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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

Synthesis and Crystal Structure of Bis(2,2'-Bipyridine-N,N')Dichloromanganese(II) Complex with Free 2,2'-Bipyridine

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Online publication date: 15 September 2010

To cite this Article Li, Zhenyu , Xu, Duanjun , Nie, Jingjing , Wu, Zhiyong , Wu, Jingyun and Chiang, Michael(2002) 'Synthesis and Crystal Structure of Bis(2,2'-Bipyridine-N,N')Dichloromanganese(II) Complex with Free 2,2'-Bipyridine', *Journal of Coordination Chemistry*, 55: 10, 1155 – 1160

To link to this Article: DOI: 10.1080/0095897021000023158

URL: <http://dx.doi.org/10.1080/0095897021000023158>

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SYNTHESIS AND CRYSTAL STRUCTURE OF BIS(2,2'-BIPYRIDINE- N,N')DICHLOROMANGANESE(II) COMPLEX WITH FREE 2,2'-BIPYRIDINE

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(Received 13 July 2001; Revised 6 November 2001; In final form 10 April 2002)

The title complex $[\text{Mn}(\text{bipy})_2\text{Cl}_2] \cdot 0.5\text{bipy} \cdot 2.5\text{H}_2\text{O}$, where $\text{bipy} = 2,2'$ -bipyridine, has been prepared and its crystal structure has been determined by X-ray diffraction methods. The complex crystallizes in the triclinic space group $P-1$, with $a = 8.814(2)$, $b = 11.335(2)$, $c = 13.347(3)$ Å, $\alpha = 76.85(2)$, $\beta = 89.55(2)$, $\gamma = 86.52(2)^\circ$. Two chloride and two bipy ligands *cis*-coordinate to a Mn(II) atom with a distorted octahedral geometry. The crystal consists of Mn(II) complex, free bipy and crystalline water. The complex crystalline water link to each other by H-bonding to form supra-molecular chains, and free bipy molecules locate between parallel chains with a van der Waals contact distance of 3.58(1) Å. A π - π interaction is also observed between adjacent bipy rings. The chelating bipy and free bipy showed different IR absorptions.

Keywords: Manganese(II); X-ray structure; π - π interactions; 2,2'-Bipyridine

INTRODUCTION

Interest has concentrated on preparing and characterizing bio-mimetic manganese-enzyme complexes in order to establish the mechanism of photosynthesis [1]. The process of water splitting arises from catalysis of the manganese cluster located in the reaction center of photosystem II [2]. In order to simulate the manganese cluster, a series of manganese complexes have been synthesized in our laboratory and several crystal structures have been reported [3–4]. In the present work we tried to prepare a 2,2'-bipyridine complex of Mn(II) bridged by a fumarate dianion, but x-ray crystal analysis showed the solid product does not contain fumarate. We report here the synthesis of the title Mn(II) complex and compare it with the corresponding synthesis of Cu(II) complexes and a Mn(II) complex bridged by fumarate. We also present

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here the crystal structure of the title complex, in which a free bipy molecule occurs unexpectedly.

EXPERIMENTAL

Synthesis

An ethanol solution (10 mL) containing bipy (0.312 g, 2 mmol) was with stirring to an aqueous solution (10 mL) containing $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.198 g, 1 mmol) slowly added. After refluxing for several minutes the mixture solution changed color to pale yellow. Then an aqueous solution (10 mL) containing fumaric acid (0.058 g, 0.5 mmol) and NaOH (0.040 g, 1 mmol) was slowly added to the reaction mixture with continuous stirring and refluxing. After half an hour a small amount of precipitate appeared. The reaction mixture was cooled to room temperature and filtered. Single crystals of pale yellow color were obtained from the filtrate by slow evaporation of the solvent over five months.

Physical Measurements

C, N and H content was analyzed using a Carlo-Erba 1160 instrument. Anal. Calc. for $\text{C}_{25}\text{H}_{24}\text{Cl}_2\text{N}_5\text{O}_{2.5}\text{Mn}$ (%): C, 53.5; N, 12.5; H, 4.5; Found: C, 53.1; N, 12.3; H, 4.5.

An infrared spectrum of the title complex was measured on KBr discs using a Nicolet 5DX FT-IR spectrophotometer (4000–400 cm^{-1}).

Diffraction intensity data for a single crystal of the complex was collected on a Rigaku AFC-7S diffractometer. The crystal structure was anisotropically refined using SHELXL-97 [5]. Data collection and structure refinement conditions are summarized in Table I.

TABLE I Crystallographic data for $\text{C}_{25}\text{H}_{24}\text{Cl}_2\text{N}_5\text{O}_{2.5}\text{Mn}$

Crystal size (mm)	$0.50 \times 0.42 \times 0.40$
Chemical formula	$\text{C}_{25}\text{H}_{24}\text{Cl}_2\text{N}_5\text{O}_{2.5}\text{Mn}$
Formula weight	561.34
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	8.814(2)
<i>b</i> (Å)	11.335(2)
<i>c</i> (Å)	13.347(3)
α (°)	76.85(2)
β (°)	89.55(2)
γ (°)	86.52(2)
<i>V</i> (Å ³)	1296.1(5)
<i>Z</i>	2
<i>F</i> (000)	578
<i>D_c</i> (g cm ⁻³)	1.438
θ range (°)	2.31–25.99
<i>T</i> (K)	293
Unique reflections	5079
Reflections with $I > 2\sigma(I)$	3529
R values	0.065
Goodness-of-fit	1.039
$(\Delta\rho)_{\text{max}}$ and $(\Delta\rho)_{\text{min}}$ (e.Å ⁻³)	0.76, -0.83

RESULTS AND DISCUSSION

Crystal structure

Fractional coordinates of non-H atoms are presented in Table II. Selected bond distances and angles are listed in Table III. The complex structure is illustrated in Fig. 1. Bipy molecules and chlorine anions coordinate to a Mn(II) atom with a *cis* configuration. The coordination bond distances and angles are comparable to those reported previously [6–7]. A small chelate angle of bipy to Mn(II) results in a distorted octahedron around the Mn(II) atom. A deviation of 0.43 Å for N(3) from the mean plane defined by N(1), N(2), Cl(1) and Mn atoms implies less overlap of the atomic orbital of N(3) and Mn(II) atoms, however the Mn–N(3) distance of 2.283(4) Å is the shortest among the four Mn–N distances in the structure, suggesting existence of an electrostatic interaction between the donor and central atoms.

TABLE II Fractional atomic coordinates [$\times 10^4$] of non-H atoms and equivalent isotropic thermal parameters [$\times 10^3$]

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{eq}(\text{Å}^2)$
Mn	8284(1)	5(1)	7820(1)	45(1)
Cl(1)	9110(2)	951(2)	9160(1)	98(1)
Cl(2)	10591(1)	– 1328(1)	7892(1)	69(1)
N(1)	8960(4)	1545(3)	6495(3)	48(1)
N(2)	7492(4)	– 386(3)	6297(3)	47(1)
N(3)	6857(4)	– 1428(3)	8810(3)	50(1)
N(4)	5888(4)	851(3)	7961(3)	44(1)
N(5)	6369(6)	4322(5)	4228(5)	86(2)
O(1)	982(7)	6357(4)	1071(4)	103(2)
O(2)	8479(12)	3981(8)	1029(7)	188(4)
O(3) ^a	9765(16)	5211(14)	2167(10)	144(7)
C(1)	9716(6)	2508(5)	6632(4)	58(2)
C(2)	10372(6)	3288(5)	5838(4)	66(1)
C(3)	10278(6)	3097(5)	4863(4)	67(1)
C(4)	9490(6)	2142(4)	4706(4)	58(1)
C(5)	8831(4)	1386(4)	5537(3)	45(1)
C(6)	7922(5)	354(4)	5421(3)	44(1)
C(7)	7528(6)	182(5)	4466(4)	59(1)
C(8)	6666(6)	– 788(5)	4417(4)	66(1)
C(9)	6230(6)	– 1536(5)	5301(4)	65(1)
C(10)	6671(6)	– 1317(5)	6229(4)	57(1)
C(11)	7389(6)	– 2560(5)	9232(5)	64(1)
C(12)	6514(8)	– 3427(5)	9793(5)	74(2)
C(13)	5028(7)	– 3117(5)	9940(5)	69(1)
C(14)	4436(6)	– 1960(4)	9509(4)	58(1)
C(15)	5401(5)	– 1127(4)	8960(3)	45(1)
C(16)	4869(5)	156(4)	8513(3)	43(1)
C(17)	3422(5)	621(4)	8679(4)	54(1)
C(18)	3023(5)	1824(5)	8263(4)	60(1)
C(19)	4073(6)	2536(5)	7676(4)	61(1)
C(20)	5477(5)	2019(4)	7547(4)	55(1)
C(21)	6412(10)	3996(7)	3320(6)	98(3)
C(22)	5181(11)	4161(6)	2675(6)	96(3)
C(23)	3847(10)	4677(6)	2968(6)	98(3)
C(24)	3755(6)	5004(5)	3904(4)	70(2)
C(25)	5017(6)	4819(4)	4504(4)	60(2)

^aThe site occupancy factor is 0.5.

TABLE III Selected bond distances [\AA] and angles [$^\circ$]

Mn–N(1)	2.288(4)	Mn–N(3)	2.283(4)
Mn–N(2)	2.300(4)	Mn–N(4)	2.290(4)
Mn–Cl(1)	2.421(2)	Mn–Cl(2)	2.448(2)
N(1)–Mn–N(2)	71.29(13)	N(1)–Mn–N(3)	160.10(13)
N(1)–Mn–N(4)	94.24(13)	N(2)–Mn–N(4)	87.23(13)
N(3)–Mn–N(4)	71.29(13)	N(2)–Mn–N(3)	93.85(13)
N(1)–Mn–Cl(1)	94.82(11)	N(2)–Mn–Cl(1)	165.13(11)
N(3)–Mn–Cl(1)	98.30(11)	N(4)–Mn–Cl(1)	88.58(11)
N(1)–Mn–Cl(2)	98.38(10)	N(2)–Mn–Cl(2)	92.83(10)
N(3)–Mn–Cl(2)	95.45(10)	N(4)–Mn–Cl(2)	166.70(10)
Cl(1)–Mn–Cl(2)	94.51(6)		

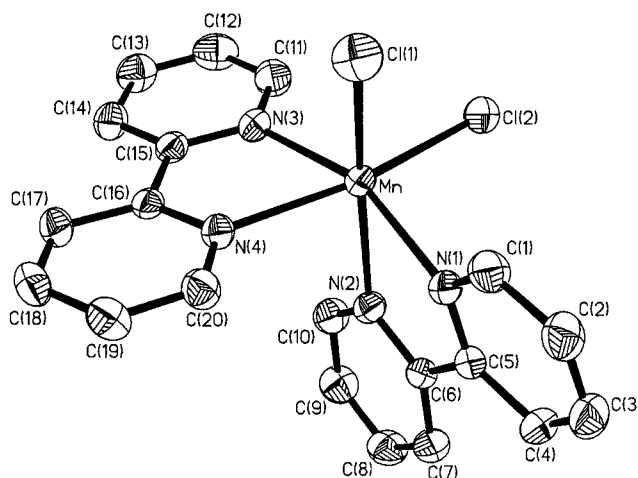


FIGURE 1 A perspective figure of the title complex structure showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

The crystal consists of Mn(II) complex, crystalline water and free bipy molecules. As shown in Fig. 2, the complex and crystalline water molecules link to each other by H-bonding to form supra-molecular chains in the crystal structure, and free bipy molecules are located between parallel chains. The free bipy molecule assumes a *trans* configuration, agreeing with that reported previously [8]. Free bipy molecules interact with complex molecules with van der Waals interactions, short contacts observed between the free bipy and complex molecule being 3.58(1) \AA of C(21)–C(4C) and 3.589(8) \AA of C(24)–C(20A). In addition to these non-covalent interactions, a π – π interaction is also observed between parallel bipy rings on adjacent chains (as shown in Fig. 3) with a separation of 3.50 \AA , which is shorter than the thickness of the aromatic ring [9].

IR Spectrum

The chelating bipy and free bipy showed different infrared absorptions with a stretching vibration of the ring structure observed at 1593 cm^{-1} for the chelating bipy and at 1573 cm^{-1} for the free bipy. The difference of 20 cm^{-1} between chelating and free bipy agrees with those reported previously [10].

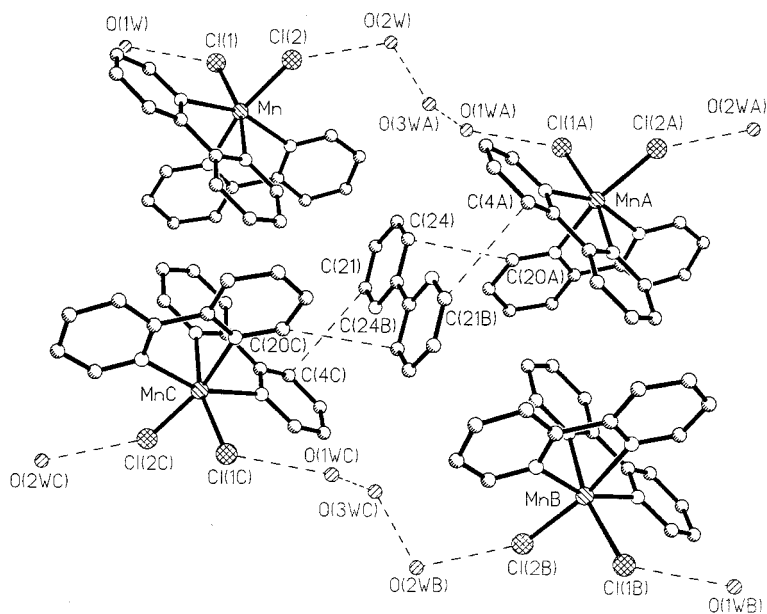


FIGURE 2 A molecular packing diagram, dashed lines showing intermolecular H-bonding between Mn(II) complex and water and van der Waals contacts between free bipy and Mn(II) complex. The atoms with a suffix of A, B or C are generated by symmetric transform as below (A) $x, 1+y, z$; (B) $1-x, 1-y, 1-z$; (C) $1-x, -y, 1-z$.

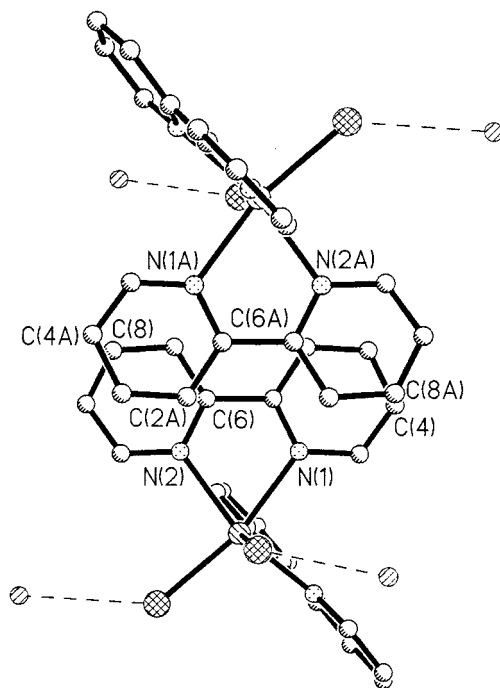


FIGURE 3 A diagram viewed along the normal line of a bipy ring plane, showing π - π interaction between parallel bipy rings on adjacent chains.

Synthesis

Although a series of bipy or phenanthrolines (phen) complexes of Cu(II) bridged by fumarate or maleate has recently been prepared in our laboratory using a similar procedure to this work [11–12], no crystalline fumarate-bridging complex of Mn(II) was obtained in this work. The different molar ratio of bipy (or phen) to metal in the reaction solution is considered to be a primary reason for the different complexes. In the case of the Cu(II) complex, equimolar bipy (or phen) and Cu(II) were used in aqueous solution, such that water may bind to Cu(II) to complete the coordination geometry before fumarate or maleate was added to the reaction mixture. The coordinated water molecules are easily replaced by fumarate or maleate, thus forming a binuclear or multinuclear Cu(II) complex bridged by fumarate or maleate. In this work, a 2:1 molar ratio of bipy to Mn(II) resulted in two bipy ligands chelating to a Mn(II) and no water coordinating to the Mn(II). The present structure shows the difficulty of replacement of chelating bipy by a fumarate anion.

When the above experiment was carried out with equimolar bipy to $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, yellow crystals with different shape were obtained. X-ray structure analysis showed a component of $[\text{Mn}(\text{fum})(\text{bipy})(\text{H}_2\text{O})]_n$, the crystal structure of which was reported previously [13].

Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

Acknowledgments

The project was supported by the National Natural Science Foundation of China (No. 29973036).

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