

2-Dimensional Manganese-Imidazoledicarboxylate Coordination Polymer: Preparation and Structure of aqua(imidazole-4,5-dicarboxylato)manganese(II), [Mn(IDC)(H₂O)]

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2차원 Manganese-Imidazoledicarboxylate 배위 고분자: aqua(imidazole-4,5-dicarboxylato)manganese(II), [Mn(IDC)(H₂O)]의 합성 및 구조

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요 약

NaOAc · 3H₂O 존재 하에서, manganese nitrate (Mn(NO₃)₂ · H₂O)와 imidazole-4,5-dicarboxylic acid (IDCH₂)가 수열반응하여, 실험식 [Mn(IDC)(H₂O)]을 가지는 2차원 배위 고분자가 합성되었다. 화합물 1의 구조가 분광학적 방법(IR) 및 X-ray 회절법으로 규명되었다. 화합물 1의 결정학적 자료: 사방정계 공간군 *Pbca*, *a* = 7.257(5) Å, *b* = 13.687(5) Å, *c* = 14.332(6) Å, *Z* = 8, *R*(*wR*₂) = 0.0498(0.0999).

Abstract

The hydrothermal reaction between manganese nitrate (Mn(NO₃)₂ · H₂O) and imidazole-4,5-dicarboxylic acid (IDCH₂) in the presence of sodium acetate (NaOAc · 3H₂O) gave a two-dimensional manganese-imidazoledicarboxylate coordination polymer with an empirical formula of [Mn(IDC)(H₂O)] (1). Compound 1 was characterized by spectroscopy (IR) and X-ray diffraction. Crystallographic data for 1: orthorhombic space group, *Pbca*, *a* = 7.257(5) Å, *b* = 13.687(5) Å, *c* = 14.332(6) Å, *Z* = 8, *R*(*wR*₂) = 0.0498(0.0999).

1. Introduction

The research in the design of infinite molecular components with specific chains and networks, or so-called crystal engineering, has become an area of current interest over recent years.¹⁻¹⁰⁾ The formation of inorganic coordination polymers with bridging multidentate ligands with transition metals has recently received much attention.

We recently reported the preparations and structures of a 3-dimensional Zn(II)-(naphthalene-2,6-dicar-

boxylate)¹¹⁾ coordination polymer and a 3-dimensional Co(II)-(pyridine-2,5-dicarboxylate)¹²⁾ coordination polymer by employing hydrothermal reactions. In an attempt to expand the scope of this methodology, we set out to prepare manganese coordination-polymers with a 5-membered ligand possessing two potentially bridging carboxylates, imidazole-4,5-dicarboxylic acid (IDCH₂). Herein we report the synthesis and structure of a 2-dimensional manganese coordination-polymer based on bridging imidazole-4,5-dicarboxylate.

2. Experimental Section

Mn(NO₃)₂·H₂O, NaOAc·3H₂O, and imidazole-4,5-dicarboxylic acid (IDCH₂) were purchased from Aldrich company. IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) by the Korea Basic Science Institute.

Preparation of [Mn(H₂O)(C₅H₃N₂O₄)_n] (1). A mixture of Mn(NO₃)₂·H₂O (0.115 g, 0.640 mmol), IDCH₂ (0.100 g, 0.640 mmol), NaOAc·3H₂O (0.174 g, 1.28 mmol), and H₂O (6.0 ml, 0.333 mol) in the mole ratio of 1.00 : 1.00 : 2.00 : 260 was heated in a 23-ml capacity Teflon-lined reaction vessel at 180 for 1 day and then cooled to room temperature by air-cooling. The colorless product was collected by filtration, washed with H₂O (2 × 5 ml), and air-dried to give [Mn(H₂O)(C₅H₃N₂O₄)_n] (0.133 g, 0.589 mmol, 92% yield).

Anal. Calcd for C₅H₄N₂O₅Mn (*M_r* = 227.04): C, 26.45; H, 1.78; N, 12.33. Found: C, 26.27; H, 1.63; N, 12.41. IR (KBr): 3432 (br), 3354 (br), 1619 (s, C=O), 1602 (s, C=O), 1562 (s, C=O), 1548 (s, C=O), 1455 (s), 1385 (s), 798 (s) cm⁻¹.

X-ray Structure Determination. All X-ray data were collected with the use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 23 reflections in the range of 15.0 < 2θ < 25.0°. Three check-reflections were measured every 100 reflections throughout data collection and showed no noticeable variations in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected for absorption with ψ-scan data. All calculations were carried out with use of the SHELXTL programs.¹³⁾

A colorless crystal of **1** of approximate dimensions 0.42 × 0.20 × 0.18 mm³, shaped as a block, was used for crystal- and intensity-data collection. The unit-cell parameters and systematic absences, 0*kl* (*k* = 2*n* + 1), *h*0*l* (*l* = 2*n* + 1), and *hk*0 (*h* = 2*n* + 1), unambiguously indicated *Pbca* as a space group. The structure was solved by direct methods. All

Table 1. X-ray data collection and structure refinement for 1

formula	C ₅ H ₄ N ₂ O ₅ Mn
fw	227.04
temperature, K	295(2)
crystal system	orthorhombic
space group	<i>Pbca</i>
<i>a</i> , Å	7.257(5)
<i>b</i> , Å	13.687(5)
<i>c</i> , Å	14.332(6)
<i>V</i> , Å ³	1423(1)
<i>Z</i>	8
<i>d</i> _{cal} , g cm ³	2.119
<i>μ</i> , mm ⁻¹	1.844
<i>T</i> _{min}	0.3941
<i>T</i> _{max}	0.7923
F(000)	904
No. of reflections measured	1222
No. of reflections unique	1222
No. of reflections with <i>I</i> > 2σ(<i>I</i>)	835
No. of parameters refined	135
2θ range (°)	3.5–50.0
scan type	ω
scan speed	variable
GOF (goodness-of-fit on <i>F</i> ²)	1.082
Max., min. in (eÅ ⁻³)	0.485, -0.450
<i>R</i>	0.0498
<i>wR</i> ₂ ^a	0.0999

$$^a wR_2 = [w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2]^{1/2}$$

Table 2. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Mn(1)	639(1)	1411(1)	853(1)	16(1)
O(1)	-1853(6)	2104(3)	1543(3)	22(1)
O(2)	2137(6)	2164(3)	1978(3)	28(1)
O(3)	2674(5)	943(3)	-183(3)	23(1)
O(4)	-1623(5)	584(3)	223(2)	21(1)
O(5)	460(8)	2689(4)	-17(4)	35(1)
N(1)	1298(7)	268(3)	1912(3)	20(1)
N(2)	1405(7)	-909(3)	2969(3)	20(1)
C(1)	1857(8)	652(4)	2759(4)	19(1)
C(2)	1930(8)	-65(4)	3429(4)	19(1)
C(3)	1055(8)	-685(4)	2071(4)	21(1)
C(4)	-2595(8)	1715(4)	2261(3)	16(1)
C(5)	2415(8)	119(4)	-582(4)	16(1)

non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located and refined isotropically.

Details on crystal data and intensity collection are

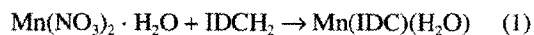
Table 3. Selected bond distances (Å) and bond angles (°) in **1**

Mn1-O5	2.152(5)	Mn1-O4	2.189(4)	Mn1-O3	2.190(4)
Mn1-O2	2.201(4)	Mn1-N1	2.231(5)	Mn1-O1	2.269(4)
O5-Mn1-O4	97.8(2)	O5-Mn1-O3	83.4(2)	O4-Mn1-O3	94.3(1)
O5-Mn1-O2	94.3(2)	O4-Mn1-O2	156.2(1)	O3-Mn1-O2	107.5(2)
O5-Mn1-N1	167.7(2)	O4-Mn1-N1	94.5(2)	O3-Mn1-N1	96.4(2)
O2-Mn1-N1	74.0(2)	O5-Mn1-O1	82.2(2)	O4-Mn1-O1	78.4(2)
O3-Mn1-O1	162.8(1)	O2-Mn1-O1	83.0(2)	N1-Mn1-O1	99.7(2)

given in Table 1. Final atomic coordinates and some selected bond distances and bond angles are shown in Tables 2 and 3, respectively.

3. Results and Discussion

Preparation. A 2-dimensional Mn(II) coordination-polymer with a nonporous, infinite network was prepared from a mixture of $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, imidazole-4,5-dicarboxylic acid (IDCH_2), $\text{NaOAc} \cdot 3\text{H}_2\text{O}$, and H_2O in the mole ratio of 1.00 : 1.00 : 2.00 : 260 by heating it at 180°C for 1 day (Eq. (1)).



This reaction was carried out under less acidic conditions ($\text{pH} \approx 5$) by adding a basic inorganic salt (sodium acetate: NaOAc) to the reaction mixture. In the absence of NaOAc , the reaction mixture has a $\text{pH} \approx 3$, and the reaction gave only a poorly crystalline product. The crystalline compound **1** is air-stable and is not soluble in common organic solvents. The FT-IR spectrum shows the asymmetric and symmetric carboxylate stretches of the IDC^{2-} ligand (1619, 1602, 1562, and 1548 cm^{-1}) and the O-H stretches of the aqua ligand (3432 and 3354 cm^{-1}).^{14,15} The disappearance of the carbonyl bands (1582 and 1538 cm^{-1}) in the free ligand suggests that the IDCH_2 ligand has been coordinated to manganese metals under the reaction conditions, together with the concurrent deprotonation of IDCH_2 to IDC^{2-} . The structure of **1** has been further confirmed by X-ray diffraction and elemental analysis.

Structure. The monomeric unit of **1** with the atom-numbering scheme is shown in Fig. 1. This unit consists of one Mn metal, one imidazole-4,5-dicarboxylate (IDC^{2-}) ligand, and one aqua ligand. The coordination sphere of Mn can be described as

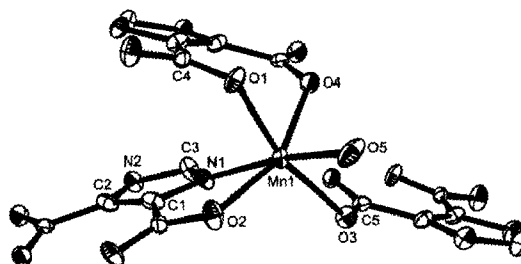


Fig. 1. A view of the local environment of **1**, showing 50% thermal ellipsoids.

a distorted octahedron. The formal oxidation state of the manganese metal is +2. The equatorial plane, defined by O2, O4, O5, and N1 atoms, is roughly planar with the average atomic displacement of 0.2014 Å. The manganese atom lies above the equatorial plane by 0.1453 Å.

Compound **1** forms a two-dimensional polymer in the *ac*-direction through the carboxylate groups and imidazole nitrogen atom of the IDC^{2-} ligand. All Mn-O and Mn-N bond distances are single bonds. The nitrogen atom of the IDC^{2-} ligand is bonded to the manganese metal. The carboxylate groups act as bidentate ligands, linking two neighboring manganese centers through the Mn-O-C-O-Mn bridge. All hydrogen atoms (HO5A, HO5B) in the aqua ligand are involved in intermolecular hydrogen bonding of the type O-H...O (O5-H...O1, O5-H...O3), as shown in Table 4.

Fig. 2 illustrates a 2-dimensional polymeric structure of **1**. Each IDC^{2-} ligand links three Mn(II) centers by the coordination of five out of six potential donor atoms (two nitrogen and four oxygen atoms). Each Mn metal is coordinated by one aqua ligand as well as three IDC^{2-} ligands. The adjacent infinite 2-D polymeric chains are separated from each other by about a half of the *b*-axis length (6.85 Å). As

Table 4. Hydrogen bonding parameters (Å, °) in 1

Bond	D-H	H···A	D-H···A	D···A	Position of A
O5-Ha···O1	0.679	2.289	162.82	2.944	$x + 0.5, -y + 0.5, -z$
O5-Hb···O3	0.871	1.923	164.25	2.771	$x - 0.5, -y + 0.5, -z$

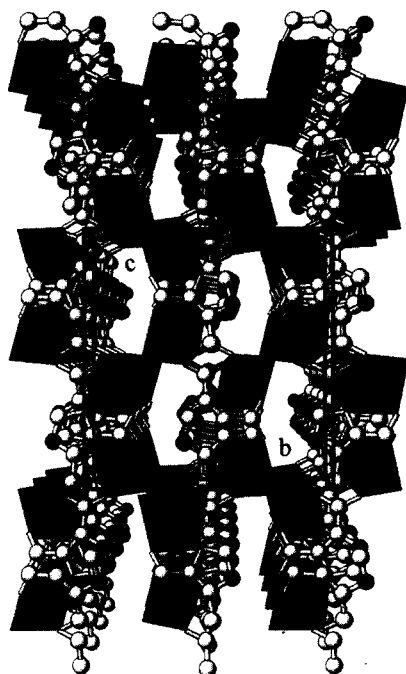


Fig. 2. A projection along the *a*-axis. MnO_5N cores are represented as light gray octahedra, nitrogen atoms as closed circles, and carbon atoms as open circles.

stated above, one imidazole nitrogen atom (N2) does not coordinate to the metal.

In summary, the hydrothermal reaction of $Mn(NO_3)_2 \cdot H_2O$ with $IDCH_2$ in the presence of sodium acetate ($NaOAc \cdot 3H_2O$), gave a 2-D coordination polymer with an empirical formula of $[Mn(IDC)(H_2O)]$, whose structure has been determined by X-ray diffraction.

4. Supplementary Material

Tables of full bond distances and bond angles, anisotropic thermal parameters, and atomic coordinates of hydrogen atoms are available from the author Soon W. Lee.

Acknowledgements

This work was supported by the Brain Korea 21 Project.

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