Guanidinium Bis(pyridine-2,6-dicarboxylato-*N,O,O*)manganese(II)

Davar M. BOGHAEE^{1*} and Mohammad Mahdi NAJAFPOUR^{*}

Department of Chemistry, Sharif University of Technology, P.O. Box 11155-9616 Tehran, Iran

The title complex was synthesized and structurally characterized by single-crystal X-ray diffraction. This complex was solved in the triclinic system, space group $P\bar{1}$, with the following unit-cell parameters: $a = 8.5657(4)\text{\AA}$, $b = 10.9848(5)\text{\AA}$, $c = 13.1681(6)\text{\AA}$, $\alpha = 112.617(1)^\circ$, $\beta = 99.646(1)^\circ$, $\gamma = 90.849(1)^\circ$, $Z = 2$, $V = 1123.28(9)\text{\AA}^3$. The final R value was $R1 = 0.0344$ for 15675 measured reflections.

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Numerous complexes of pyridinecarboxylic acids with transition metals have been investigated because of their

interesting structural, redox and water oxidation properties.^{1,2} Pyridine-2,6-dicarboxylic (dipicolinic) acid has been demonstrated in spores of aerobic and anaerobic bacteria. It is released during the germination of spores of aerobes. Pyridine-2,6-dicarboxylic forms a metal complex with divalent metal ions, especially with manganese and calcium.³ Also the guanidinium cation has an important role in enzymes; for example, X-ray structural evidence places the guanidinium cation of the conserved arginine 357 residue of CP43 within a few Å to the Mn_4Ca cluster of the water-oxidizing complex (WOC) in photosystem II.⁴

Fig. 1 Chemical structure of the title complex.

Table 1 Crystal and experimental data

Empirical formula	$\text{C}_{16}\text{H}_{22}\text{MnN}_8\text{O}_{10}$
Formula weight	541.36
Temperature	100(2)K
Crystal system	triclinic
Wavelength	0.71073 Å
Space group	$P\bar{1}$
Unit cell dimensions	$a = 8.5657(4)\text{\AA}$ $\alpha = 112.617(1)^\circ$ $b = 10.9848(5)\text{\AA}$ $\beta = 99.646(1)^\circ$ $c = 13.1681(6)\text{\AA}$ $\gamma = 90.849(1)^\circ$
V	$1123.28(9)\text{\AA}^3$
Z	2
D_x	1.601 Mg/m^3
Absorption coefficient	0.659 mm^{-1}
Crystal size, color	$0.29 \times 0.20 \times 0.07 \text{ mm}^3$, yellow
$2\theta_{\text{max}}$	61.98°
$R1$ indices [6168 refs $I > 2\sigma(I)$]	$R1 = 0.0344$, $wR2 = 0.0887$
Reflections collected	15675
Max. and min. transmission	0.960 and 0.851
$(\Delta\rho)_{\text{max,min}}$	0.486 and $-0.546 \text{ e.\AA}^{-3}$
Diffractometer	Bruker APEX II CCD
Program system	SHELXL-97
Structure determination	SHELXS-97
Refinement	full matrix least
CCDC deposition number	661203

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the complex

Atom	x	y	z	$U(\text{eq})$
Mn(1)	7444(1)	2480(1)	2225(1)	12(1)
O(1)	5842(1)	1921(1)	3183(1)	15(1)
O(2)	5139(1)	2470(1)	4860(1)	17(1)
O(3)	8962(1)	4191(1)	2214(1)	16(1)
O(4)	9588(1)	6391(1)	3079(1)	19(1)
O(5)	5862(1)	2410(1)	728(1)	16(1)
O(6)	5068(1)	1340(1)	-1129(1)	22(1)
O(7)	9277(1)	1402(1)	2912(1)	14(1)
O(8)	10559(1)	-430(1)	2541(1)	19(1)
N(1)	7523(1)	4157(1)	3806(1)	11(1)
N(2)	7805(1)	672(1)	857(1)	12(1)
N(3)	8006(2)	4674(1)	180(1)	19(1)
N(4)	6212(2)	5610(1)	-755(1)	17(1)
N(5)	7047(2)	6656(1)	1153(1)	17(1)
N(6)	7287(2)	9505(1)	5373(1)	17(1)
N(7)	8485(1)	11010(1)	4849(1)	16(1)
N(8)	6546(2)	9439(1)	3576(1)	16(1)
C(1)	6837(2)	4008(1)	4594(1)	12(1)
C(2)	7013(2)	5002(1)	5664(1)	15(1)
C(3)	7885(2)	6181(1)	5881(1)	17(1)
C(4)	8554(2)	6344(1)	5045(1)	15(1)
C(5)	8361(2)	5292(1)	4012(1)	12(1)
C(6)	5858(2)	2689(1)	4191(1)	13(1)
C(7)	9042(2)	5303(1)	3029(1)	14(1)
C(8)	6970(2)	405(1)	-171(1)	12(1)
C(9)	7107(2)	-748(1)	-1073(1)	15(1)
C(10)	8124(2)	-1644(1)	-874(1)	15(1)
C(11)	8979(2)	-1366(1)	199(1)	14(1)
C(12)	8788(2)	-179(1)	1047(1)	12(1)
C(13)	5868(2)	1466(1)	-218(1)	14(1)
C(14)	9618(2)	288(1)	2260(1)	12(1)
C(15)	7086(2)	5641(1)	198(1)	14(1)
C(16)	7426(2)	9984(1)	4605(1)	13(1)
O(1W)	4582(1)	6927(1)	2895(1)	20(1)
O(2W)	1539(1)	7125(1)	1952(1)	18(1)

[†] To whom correspondence should be addressed.
E-mail: dboghaei@sharif.edu

$$U_{\text{eq}} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha).$$

Table 3 Selected bond distances (Å) and angles (°)

Bond distances

Mn(1)-O(5)	2.171(1)	Mn(1)-O(1)	2.237(1)
Mn(1)-N(1)	2.174(1)	Mn(1)-O(7)	2.256(1)
Mn(1)-N(2)	2.177(1)	Mn(1)-O(3)	2.276(1)

Bond Angles

O(5)-Mn(1)-N(1)	119.81(4)	O(5)-Mn(1)-O(1)	104.17(4)
O(5)-Mn(1)-N(2)	73.00(4)	N(1)-Mn(1)-O(1)	72.01(4)
N(1)-Mn(1)-N(2)	167.13(4)	N(2)-Mn(1)-O(1)	107.43(4)

Torsion Angles

O(5)-Mn(1)-O(1)-C(6)	-126.00(1)
N(1)-Mn(1)-O(1)-C(6)	-8.79(9)
N(2)-Mn(1)-O(1)-C(6)	157.71(9)
O(7)-Mn(1)-O(1)-C(6)	88.57(1)
O(3)-Mn(1)-O(1)-C(6)	-16.16(1)

Fig. 3 Crystal packing fragment. Hydrogen atoms are omitted for clarity.

The complex (Fig. 1) was prepared by dissolving guanidinium carbonate (4 mmol, 720 mg) and pyridine-2,6-dicarboxylic acid (2 mmol, 334 mg) in water (20 ml); the mixture was stirred for about 1 h at room temperature; then manganese(II) chloride (1 mmol, 126 mg) was added to this solution and stirred for about 3 h at room temperature. This solution yielded yellow crystals of the complex after 10 d.

Data were collected on a Bruker APEX II CCD. The structures were solved using direct methods (SHELXS-97) and refined against F^2 using the SHELXL-97 software.⁵ All of the hydrogen atoms were treated in riding model with the equivalent thermal parameters of the atoms to which

Fig. 3 Crystal packing fragment. Hydrogen atoms are omitted for clarity.

corresponding H atoms are bonded. The crystal and experimental data are given in Table 1. The atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms are listed in Table 2. Selected bond distances, angles and torsion angles are listed in Table 3. Mn is hexacoordinated in an approximately octahedral geometry, chelated by four O atoms and two N atoms from two pyridine-2,6-dicarboxylate ligands (Mn(1)-O(1)=2.237(1) Å, Mn(1)-N(1)=2.174(1) Å, Mn(1)-O(3)=2.276(1) Å, Mn(1)-N(2)=2.177(1) Å, Mn(1)-O(5)=2.171(1) Å, Mn(1)-O(7)=2.256(1) Å).

Hydrogen bonds between the water molecules, the O atoms of the carboxylate groups and the guanidinium link the molecules into a three-dimensional network (for example H(3A)⋯O(3)^{#1} = 2.11 Å, H(5A)⋯O(4)^{#1} = 2.31 Å, H(5B)⋯O(6)^{#2} = 2.00 Å, H(4B)⋯O(5)^{#2} = 1.94 Å, #1 = x, y, z , #2 = $-x+1, -y+1, -z$). The ORTEP structure of the title complex is shown in Fig. 2. A packing diagram of the title complex is shown in Fig. 3.

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