental Section

Materials and Physical Measurements: All chemicals were of analytical reagent grade and were used as received. C, H, and N analysis were carried out with a Perkin–Elmer 2400 analyzer. Fourier transform infrared (FTIR) spectra were recorded with a Vertex 70 FTIR spectrophotometer using the reflectance technique (4000–400 cm^{-1}). Samples were prepared as KBr disks. X-ray measurements for **1** and **2** were taken at room temperature with a Bruker ApexII CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), operating in ω–2θ scanning mode using suitable crystals for data collection. Variable temperature magnetic susceptibility measurements were performed in the temperature range 1.8–300 K with a Quantum Design MPMS XL-7 SQUID magnetometer equipped with a 7 T magnet. The diamagnetic corrections for the compounds were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

Synthesis: The 2-hydrazino benzothiazole was prepared by a literature procedure described elsewhere.[44] The Schiff-base ligand HL [2-(benzothiazol-2-yl-hydrazonomethyl)-6-methoxyphenol] was synthesized by a condensation reaction between 2-hydrazino benzothiazole (0.33 g, 2 mmol) and *o*-vanillin (0.34 g, 2.2 mmol) in methanol (80 mL). The mixture was refluxed for 3 h. The resulting light yellow precipitate was filtered.

$[Cu_2L(\mu\text{-}Cl)Cl_2(CH_3OH)_2]$ (1): A solution of Schiff-base ligand (HL, 44.9 mg, 0.15 mmol) in methanol/ethanol (2:1, 15 mL) was added to $CuCl_2 \cdot 4H_2O$ (62.1 mg, 0.3 mmol) dissolved in distilled water (10 mL) whilst stirring. The mixture was further stirred for 30 min and filtered. Several days later, well-shaped blue crystals that appeared were separated by filtration, washed with cold water and methanol, Yield 45.4 mg [51 % based on copper(II) chloride]. **IR** (KBr): $\tilde{\nu}$ = 3354 (b), 2842 (w), 1601 (m), 1572 (s), 1516 (w), 1452 (s), 1384 (w), 1270 (m), 1243 (m), 1227 (s), 1121 (s), 942 (w), 743 (m), 637 (w) cm^{-1}. Anal. calcd (found) for $C_{17}H_{18}Cl_3Cu_2N_3O_4S$: C 30.31 (30.76); N 7.07 (7.23); H 3.03 (3.27) %.

$[Mn_2L_3](ClO_4)(CH_3CH_2OH)_3$ (2): The compound was prepared using the same procedure as described above for the synthesis of complex **1** but using $Mn(ClO_4)_2 \cdot 6H_2O$ instead of $CuCl_2 \cdot 4H_2O$. Finally, the product was obtained as block-shaped orange crystals after 3 days. Yield 85.7 mg (46 % based on magnesium perchlorate hexahydrate). **IR** (KBr): $\tilde{\nu}$ = 3354 (b), 2842 (w), 1601 (m), 1572 (s), 1516 (w), 1452 (s), 1384 (w), 1270 (m), 1243 (m), 1227 (s), 1121 (s), 942 (w), 743 (m), 637 (w) cm^{-1}. Anal. calcd (found) for $C_{51}H_{54}ClMn_2N_9O_{13}S_3$: C 49.25 (49.64); N 10.14 (10.38); H 4.34 (4.62) %.

X-ray Structure Determination: Crystallographic data and refinement details are given in Table 3. Suitable single crystals with dimensions of 0.19 × 0.16 × 0.09 and 0.19 × 0.14 × 0.11 mm for **1** and **2** respectively, were selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at a temperature of 296 K with a Bruker ApexII CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data processing was accomplished with the SAINT processing program.[45] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL.[46] The location of metal atoms was easily determined, and oxygen, nitrogen, and carbon atoms were subsequently determined from the difference Fourier maps. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced in calculated positions and refined with a fixed geometry with respect to their carrier atoms.

Table 3. Crystallographic data and structure refinement for **1** and **2**.

	1	**2**
Empirical Formula	$C_{17}H_{18}Cl_3Cu_2N_3O_4S$	$C_{51}H_{54}ClMn_2N_9O_{13}S_3$
Formula weight	595.88	1242.57
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a /Å	8.6282(5)	15.8246(6)
b /Å	17.6418(10)	21.5242(8)
c /Å	14.6886(8)	22.3661(6)
α, β, γ /°	90, 97.9590(10), 90	90, 133.987(2), 90
V /Å^3	2214.3(2)	5481.2(3)
Z	4	4
T /K	296(2)	293(2)
$\rho_{\text{calcd.}}$ /g·cm^{-3}	1.787	1.506
μ /mm^{-1}	2.407	0.696
$F(000)$	1200	2568
θ Range /°	$1.81 < \theta < 26.05$	$1.58 < \theta < 25.91$
Measured reflections	$-10 \le h \le 10$	$-11 \le h \le 19$
	$-17 \le k \le 21$	$-24 \le k \le 26$
	$-18 \le l \le 17$	$-27 \le l \le 25$
Reflections collected	12144	29966
Unique reflection, R_{int}	4373, 0.0234	10631, 0.0510
GOF on F^2	1.067	1.002
Final R indices $[I > 2\sigma(I)]$	$R^{a)}$ = 0.0243 $wR^{b)}$ = 0.0645	$R^{a)}$ = 0.0435 $wR^{b)}$ = 0.1013
R indices (all data)	R = 0.0288, wR = 0.0668	R = 0.0801, wR = 0.1222
Largest difference peak and hole /e·Å^{-3}	0.413 and –0.360	0.679 and –0.578

a) $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. b) $wR = [\Sigma w(F_o^2-F_c^2)^2/\Sigma(wF_0^4)]^{1/2}$.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-820979 and CCDC-820980 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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