

## Synthesis and Crystal Structure of Charge Separate Manganese Complex

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A novel complex  $Mn(tab_a)_2 \cdot 4H_2O$  [ $Htab_a = 4-(1H-1,2,4-triazol-1-yl)$  benzoic acid] containing carboxylate-triazole ligands has been synthesized and characterized by elemental analyses, IR and X-ray single crystal diffraction. The crystal of the complex belongs to the triclinic system and  $P\bar{1}$  space group with  $a = 6.153(5) \text{ \AA}$ ,  $b = 7.047(5) \text{ \AA}$ ,  $c = 12.257(5) \text{ \AA}$ ,  $\alpha = 80.366(5)^\circ$ ,  $\beta = 87.997(5)^\circ$ ,  $\gamma = 72.673(5)^\circ$ ,  $Z = 1$ ,  $V = 500.1(6) \text{ \AA}^3$ ,  $D_c = 1.671 \text{ g cm}^{-3}$ ,  $\mu = 0.723 \text{ mm}^{-1}$ ,  $F(000) = 259$ ,  $R_{int} = 0.0373$ ,  $wR = 0.0993$ . X-ray crystallography shows the manganese(II) ion is coordinated with two triazole nitrogen atoms from two ligands and four oxygen atoms from four water molecules. However, manganese(II) ions only coordinate with N from triazole and not with O from carboxylate group of the ligand, which is different with the reported manganese complexes. In addition, the title complex is a charge separate style that the positive charge center is in manganese atom and the negative charge center is in the carboxylic root of the ligand.

**Keywords:** Manganese complex, Crystal structure, Charge separate structure.

### INTRODUCTION

Manganese compounds are not only low cost but also environmentally friendly<sup>1-3</sup>. Thus, these complexes based on functional organic building blocks have been rapidly developed in recent years because of their fascinating structural diversities and potential applications in magnetism, catalysis, electrical conductivity, cancer research and nucleic acid chemistry<sup>4-7</sup>. As is known to all, the framework structure is primarily dependent on the coordination properties of the metal centers and the functionality of the ligands. In addition to coordination bonding, various weak interactions, especially strong hydrogen bonding and aromatic  $\pi$ - $\pi$  stacking interactions also play very important roles in determining the ultimate architectures<sup>8-10</sup>.

To get anticipant and interesting structures and desired properties, an enormous amount of researches have been carried on by choosing versatile binding-ligand. The heterocyclic carboxylic acids as multifunctional building blocks have attracted great attention, such as pyridine-, triazole-, imidazole- and pyrazole-carboxylic acids<sup>11-12</sup>. The heterocyclic nitrogen atoms can coordinate to the metal centers, while carboxylate groups can coordinate in monodentate, chelate or bridged modes resulting in the formations of various MOFs with novel structures and useful properties.

1H-1,2,4-triazoles are a common component of a large number of natural products and pharmacologically active molecules<sup>13,14</sup>. The triazoles ring functions as a rigid ligand toward transition metal ions in a number of biologically important systems. These facts make triazoles and its derivatives important target analytes. In order to balance the rigidity and flexibility of the ligands and use their multifunctional coordination ability, we synthesized  $Htab_a$  as organic ligand which both nitrogen and oxygen donor atoms could bond to transition metal ions with versatile coordination modes.

In this paper we reported the crystal structure of a complex synthesized by  $Mn(AcO)_2 \cdot 4H_2O$  with  $Htab_a$  and showed the intriguing three-dimensional (3D) layers structure with a six coordinated Mn(II) ion. However, Mn was only coordinated with nitrogen from triazole not oxygen from carboxylate group. It was probably attribute to the intermolecular weak interactions in the supermolecular system. In addition, we found that the title complex was a charge separate style that the positive charge center was in manganese atom and the negative charge center was in the carboxylic root of the ligand and this was rare reported.

### EXPERIMENTAL

All chemicals used were of analytical pure. The solvents were purified by conventional methods. <sup>1</sup>H NMR spectrum

(acetone- $d_6$ ) was performed on Bruker 400 spectrometer with TMS as an internal standard. IR spectra were recorded using a Nicolet FT-IR with KBr disks in the range of 4000-400  $\text{cm}^{-1}$ . Element analysis was performed using a Perkin-Elmer 240 analyzer. The mass spectra were obtained on ZAB-HS mass spectrometer (EI source).

**Synthesis of 4-(1H-1,2,4-triazol-1-yl)benzaldehyde (TABA):** 1H-1,2,4-triazole (3 g, 43 mmol),  $\text{K}_2\text{CO}_3$  (6 g, 43 mmol), 30 mL DMSO and a little Aliquat 336 were added to a round-bottom flask equipped with a magnetic stirrer and a reflux condenser. 4-Fluorobenzaldehyde (3.5 mL, 33 mmol) was added dropwise to the mixture at 90 °C for 5 min. The reaction mixture was refluxed for 24 h at 80 °C, cooled to room temperature and filter after adding 150 mL ice-water. The product was washed with water, dried and obtained as yellow crystals (2.7 g), Yield: 47.79 %.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) [ppm]  $\delta$ : 10.504 (s, 1H, CHO), 9.478 (s, 1H, triazoleH), 8.326 (s, 1H, triazoleH), 8.121-8.113 (m, 4H, ArH). MS  $m/z$  (%): 173.1 ( $\text{M}^+$ , 100), 174.1 ( $\text{M}^++1$ ), IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3435 (m), 3119 (m), 2931 (m), 2958 (s), 1698 (m), 1604 (m), 1403 (m), 1289 (m), 1216 (m), 1139 (m), 1049 (m), 977 (m), 840 (m), 672 (m), 510 (m). Anal. Calcd. (%) for  $\text{C}_9\text{H}_7\text{N}_3\text{O}$  (173.1): C, 62.42; H, 4.07; N, 24.27; O, 9.24 %. Found: C, 62.39; H, 4.10; N, 24.25; O, 9.26 %.

**Synthesis of the ligand Htaba:** TABA (2.15 g, 12.4 mmol) and 60 mL 6.5 % (wt) NaOH (aq.) were added to a round-bottom flask equipped with a magnetic stirrer and a reflux condenser at 60 °C for 0.5 h. Then  $\text{AgNO}_3$  (4 g, 24 mmol) was added to the mixture. The reaction mixture was refluxed for 24 h at 60 °C, cooled to room temperature and filter. Added HCl to adjust pH to 2 and a great deal of ivory white sediments were obtained. The product was filtered and dried. Weight: 1.06 g, Yield: 45 %.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) [ppm]  $\delta$ : 13.147 (s, 1H, COOH), 9.428 (s, 1H, triazoleH), 8.300 (s, 1H, triazoleH), 8.125-8.103 (d,  $J = 8.80$  Hz, 2H, ArH), 8.028-8.006 (d,  $J = 8.80$  Hz, 2H, ArH). MS  $m/z$  (%): 189.1 ( $\text{M}^+$ , 100), 162.1 ( $\text{M}^+-\text{OH}$ ), 134.1 ( $\text{M}^+-\text{COOH}$ ). IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3133 (w), 2907 (m), 2788 (m), 2618 (m), 2522 (m), 1902 (m), 1694 (s), 1620 (s), 1524 (s), 1444 (s), 1275 (s), 1155 (s), 977 (s), 769 (s), 680 (m), 526 (m). Anal. calcd. (%) for  $\text{C}_9\text{H}_7\text{N}_3\text{O}_2$  (189.1): C, 57.14; H, 3.73; N, 22.21; O, 16.92 %. Found: C, 57.11; H, 3.76; N, 22.23; O, 16.90 %.

**Synthesis of complex  $\text{Mn}(\text{taba})_2 \cdot 4\text{H}_2\text{O}$ :** Htaba (0.0189 g, 0.1000 mmol) was dissolved in 1.5 mL DMSO, then the solution was filtered, DMSO (0.25 mL) and methanol was respectively added to the filtrate as a cushion.  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.0800 g, 0.4300 mmol) was dissolved in 1.5 mL methanol and was added over the cushion. Colourless needle single crystals suitable for X-ray diffraction were obtained after two months by slow evaporation of the filtrate at room temperature. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3391 (m), 3116 (m), 1607 (m), 1528 (s), 1387 (s), 1279 (s), 1147 (m), 977 (m), 861 (m), 784 (m), 672 (m), Anal. calcd. (%) for  $\text{C}_{18}\text{H}_{20}\text{N}_6\text{O}_8\text{Mn}$  (503.3): C, 42.95; H, 4.01; N, 16.70; O, 25.43 %. Found: C, 42.93; H, 4.03; N, 16.73; O, 25.40 %.

The IR spectrum of the ligand in complex shows a series of peaks at 1607, 1477, 1279, 861 and 784  $\text{cm}^{-1}$  are the characteristic of aromatic ring<sup>15</sup>. To compare with the IR spectrum

of raw material Htaba, the absence of a strong peak at 1694  $\text{cm}^{-1}$  indicates that the carbonyl group has been completely clear away. Moreover, the new double peaks at 1528  $\text{cm}^{-1}$  and 1387  $\text{cm}^{-1}$  show that the carboxyl is deprotonated to generate  $\text{COO}^-$  anion, which is agreement with its X-ray single structure. The double peaks are the characteristics of  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$ , respectively<sup>16</sup>. And the difference between the asymmetric stretching and symmetric stretching bands of the carboxyl group ( $\Delta\nu = \nu_{\text{as}}(\text{C}=\text{O}) - \nu_{\text{s}}(\text{C}-\text{O})$ ) is 141  $\text{cm}^{-1}$ , which indicates strong conjugative effect has been occurred. The broad band around 3391  $\text{cm}^{-1}$  indicates the presence of  $\nu(\text{O}-\text{H})$  stretching frequency of coordinated water molecule<sup>17</sup>.

**X-ray crystallography:** Data collections [ $0.99^\circ < \theta < 25.00^\circ$ ] were performed using a Bruker Smart 1000 CCD diffractometer with MoK $\alpha$  radiation with a multi-scan mode [ $\gamma = 0.71069 \times 10^{-10}$  m] at room temperature. The structure was solved with direct methods using the SHELXL-97 program<sup>18</sup> and refined anisotropically with SHELXL-97 using full-matrix least-squares procedure giving for the complex, a final  $R_1$  value of 0.0373 for 163 parameters and 1743 unique reflections with  $I \geq 2\sigma(I)$  and  $wR_2$  of 0.0993 for all 4680 reflections. All the nonhydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-97 using full matrix least-squares procedure. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atoms and fixed displacement parameters (Table-1).

TABLE-1  
CRYSTALLOGRAPHIC DATA FOR THE  $\text{Mn}(\text{II})$  COMPLEX

Compound	$\text{Mn}(\text{taba})_2 \cdot 4\text{H}_2\text{O}$
Empirical formula	$\text{C}_{18}\text{H}_{20}\text{N}_6\text{O}_8\text{Mn}$
Fw	503.34
Crystal system	$\text{P}\bar{1}$
Space group	triclinic
a (Å)	6.153(5)
b (Å)	7.047(5)
c (Å)	12.257(5)
$\alpha$ (deg)	80.366(5)
$\beta$ (deg)	87.997(5)
$\gamma$ (deg)	72.673(5)
V (Å <sup>3</sup> )	500.1(6)
Z	1
T (K)	298(2)
$D_{\text{calcd}}$ ( $\text{g cm}^{-3}$ )	1.671
$\mu$ ( $\text{mm}^{-1}$ )	0.723
$2\theta$ max (deg)	50.00
Tot. no. data	4680
No. unique data	1743
No. params refined	163
R1	0.0373
wR2	0.0993
GOF	1.092

CCDC 719381 (for the coordination compound) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

**X-ray crystal structure analysis:** The metal coordination compound,  $\text{Mn}(\text{taba})_2 \cdot 4\text{H}_2\text{O}$ , crystallizes in the triclinic system and  $P\bar{1}$  space group as shown in Fig. 1. A six-coordinate Mn(II) cationic with octahedron geometry coordinated with two triazole nitrogen atoms from the different ligands and four oxygen atoms from four water molecules can be seen. The bond lengths,  $\text{Mn}(1)-\text{O}(1) = 2.169(2)$  Å,  $\text{Mn}(1)-\text{O}(2) = 2.223(3)$  Å and  $\text{Mn}(1)-\text{N}(2) = 2.249(2)$  Å, which are consistent with those values reported for Mn-carboxylate and Mn-triazole complexes<sup>19-20</sup>. The bond angles,  $\text{O}(1)-\text{Mn}(1)-\text{O}(1)a$ ,  $\text{O}(2)-\text{Mn}(1)-\text{O}(2)a$  and  $\text{N}(2)-\text{Mn}(1)-\text{N}(2)a$  being quite close to  $180^\circ$  and reveals that the complex is an almost perfect octahedral geometry. The selected bond lengths and bond angles for the complex are listed in Table-2. The dihedral angle between the phenyl ring and the 1,2,4-triazole ring is  $8.63^\circ$  and the terminal carboxylate moiety has a  $13.21^\circ$  dihedral angle with the plane of the attached phenyl ring, which likes wings and reveals perfect planarity. Unlike the reported complexes  $\text{Mn}(\text{atza})_2(\text{H}_2\text{O})_4$  (Hatza = 5-aminotriazole-1-acetic acid) and  $\text{Mn}(\text{nptza})_2(\text{CH}_3\text{OH})_4$  (Hnptza = 5-[(4-nitryl) phenyl] tetrazole-1-acetic acid)<sup>21</sup>, the Mn(II) cationic of the title complex is coordinated with triazole nitrogen atoms but not carboxyl oxygen atoms perhaps because of the perfect planarity of the ligand and strong  $\pi$ - $\pi$  conjugate effect between the carboxylate and the phenyl ring which reduce the coordination ability of the carboxylate. This is also the reason for the formation of the charge separate complex; furthermore, the charge separate structure is rare reported.

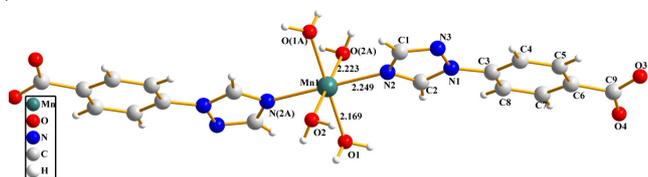


Fig. 1. Coordination environments of Mn with the atom numbering scheme

TABLE-2  
SELECTED BOND LENGTHS (Å) AND  
ANGLES ( $^\circ$ ) FOR  $\text{Mn}(\text{taba})_2 \cdot 4\text{H}_2\text{O}$

Complex $\text{Mn}(\text{taba})_2 \cdot 4\text{H}_2\text{O}$			
$\text{Mn}(1)-\text{O}(1)$	2.169(2)	$\text{O}(1)-\text{Mn}(1)-\text{O}(1)a$	180.0(1)
$\text{Mn}(1)-\text{O}(2)$	2.223(3)	$\text{O}(2)-\text{Mn}(1)-\text{O}(2)a$	180.0(1)
$\text{Mn}(1)-\text{N}(2)$	2.249(2)	$\text{N}(2)-\text{Mn}(1)-\text{N}(2)a$	180.0(1)
$\text{C}(9)-\text{O}(3)$	1.254(3)	$\text{O}(1)-\text{Mn}(1)-\text{O}(2)$	88.0(1)
$\text{C}(9)-\text{O}(3)$	1.248(4)	$\text{O}(2)-\text{Mn}(1)-\text{N}(2)$	87.6(1)
Symmetry codes: $\text{O}(1)a, x, y, z$ ; $\text{O}(2)a, x, y, z$ ; $\text{N}(2)a, 1-x, 1-y, -z$			

Weak interactions play significant roles in forming the topological structures. It can be seen from Fig. 2 that adjacent molecules are interacted with each other through weak  $\text{C}-\text{H}\cdots\text{O}$  interactions [ $d(\text{C}(2)\cdots\text{O}(2)) = 3.503(4)$  Å,  $d(\text{H}(1)\cdots\text{O}(2)) = 2.576(3)$  Å,  $\angle(\text{C}(2)-\text{H}(1)\cdots\text{O}(2)) = 174.46(20)^\circ$ ] forming a 1D chain structure along the  $a$ -axis and the Mn(II) ions ( $\text{Mn}(1)\cdots\text{Mn}(2) = 6.153(5)$  Å) are linearly arranged along the  $a$ -axis. As shown in Fig. 3, the 1-D chains further link along the  $c$ -axis direction to form a mimic-2D sandwich structure

through hydrogen bonds with the H from the coordinated water molecule and the O from carboxyl [ $d(\text{O}(2)\cdots\text{O}(3)) = 2.703(3)$  Å,  $d(\text{H}(12)\cdots\text{O}(3)) = 1.926(3)$  Å,  $\angle(\text{O}(2)-\text{H}(12)\cdots\text{O}(3)) = 162.86(57)^\circ$ ], at the same time,  $\pi$ - $\pi$  stacking interactions between the phenyl of the ligand and the triazole ring in neighbouring complexes with distance of 3.754 Å and an angle of  $0.39^\circ$  play concernful roles in forming the 2D layer structure. Finally, the extended mimic-3D topological structures were formed *via* hydrogen bonds with the H from the coordinated water molecule and the O from carboxyl [ $d(\text{O}(1)\cdots\text{O}(4)) = 2.608(3)$  Å,  $d(\text{H}(9)\cdots\text{O}(4)) = 1.694(3)$  Å,  $\angle(\text{O}(1)-\text{H}(9)\cdots\text{O}(4)) = 176.24(34)^\circ$ ] (Fig. 4).

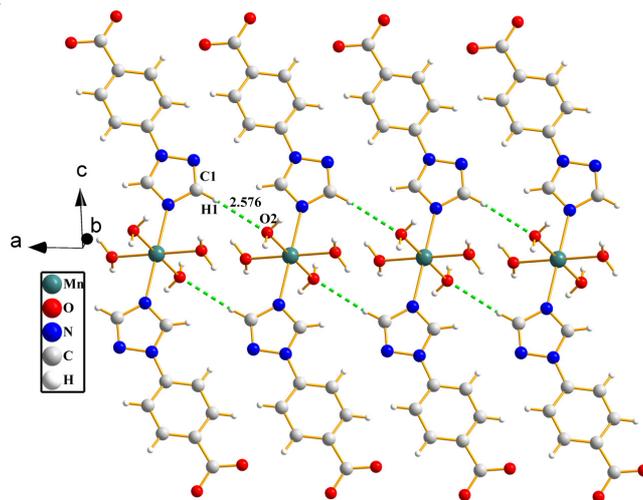


Fig. 2. 1-D framework of complex showing the weak  $\text{C}-\text{H}\cdots\text{O}$  interactions along the  $a$ -axis

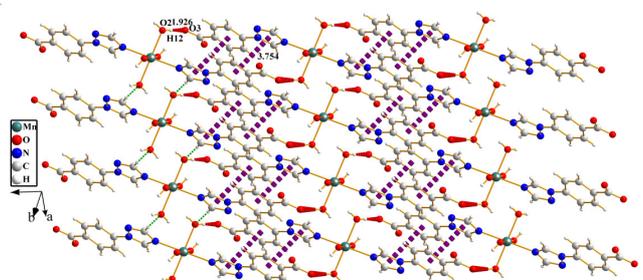


Fig. 3. 2-D architecture is connected by the  $\pi$ - $\pi$  stacking interactions and  $\text{O}-\text{H}\cdots\text{O}$  strong hydrogen bonding interactions along the  $c$ -axis

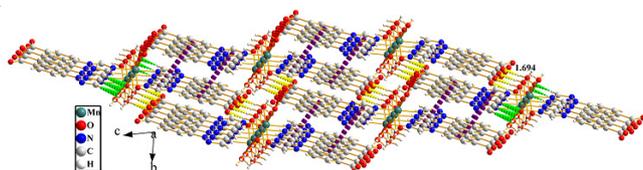


Fig. 4. 3-D layer structure resulting from strong hydrogen bonding interactions between carbonyl O and  $\text{H}_2\text{O}$  along the  $b$ -axis

**Single-photon excited fluorescence (SPEF):** There is considerable contemporary interest in the development of new organic/organometallic luminescent compounds. This is because of the enormous potential of such materials in niche technological applications based on the possibility of using

them as photo- and electroluminescent devices<sup>22</sup>. Therefore the photoluminescence properties of the ligands and complex were measured in the solid state at room temperature. The nanosecond range of lifetime in the solid state at 298 K reveals that the emission is fluorescent in nature. The measurements were carried out under the same experimental conditions and excited at a wavelength of 320 nm. Then we found that the ligand exhibits photoluminescence with emission at 368 nm and the complex has no emissions perhaps due to the centrosymmetric configuration of the complex.

### Conclusion

In summary, a new complex  $\text{Mn}(\text{taba})_2 \cdot 4\text{H}_2\text{O}$  is constructed by two Htaba ligands and four water molecules has been synthesized by the reaction of  $\text{Mn}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$  with Htaba. The complex exhibits an intriguing three-dimensional (3D) layer structure with six coordinated metal ions Mn(II) and a rare reported charge separate style. The successful synthesis of the complex confirms that it is crucial to choose an appropriate ligand for the formation of unique complex. Unfortunately, the complex has no UV absorption and fluorescent properties at solid state and further studies of the complex are in progress.

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