Asian Journal of Chemistry Vol. 21, No. 8 (2009), 6613-6615

NOTE

Synthesis and Crystal Structure of $MnL_3 \cdot (ClO_4)_2$ (L = Diacetyl dihydrazone)

JIAN-HONG BI*, ZI-XIAN HUANG† and MENG LI‡
Department of Chemistry and Chemical Engineering,
Hefei Teachers College, Hefei 230061, P.R. China
E-mail: bi010101@126.com

A new complex $MnL_3 \cdot (ClO_4)_2$ (L = diacetyl dihydrazone) has been synthesized and characterized by IR spectra, elemental analysis and single-crystal X-ray. The crystal is trigonal, space P-3c1 with unit cell parameters: a = 9.6546(4)Å, b = 9.6546(4)Å, c = 15.3525 (11)A, α = 90º, β = 90º, γ = 120º, V = 1239.30(11)Å^3, Z = 2, Mr = 596.32, Dc = 1.598 Mg/cm^3, μ = 0.811 mm^{-1}, F(000) = 618, T = 293(2) K, R = 0.0481, wR = 0.1627 for 3899 reflections with $I > 2\sigma(I)$.

Key Words: Manganese(II) complex, Diacetyl dihydrazone, Crystal sructure.

Recently, the chemistry of transition metal coordination with nitrogen donor ligands has become increasingly important. It has been reported useful catalysts for many reactions, resulting in higher selectivity and easier operation[1-3]. The study of inorganic-organic hybrid materials may contribute to the development of modern chemistry[4-6]. In this paper, a Mn(II) complex $MnL_3 \cdot (ClO_4)_2$, (L = diacetyl dihydrazone) is reported.

$Mn(ClO_4)_2 \cdot 6H_2O$ was prepared by our laboratory. Diacetyl dihydrazone was prepared by similar procedure given in the literature[7,8]. All reagents were of AR grade and used without further purification. IR spectra were recorded on a Nexus-870 spectrophotometer. Elemental analysis were performed on an Elementar Vario EL-III analyzer.

Synthesis: An aqueous solution (10 mL) of $Mn(ClO_4)_2 \cdot 6H_2O$ (370 mg, 1 mmol) and and a solution (20 mL) of diacetyl dihydrazone (350 mg, 3 mmol) were allowed to diffuse slowly in a U-shaped tube, across an agar-gel medium, the temperature was maintained at 25 ± 0.5 ºC in a constant-temperature box. Well-shaped brown single crystals grew within 2 weeks and were isolated in about a 45 % yield. IR (KBr, ν_{max}, cm^{-1}): (N-H) 3230; (C=N) 1642; (Cl-O) 1090, 625. Calcd. (%) for $C_{12}H_{30}N_{12}O_8Cl_2Mn$: C, 24.15; H, 5.03; N, 28.17. Found (%): C, 24.13; H, 4.98; N, 28.20.

†Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou 350002, P.R. China.

‡School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, P.R. China.

Crystal structure determination: A dark golden colour crystal 0.60 mm × 0.45 mm × 0.35 mm was selected for crystallographic data collection at 293(2) K, and structure determined with graphite monochromatic MoKα radiation (λ = 0.71073Å). A total of 3899 reflections were collected in the range of $2.44° \leq \theta \leq 27.46°$, of which 948 reflections were unique with $R_{int} = 0.0183$ and R = 0.0481 and wR = 0.1627, where $w = 1/[s^2(F_0^2) + (0.1118P)^2 + 0.2693P]$, $P = (F_0^2 + 2F_0^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.744 and -0.474e/A^3, respectively. The CCDC numbers was 607364.

The atomic coordinates and thermal parameters are listed in Table-1 and the selected bond lengths and bond angles in Table-2, respectively. Fig. 1 shows diagram of the the molecular structure of $[MnL_3](ClO_4)_2$. Fig. 2 shows a perspective view of the crystal packing in the unit cell.

TABLE-1
NON-HYDROGEN ATOMIC COORDINATES (× 10^4)
AND THERMAL PARAMETERS (× 10^3 $Å^2$)

Atom	X	Y	Z	U (eq)
Mn	0	0	2500	32(1)
N(1)	2199(2)	659(2)	1722(1)	39(1)
N(2)	2383(3)	1238(3)	886(2)	53(1)
C(1)	3249(2)	370(2)	2060(1)	36(1)
C(2)	4771(3)	743(3)	1618(2)	53(1)

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (°) OF $[MnL_3](ClO_4)_2$

Bond	Length	Angle	(°)	Angle	(°)
Mn-N(1)#1	2.2331(18)	C(1)-N(1)-N(2)	120.51(19)	N(1)#1-Mn-N(1)	94.08(6)
Mn-N(1)	2.2331(17)	C(1)-N(1)-Mn	117.54(13)	N(1)#2-Mn-N(1)	103.69(10)
N(1)-C(1)	1.287(3)	N(2)-N(1)-Mn	121.76(15)	N(1)#3-Mn-N(1)	158.04(10)
N(1)-N(2)	1.377(3)	N(1)-C(1)-C(2)	123.53(19)	C(1)#4-C(1)-C(2)	120.09(13)
Cl-O(1)	1.427(3)	O(2)-Cl-O(1)	108.05(16)	O(1)-Cl-O(1)#6	110.86(15)

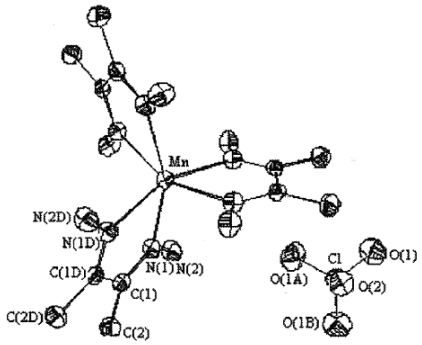

Fig. 1. Molecular structure of the title compound

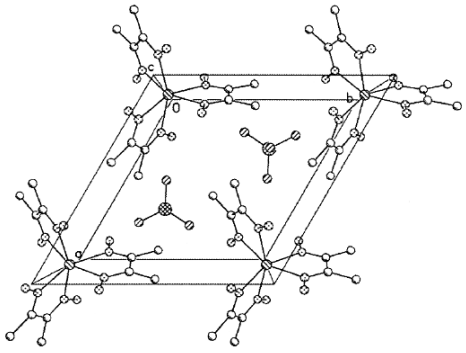

Fig. 2. Molecular packing arrangement in the unit cell

From the Fig. 1, it is easy to see that the manganese(II) ion is six-coordinated with six N atoms having octahedral geometry. There is a positive negative charge interaction between $[MnL_3]^{2+}$ and ClO_4^-.

ACKNOWLEDGEMENTS

This work is financially supported by the National Natural Science Foundation of China (20871039) and Anhui Colleges and Universities Provincial Natural Science key research projects (KJ2008A24ZC).

REFERENCES

1. B. Moulton and M.J. Zaworotko, *Chem. Rev.*, **107**, 1629 (2001).
2. J.H. Bi, L.T. Kong, Z.X. Huang and J.H. Liu, *Inorg. Chem.*, **47**, 4564 (2008).
3. J.H. Bi, H.F. Wang, Z.X. Huang, W.T. Bi and N.L. Hu, *Asian J. Chem.*, **20**, 4966 (2008).
4. X.M. Chen and M.L. Tong, *Acc. Chem. Res.*, **40**, 162 (2007).
5. J.H. Bi, R.J. Ding, Z.X. Huang, Y. Cheng and N.L. Hu, *Asian J. Chem.*, **20**, 4963 (2008).
6. J.H. Bi, X.C. Meng, Z.X. Huang and N.L. Hu, *Asian J. Chem.*, **20**, 6615 (2008).
7. D.H. Busch and J.C. Bailar, *J. Am. Chem. Soc.*, **78**, 1137 (1956).
8. J.H. Bi, W.B. Tao, Z.X. Huang and W.T. Bi, *Asian J. Chem.*, **20**, 6618 (2008).

(*Received*: 2 February 2009; *Accepted*: 16 June 2009) AJC-7663