Asian Journal of Chemistry Vol. 20, No. 5 (2008), 3673-3676

Synthesis and Crystal Structure of a $[(Phen)_3Mn]Ni(CN)_4$

JIAN-HONG BI*, HONG-LIANG WANG†, ZI-XIAN HUANG‡,
NAI-LIANG HU† and LING-TAO KONG†
Department of Chemistry, Hefei Teachers College, 327, Jinzhai Street
Hefei, Anhui 230061, P.R. China
E-mail: hxx010101@126.com

A novel complex $[(Phen)_3Mn]Ni(CN)_4$ where phen is 1,10-phenanthroline, was synthesized and characterized by IR spectra, elemental analysis and single-crystal X-ray. The crystal is monoclinic, space group P2(1)/n with unit cell parameters: a = 10.46930 (10) Å, b = 20.9570 (3) Å, c = 17.07300 (10) Å, $\alpha = 90°$, $\beta = 96.7380\ (10)°$, $\gamma = 90°$, V = 3720.03 (7) $Å^3$, Z = 4, Mr = 812.39, Dc = 1.451 Mg/cm^3, $\mu = 0.899\ mm^{-1}$, F(000) = 1668, T = 293 ± 2 K, R = 0.0763, wR = 0.1741 for 6535 reflections with $I > 2\sigma(I)$. The crystal structure analysis shows that the manganese(II) is a six-coordinated in a slightly distorted octahedron environment, then complex forms layer structure and packs in 3-D net structure through hydrogen bonds and π-π stacking interactions.

Key Words: Manganese(II) compound, π-π Stacking interactions, Crystal structure, Hydrogen bonds.

INTRODUCTION

There has been increasing interest of Mn(II) and phenanthroline complexes in the field of coordination chemistry[1-3]. At the same time, cyanide have played a prominent role in the design and construction of molecular magnetic material due to their stability and ease of chemical modification[4-7]. In an effort to bring these two research areas together, recently, in our laboratory, a series of transition metal compounds have been synthesized and studied[8-10]. In this paper, the synthesis and crystal structure of manganese(II) complex $[(Phen)_3Mn]Ni(CN)_4$ is reported.

EXPERIMENTAL

$Mn(ClO_4)_2 \cdot 6H_2O$ was prepared by our laboratory, the other reagents were of AR grade and used without further purification. IR spectra were recorded on a Nexus-870 spectrophotometer. Elemental analysis were performed on a Elementar Vario ELZ(III) analyzer.

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

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

Synthesis: An aqueous solution (10 mL) of $Na_2Ni(CN)_4$ (210 mg, 1 mmol) and a mixed solution (20 mL) of $Mn(ClO_4)_2 \cdot 6H_2O$ (370 mg, 1 mmol, 10 mL water) and 1,10-phenanthroline (198 mg, 1 mmol, 10 mL alcohol) were allowed to diffuse slowly in a U-shaped tube, across an agar-gel medium, the temperature was maintained at 4 ± 0.5 ºC in a constant-temperature box. Well-shaped red single crystals grew within 3 weeks and were isolated in about a 30 % yield. IR (KBr, ν_{max}, cm^{-1}): (N-H) 3390, (C=N) 2120, (C=N) 1660, (C=C) 1520, 1420, (phen) 848, 725. Elemental analysis: Calcd. (%) for $[(Phen)_3Mn]Ni(CN)_4$: C, 59.13; H, 3.72; N, 17.24; Found (%): C, 59.10; H, 3.70; N, 17.23.

Crystal structure determination: A single crystal of compound with dimensions of 0.46 mm × 0.46 mm × 0.36 mm was selected for crystallographic data collection at 293 ± 2 K and structure determination on a Siemens SMART CCD area-detector diffractometer with graphite-monochromatic MoK_α radiation (λ = 0.71073 Å). A total of 11372 reflections were collected in the range of $3.04^\circ \leq \theta \leq 27.48^\circ$, of which 6535 reflections were unique with Rint = 0.0358. Lp effects and empirical absorption were applied in data corrections. The structure was solved by direct methods and expanded using Fourier techniques, and SHELXS-97 program system was used in the solution and refinement of the structure. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 220 variable parameters for 6535 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R_1 = \Sigma(||F_0|-|F_c||) / \Sigma|F_0| = 0.0763 \quad (1)$$

and

$$wR_2 = \{\Sigma[w(F_0^2-F_C^2)^2] / \Sigma w(F_0^2)^2\}^{1/2} = 0.1741 \quad (2)$$

where $w = 1/[\sigma^2(F_0^2) + (0.0537P)^2 + 16.3288P]$, and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.917 and -0.645e/$Å^3$, respectively.

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters are listed in Table-1, and the selected bond lengths and bond angles in Table-2. Fig. 1 shows the molecular structure of the title compound. Fig. 2 shows the packing diagram of the title compound. From the Fig. 1, it is easy to see that the manganese(II) ion is six-coordinated with six N atoms.

The hydrogen-bonded geometry involving two kinds of water molecules is characterized in Table-3. One is between crystal waters, and the other is between crystal water and $[Ni(CN)_4]^{2-}$. In one layer, the distance between superpositional phenanthroline rings, which are from adjacent two $[(Phen)_3Mn]^{2+}$,

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

Atom	x	y	z	U(eq)
Ni	696(1)	2783(1)	5498(1)	52(1)
Mn	2202(1)	499(1)	2799(1)	28(1)
N(1)	2932(8)	1887(4)	5935(6)	117(3)
N(2)	2142(7)	3208(4)	4169(4)	77(2)
C(1)	2053(7)	2225(4)	5776(5)	70(2)
C(2)	1589(7)	3060(3)	4682(5)	60(2)
O(1)	1953(6)	3183(4)	2478(4)	100(2)
O(2)	-1761(8)	2931(5)	3476(6)	60(2)

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (º)

Bond	Length	Angle	(º)	Angle	(º)
Ni-C(4)	1.849(8)	O(5)-O(4)-N(1)	61.2(10)	Ni(11)-Mn-N(12)	79.70(2)
Ni-C(3)	1.858(7)	C(2)-N(2)-O(1)	141.3(6)	C(20)-N(12)-Mn	129.00(4)
N(1)-C(1)	1.168(10)	C(1)-N(1)-O(5)	138.8(10)	N(14)-Mn-N(11)	169.51(19)
N(2)-O(1)	2.871(10)	O(4)-O(5)-N(1)	90.4(12)	C(21-N(12)-Mn	112.20(4)
Mn-N(11)	2.083(5)	O(5)-N(1)-O(4)	28.4(6)	N(4)-C(4)-Ni	174.70(7)

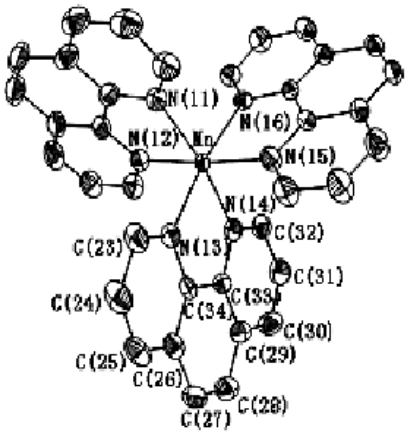

Fig. 1. Atom labelling scheme for $[Mn(Phen)_3]^{2+}$

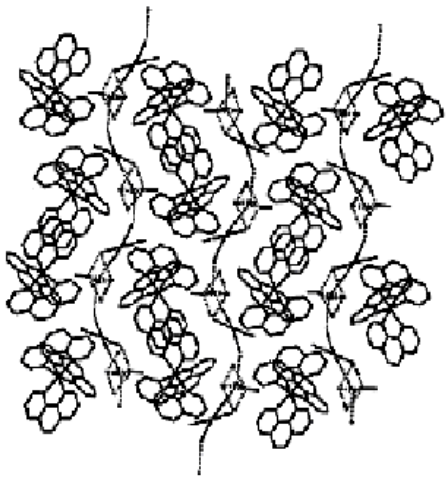

Fig. 2. Packing diagram of the title compound

TABLE-3
HYDROGEN BOND DISTANCES (Å) AND ANGLES (°)

D–H···A	D–H	H···A	D···A	∠ DHA
O(5)–H(1)···O(4)	0.894(16)	1.845(16)	2.7392(17)	178.0(2)
O(5)#1–H(2)···O(1)	0.864(16)	2.067(16)	2.9287(18)	169.0(2)
O(1)–H(4)···O(3)#1	0.876(15)	1.977(16)	2.8486(17)	172.6(19)
O(2)–H(3)···O(3)#1	0.875(15)	2.099(16)	2.9305(18)	158.0(2)

is about 3.317 Å. That means there is π-π stacking interaction. Between $[(Phen)_3Mn]^{2+}$ and $[Ni(CN)_4]^{2-}$ has the static electricity attraction, as shown in Fig. 2. In layers, the distance of two adjacent phenanthroline rings is about 3.538 Å. That means there is also π-π stacking interaction. By the hydrogen-bonding and π-π stacking interactions, the title compound molecules pack in a three-dimensional net structure.

Conclusion

Crystal structure of a novel manganese(II) complex has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis.

ACKNOWLEDGEMENT

This work is financially supported by the Nature Science Foundation of Anhui Universities.

REFERENCES

1. B. Moulton and M.J. Zaworotko, *Chem. Rev.*, **101**, 1629 (2001).
2. J. Fan, W.Y. Sun, T.A. Okamura, K.-B. Yu and N. Ueyama, *Inorg. Chem. Acta*, **319**, 240 (2001).
3. J.Y. Lu, M.A. Lawandy and J. Li, *Inorg. Chem.*, **38**, 2695 (1999).
4. G.F. Swiegers and T.J. Malefetse, *Chem. Rev.*, **100**, 3483 (2000).
5. F.L. De Paththou, E. Belorizky, R. Calemczuk, D. Luneau, C. Marcenat, E. Ressouche, P. Turek and P. Rey, *J. Am. Chem. Soc.*, **117**, 11247 (1995).
6. Y. Yamamoto and S. Suzuki, *J. Chem. Soc., Daltons Trans.*, 1566 (2001).
7. F.A. Cotton, S.M. Morehouse and J.S. Wood, *Inorg. Chem.*, **3**, 1603 (1964).
8. J.H. Bi, F.X. Xie, X.D. Zhao, Q. Chen, J.D. Xu and S.S. Ni, *Asian J. Chem.*, **16**, 137 (2004).
9. N.L. Hu, H.Z. Dong, Z.X. Huang and F.X. Xie, *Asian J. Chem.*, **17**, 1276 (2005).
10. J.H. Bi, J.M. Song, Z.X. Huang, Y.H. Wang and L.T. Kong, *Asian J. Chem.*, **18**, 2365 (2006).

(*Received*: 31 August 2007; *Accepted*: 4 February 2008) AJC-6301