第 25 卷第 5 期 无 机 化 学 学 报 Vol.25 No.5
2009 年 5 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 906~909

研究简报

3-甲基-4-对甲基苯基-5-(2-吡啶基)-1,2,4-三唑双核锰(Ⅱ)配合物的合成及晶体结构

王作祥 徐海军* 宫晓宁 吴平锋
(东南大学化学化工学院有序物质科学研究中心,南京 211189)

关键词:1,2,4-三唑;晶体结构;双核锰配合物
中图分类号:O614.7+11 **文献标识码**:A **文章编号**:1001-4861(2009)05-0906-04

Synthesis and Crystal Structure of A Dinuclear Manganese(Ⅱ) Complex with 3-Methyl-4-(4-Methylphenyl)-5-(2-Pyridyl)-1,2,4-Triazole

WANG Zuo-Xiang XU Hai-Jun* GONG Xiao-Ning WU Ping-Feng
(*Ordered Matter Science Research Center, School of Chemistry and Chemical Engineering, Southeast University, Nanjing* 211189)

Abstract: A dinuclear Mn(Ⅱ) complex $[Mn_2L_2(\mu\text{-}Cl)_2Cl_2(H_2O)_2]$ (**1**) was synthesized by reaction of ligand L with $MnCl_2\cdot 4H_2O$ and its structure was determined by X-ray crystal structure analysis. The structure indicates that the complex crystallizes in monoclinic, space group *C*2/*c* with *a*=2.018 0(15) nm, *b*=0.894 0(6) nm, *c*=1.932 1(14) nm, β=97.506(12)°. *V*=3 456(4) nm^3, *Z*=4, D_c=1.515 Mg·m^{-3}, μ=1.081 mm^{-1}, *F*(000)=1 608, and final R_1=0.043 8, wR_2=0.109 9. The result shows a Mn(Ⅱ) ion was six-coordinated by a bidentate 3-methyl-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole, one chlorine and one bridging chlorine atom in the basal positions and one chloride atom and one water molecule in the axial one, to form a distorted octahedral-pyramidal geometry. CCDC: 713047.

Key words: 1,2,4-triazoles; crystal structure; dinuclear manganese complex

1,2,4-Triazole and its derivatives represent an important class of heterocycles that find many useful applications as biological reagents: They are used as fungicides, insecticides, antimicrobe, herbicides and anti animal parasites[1]. Moreover, The coordination chemistry of substituted 1,2,4-triazoles has also received considerable attention in latest decade due to the fact that some of their complexes have spin-crossover properties which can be used as molecular-based memory devices, dispays and switching materials[2~11]. Recently we have reported the syntheses, crystal structures and properties of one new cobalt(Ⅱ) complexes with 4-(*p*-methylphenyl)-3,5-bis(pyridin-2-yl)-1,2,4-triazole (MBPT)[12]. As a continuation of our investigation, we report here the synthesis, crystal structure and magnetic properties of a novel mamganese (Ⅱ) complex with ligand L: $[Mn_2L_2(\mu\text{-}Cl)_2Cl_2(H_2O)_2]$.

1 Experimental

1.1 General procedures

All chemicals were reagent grade and used as received. All solvents were of analytical grade and used directly. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240 analyzer. Variable

收稿日期:2009-01-05。收修改稿日期:2008-03-17。
*通讯联系人。E-mail:xuhaijun_jx@yahoo.com.cn
第一作者:王作祥,男,44 岁,副教授,研究方向:有机合成,配位化学。

temperature magnetic susceptibilities of crystalline of the complex were measured on a Quantum Design MPMS SQUID-XL7 magnetometer in the temperature range of 1.8 ~300 K. Diamagnetic corrections were made with Pascalt′s constants for all the constituent atoms. The IR spectra were taken on a Vector22 Bruker Spectrophotometer (400~4 000 cm^{-1}) with KBr pellets.

1.2 Syntheses of 3-methyl-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (L)[13]

N-propionyl-*N*′-(2-pyridoyl)hydrazine (5.0 g, 25 mmol) was added to the solution of di(*p*-methylphenyl) phosphazoanilide (6.9 g, 28.5 mmol) in *N*,*N*′-dimethylaniline (40 mL). The mixture was refluxing for 3 hours, and then the solvent was removed by vacuum distillation. To the residue concentrated chlorhydric acid (10 mL) was added and refluxing for 1 hour. After cooling, the solution was filtered, and the filtrate was neutralized to pH=8 with potassium carbonate, the white precipitate was formed and collected. The crude product recrystallized from water (4.3 g, yield 63.5%). m.p. 172~174 ℃. $C_{15}H_{14}N_4$ (%): Calcd. C 71.98, H 5.64, N 22.38; Found(%): C 71.73, H 5.81, N 22.26. IR(KBr): 3 056.7, 3 031.6, 2 925.5, 2 856.1, 1 589.1, 1 496.5, 1 450.2, 1 413.6, 1 373.1, 1 282.5, 1 152.2, 999.0, 827.3, 711.6. ^{1}H NMR ($CDCl_3$): 2.336 7(3H, single), 2.425 2(3H, single), 7.061 8~7.268 2(4H, symmetry), 7.159 4~8.042 0(4H, multiple, pyridine ring). ESI-MS: 251.28(M^+).

1.3 Preparation of the complexes of $[Mn_2L_2(\mu\text{-}Cl)_2Cl_2(H_2O)_2]$

To the warm solution of 3-methyl-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (0.500 g, 2.0 mmol) in 20 mL ethanol, manganese(Ⅱ) chloride ($MnCl_2\cdot 4H_2O$, 0.792 g, 4.0 mmol) in distilled water (10 mL) was added. The mixture was filtered, and the filtrate was left to stand at room temperature for several days. Colorless solid product formed and collected (0.865 g, yield 67%). Single crystals suitable for X-ray diffraction were selected. Anal. Calcd. for $C_{30}H_{32}Cl_4Mn_2N_8O_2$ (%): C 45.71, H 4.09, N 14.21; Found(%): C 45.53, H 4.25, N 14.38.

1.4 Crystal structure determination

A single crystal with dimensions of 0.3 mm×0.2 mm×0.05 mm was selected for X-ray structure analysis. The data were collected on a Rigaku SCX Mini CCD diffractometer using a graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293(2) K. A total of 16 705 reflections were collected in the range of $3.13° \leqslant \theta \leqslant 27.52°$ by using an ω-2θ scan mode, of which 3 953 were unique with R_{int}=0.060 8 and 3 356 with $I>2\sigma(I)$ were considered as observed. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 program[14,15]. The hydrogen atom positions were geometrically idealized and allowed to ride on their respective parent atoms and fixed displacement parameters. The weighting scheme was $w=1/[\sigma^2(F_o^2)+(0.045\ 3P)^2]$ where $P=(F_o^2+2F_c^2)/3$, the refinement was converged to the final R_1=0.043 8, wR_2=0.109 9, and S=1.135. The highest peak and deepest hole in the final difference Fourier map are 336 and −457 e·nm^{-3}, respectively. The crystal data and structure refinement datails for the title complex are listed in Table 1.

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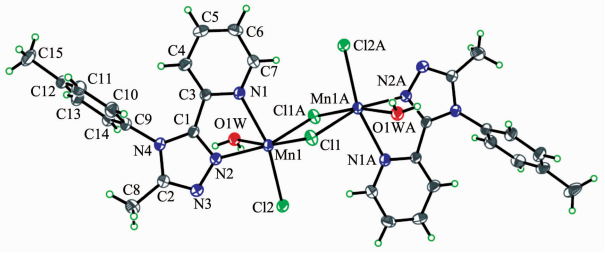
Table 1　Crysta data and structure refinement parameters for the title complex

Empirical formula	$C_{30}H_{32}Cl_4Mn_2N_8O_2$	F(000)	1 608
Formula weight	788.32	Crystal size / mm	0.30×0.26×0.24
T / K	293(2)	θ range for data collection / (°)	3.13~27.52
Crystal system	Monoclinic	Index ranges	$-26 \leqslant h \leqslant 26, -11 \leqslant k \leqslant 11, -25 \leqslant l \leqslant 25$
Space group	$C2/c$	Reflections collected / unique (R_{int})	16 705 / 3 953 (0.060 8)
a / nm	2.018 0(15))	Refinement method	Full-matrix least-squares on F^2
b / nm	0.894 0(6)	Data / restraints / parameters	3 953 / 0 / 210
c / nm	1.932 1(14)	Goodness-of-fit on F^2	1.135
β / (°)	97.506(12)	R_1 (on F) [$I>2\sigma(I)$]	0.043 8
Z	4	wR_2 (on F^2)	0.1099
D_c / (Mg·m^{-3})	1.515	Largest diff. peak and hole / (e·nm^{-3})	336 and −457
μ / mm^{-1}	1.081	Absorption correction	Multi-scan

2 Results and discussion

2.1 Structural analysis

An ORTEP drawing of the structure with atomic numbering are shown in Fig.1. The crystal structure of complex **1** reveals that the crystallographic unit of the title complex consists of two Mn(Ⅱ) ions, four chlorine anions, two 3-methyl-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole and two water molecules in which the two Mn(Ⅱ) ions are bridged by two chlorine anions. The selected bond lengths and angles of this compound are listed in Table 2. The Mn(Ⅱ) center is six-coordinated with a slightly distorted octahedral geometry. The equatorial positions are occupied by the two nitrogen atoms of 3-methyl-4-(4-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole and two chlorine atoms. In the axial position, one oxygen atom from the water molecule and other chlorine atom, belonging to the other of the dimmer, complete the coordination sphere.



Displacement ellipsoids are drawn at the 30% probability level
Symmetry code: A: $-x$, $1-y$, $-z$

Fig.1 A view of the title compound with the atomic numbering scheme

As can be seen in Table 2 for the title compound, The N1-Mn1-N2 angle is 70.12(7)°. the bridge between metallic cations shows nearly same distances [Mn-Cl1 and Mn-Cl1A (A: $-x$, $1-y$, $-z$) are 0.252 30(15) nm and 0.255 63(15) nm, respectively], The interior Cl1-Mn1-Cl1 (A) angle of the bridging arrangement is 85.74(6)° while the Mn1-Cl1-Mn1(A) bridge-angle being 94.26(6)°. The distance between metallic cations and water mole-cule is intermediate between the Mn-O1W distances [Mn1-O1W is 0.222 4(2) nm]. The dimmer sits on an inversion center, hence the Mn2Cl2 bridging unit is planar. The Mn1-Mn1 (A) distance is 0.372(3) nm, which is significantly larger than the sum of the two manganese radii (0.091 nm for Mn(Ⅱ)) and precludes any direct Mn-Mn bonding. The pyridine ring where nitrogen atom is involved in coordination makes an angle of 7.11(17)° with respect to the triazole ring, and they are are approximately coplanar. While the pendant substituted phenyl rings are twisted away from coplanarity and almost perpendicular to the adjacent triazole unit, forming dihedral angles of 87.80(9)°. The C-C and C-N bond lengths within the aromatic rings are normal [C-C distances range from 0.136 0(4) to 0.139 5(4) nm and C-N distances from 0.131 8(3) to 0.135 1(3) nm]. These bond lengths are similar to those observed for other 1,2,4-triazole complexes[16,17]. In the crystal structure, the molecules are further connected through O−H⋯Cl and O−H⋯N hydrogen bond building up a one dimensional network (Table 3). However, there is not any observed existence of intermolecular aromatic π-π stacking interactions between the triazole unit molecules.

Table 2 Selected bond lengths (nm) and bond angles (°) for the title compex

Mn1-N1	0.234 6(3)	Cl1-Mn1(A)	0.255 63(15)	C2-N3	0.130 9(3)
Mn1-N2	0.232 4(2)	Mn1-O1W	0.222 4(2)	C2-N4	0.137 2(3)
Mn1-Cl2	0.248 75(17)	C1-N2	0.131 8(3)	N2-N3	0.138 8(3)
Mn1-Cl1	0.252 30(15)	C7-N1	0.133 9(3)	C1-N4	0.136 6(3)
Mn1-Cl1(A)	0.255 63(15)	C3-N1	0.135 1(3)		
O1W-Mn1-N1	80.55(7)	O1W-Mn1-Cl1	167.07(5)	N2-Mn1-N1	70.12(7)
O1W-Mn1-Cl2	92.80(6)	N2 Mn1 Cl1	99.94(8)	O1W-Mn1-N2	84.80(9)
N2 -Mn1-Cl2	96.12(6)	N1-Mn1-Cl1	89.71(6)		
N1-Mn1-Cl2	165.08(6)	Cl2-Mn1-Cl1	98.60(4)		

Symmetry code: A: $-x$, $1-y$, $-z$.

Table 3　Hydrogen-bond geometry

D–H···A	D-H / nm	H···A / nm	D···A / nm	∠D–H···A / (°)
O1W–H1W···Cl2^{i}	0.082	0.229	0.307 6(3)	161
O1W–H2W···N3^{i}	0.080	0.207	0.282 7(3)	158

Symmetry codes: ^{i} $-x$, $-y+2$, $-z$.

2.2　Magnetic property

The magnetic susceptibility of $[Mn_2L_2(\mu\text{-}Cl)_2Cl_2(H_2O)_2]$ was measured in the temperature range of 1.8~300 K, and the data are shown in Fig.2 as plot of χ_m vs T. A weakly antiferromagnetic coupling was observed. The χ_m data is fitted to the equation (**1**). According to the isotopic Heisenberg exchange Hamiltonian $H=-2JS_1S_2$, the $S_1=S_2=5/2$ for Mn^{II} high-spin d^5 ion systems[18]. N is the Avogadro′s number, μ_B is Bohr magneton, g is the Landé g value, J is the exchange integral, and k is the Boltzmann′s constant. A good fit was obtained using the parameters $J=-0.165\,09$ cm^{-1} and $g=2.087\,27$.

$$\chi_m=2Ng^2\mu_B^2(A/B)/(kT) \quad (1)$$

$$A=55+30\exp[-10J/(kT)]+14\exp[-18J/(kT)]+5\exp[-24J/(kT)]+\exp[-28J/(kT)]$$

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

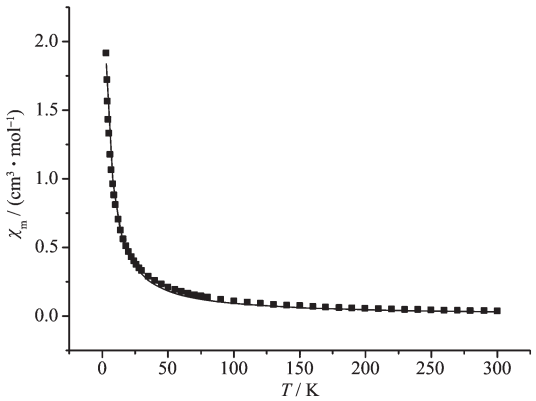


Fig.2　Plot of χ_m vs T for $[Mn_2(mmppt)_2(\mu\text{-}Cl)_2Cl_2(H_2O)_2]$

3　Conclusion

In this paper a new manganese(Ⅱ) Complex with 3-methyl-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole has been synthesized and characterized by elemental analyses and crystal structure determination. The manganese atom is in a distorted octahedral environment. Each 1,2,4-triazole entity coordinates to Mn(Ⅱ) with one triazole nitrogen atom and one pyridine nitrogen atom. Magnetic measurements show that the complex is a weakly antiferromagnetic coupling.

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