

Structure of *cis*-dichlorobis(1,10-phenanthroline)manganese(II) and *cis*-dichlorobis(2,2'-bipyridine)manganese(II)

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Abstract: The crystal structures of the title compounds, $[\text{Mn}(\text{phen})_2\text{Cl}_2]$ (**I**) and $[\text{Mn}(\text{bipy})_2\text{Cl}_2]$ (**II**), have been determined at 150 K. The manganese atoms in both compounds are coordinated by four pyridine nitrogen atoms from two 1,10-phenanthroline or 4,4'-bipyridine ligands and two chloride anions, resulting in a distorted *cis*- MnN_4Cl_2 octahedral geometry. Both complexes are connected through C—H...Cl hydrogen bonds into frameworks. The π - π stacking interactions are observed in crystal structure of both ones.

Keywords: manganese, X-ray, crystal structure, 1,10-phenanthroline, 2,2'-bipyridine

Introduction

Manganese complexes are of current interest in studies of molecular magnetism and in applications as magnetic recording (Ako et al., 2006; Aromi & Brechin, 2006) and manganese-enhanced MRI (Koretsky & Silva, 2004), and they can serve as model compounds of the bioinorganic chemistry of manganese (Deeth, 2008; Dismukes, 2006) including O_2 -evolving center of photosystem II (Umena et al., 2011) and various manganese-containing redox enzymes as dioxygenases (Georgiev et al., 2006), oxalate oxidase (Opaleye et al., 2006), catalase (Whittaker, 2012), superoxid dismutase (Friedel et al., 2004) and peroxidase (Sundaramoorthy et al., 2010). More manganese complexes especially for catalase and/or superoxide dismutase mimetics contain chelating N,N-donor ligands as 1,10-phenanthroline or 2,2'-bipyridine (Devereux et al., 1996; Geraghty et al., 1998; Kani et al., 2008; McCann et al., 1998; Viossat et al., 2003). Our effort in this field has been targeted to monomeric and dimeric manganese(II) complexes with chelating N,N-donor ligands. The aim of this paper is to report an X-ray structures of the mononuclear complexes $[\text{Mn}(\text{phen})_2\text{Cl}_2]$ (**I**) and $[\text{Mn}(\text{bipy})_2\text{Cl}_2]$ (**II**).

Experimental

Synthesis

The $[\text{Mn}(\text{phen})_2\text{Cl}_2]$ (**I**) and $[\text{Mn}(\text{bipy})_2\text{Cl}_2]$ (**II**), were prepared by following method. To a solution of 1,10-phenanthroline monohydrate (0.396 g, 2 mmol, for **I**) or 2,2'-bipyridine (0.312 g, 2 mmol, for **II**) in ethanol (40 cm^3) was added $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.198 g, 1 mmol). These mixtures were stirred for

1 day resulting in a yellow suspensions. The main products of **I** or **II** were filtered off and dried at ambient temperature and a yellow mother liquid were left crystallization. Yellow needle crystals of **I** and **II** were separated from the mother liquor after several weeks.

X-ray Crystallography

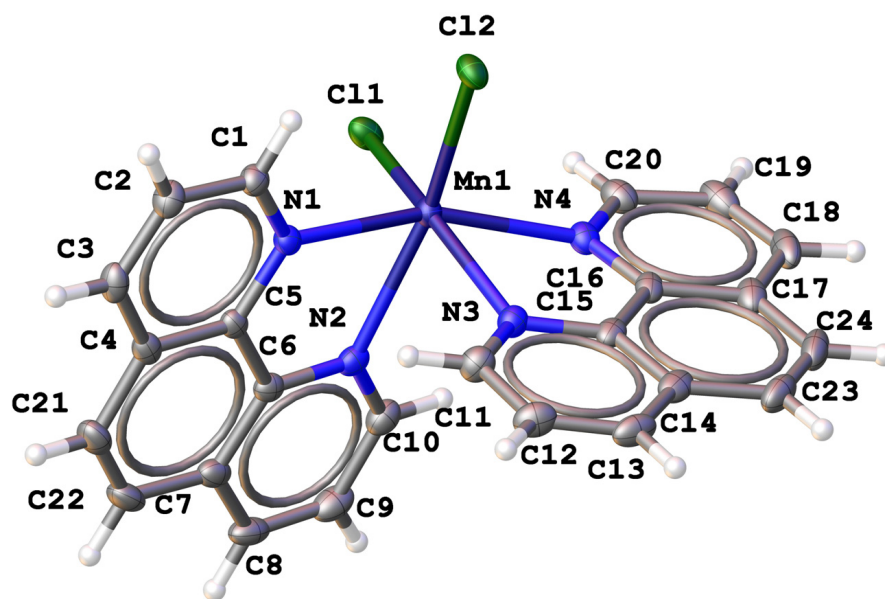
Crystal data and conditions of data collection and refinement are reported in Table 1. Data collection and cell refinement were carried out using diffractometer Bruker Kappa APEXII CCD (Bruker, 2008) at 150 K with graphite monochromated Mo $\text{K}\alpha$ radiation. The semi-empirical absorption corrections were applied the using multi-scan method. The structures were solved by direct methods using SIR-2011 (Burla et al., 2012) and refined by the full-matrix least-squares procedure with SHELXL-2014 (Sheldrick, 2008) or CRYSTALS (Betteridge et al., 2003). Geometrical analyses were performed with SHELXL-2014 or CRYSTALS. The structures were drawn with OLEX2 (Dolomanov et al., 2009).

Results and discussion

The principle structure features of $[\text{Mn}(\text{phen})_2\text{Cl}_2]$ (**I**) and $[\text{Mn}(\text{bipy})_2\text{Cl}_2]$ (**II**) are illustrated in Figs. 1 and 2, respectively, and selected bond distances and angles are given in Table 2. The both compounds crystallize in the monoclinic system (space group $\text{P}2_1/c$). The manganese atom in both compounds are coordinated by four pyridine nitrogen atoms of two 1,10-phenanthroline ligands (**I**) or 2,2'-bipyridine ligands (**II**), and two chloride anions with a distorted octahedral geometry (Table 2). The Mn—N bonds located in the *trans* positions relative to the Mn—Cl

Tab. 1. Experimental details.

	1	2
Chemical formula	C ₂₄ H ₁₆ Cl ₂ MnN ₄	C ₂₀ H ₁₆ Cl ₂ MnN ₄
M_r	486.25	438.21
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	150	150
a, b, c (Å)	9.4130(7), 15.161(1), 14.3470(7)	8.5710(4), 14.254(1), 15.693(1)
β (°)	98.723(4)	98.842(4)
V (Å ³)	2023.8(2)	1894.4(2)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	0.94	0.99
Crystal size (mm)	0.33 × 0.19 × 0.15	0.35 × 0.19 × 0.18
Diffractometer	Bruker Kappa APEXII	Bruker Kappa APEXII
Absorption correction	Multi-scan	Multi-scan
T_{\min}, T_{\max}	0.744, 0.869	0.83, 0.84
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	28914, 4115, 3319	14933, 4295, 3242
R_{int}	0.047	0.038
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.031, 0.067, 1.06	0.040, 0.073, 1.07
No. of reflections	4115	3242
No. of parameters	280	244
$\Delta_{\text{max}}, \Delta_{\text{min}}$ (e Å ⁻³)	0.28, -0.32	0.55, -0.42
CCDC	991690	991691

**Fig. 1.** Perspective view of **I**, with the atom numbering scheme.

bonds are significantly longer than the other Mn—N bonds to the same 1,10-phenanthroline or 2,2'-bipyridine ligands. The large Cl11—Mn1—Cl12 bond angle of 103.94(2)° for **I** and 100.24(3)° for **II** may be result of the repulsion between the neighboring chloride anions.

The crystal packing of **I** and **II** are shown in Figs. 3 and 4, respectively. The complex molecules of **I** are connected through C—H...Cl hydrogen bonds between carbon atoms of 1,10-phenanthroline ligands and chloride atoms of neighboring complex molecules [C3—H3...Clⁱ, C22—H22...Clⁱⁱ and

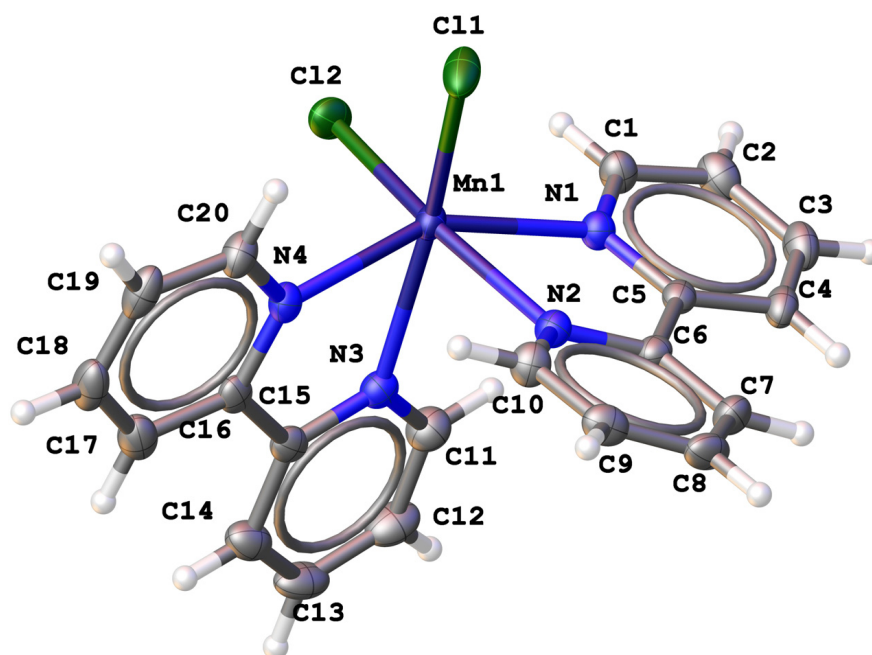


Fig. 2. Perspective view of **II**, with the atom numbering scheme.

Tab. 2. Selected geometric parameters (Å, °).

	1	2
Mn1—Cl1	2.443(1)	2.441(1)
Mn1—Cl2	2.456(1)	2.441(1)
Mn1—N1	2.283(2)	2.273(2)
Mn1—N2	2.369(2)	2.318(2)
Mn1—N3	2.335(2)	2.356(2)
Mn1—N4	2.291(2)	2.275(2)
Cl1—Mn1—Cl2	103.94(2)	100.24(3)
Cl1—Mn1—N1	103.03(4)	102.03(6)
Cl1—Mn1—N2	87.06(4)	86.62(5)
Cl1—Mn1—N3	160.92(4)	164.93(6)
Cl1—Mn1—N4	94.01(4)	95.86(6)
Cl2—Mn1—N1	90.64(4)	97.55(5)
Cl2—Mn1—N2	160.59(4)	167.48(5)
Cl2—Mn1—N3	90.66(4)	88.49(5)
Cl2—Mn1—N4	96.96(4)	100.06(5)
N1—Mn1—N2	71.10(5)	70.62(7)
N1—Mn1—N3	88.80(6)	88.81(7)
N1—Mn1—N4	159.11(6)	152.16(7)
N2—Mn1—N3	82.64(5)	87.19(7)
N2—Mn1—N4	98.17(6)	89.54(7)
N3—Mn1—N4	71.75(6)	70.36(7)

C24—H24...Cl2ⁱⁱⁱ (Symmetry codes: (i) $-x + 2, -y + 1, -z$; (ii) $x + 1, y, z$; (iii) $-x + 1, -y, -z$) with C...Cl distances of 3.638(2), 3.552(2) and 3.725(2) Å, respectively] (Table 3) into 2-D supramolecular framework in the *ab* plane (Figure 3). The 2-D supramolecular framework of **I** is also observed $\pi \cdots \pi$ stacking interaction (Janiak, 2000) between aromatic rings of from both 1,10-phenanthroline ligands.

The complex molecules of **II** are linked to 2-D supramolecular framework through C—H...Cl hydrogen bonds between carbon atoms of 2,2'-bipyridine ligands and chloride atoms of neighboring complex molecules [C3—H3...Cl1^{iv}, C7—H7...Cl1ⁱⁱ and C17—H17...Cl2^v (Symmetry codes: (ii) $x + 1, y, z$; (iii) $-x + 1, -y, -z$; (iv) $-x + 1, -y + 1, -z$; (v) $-x, -y, -z$) with C...Cl distances of 3.618(2), 3.552(2) and 3.591(2) Å, respectively] (Table 3) in the *ab* plane (Figure 4). The 2-D supramolecular framework of **I** is connected to 3-D supramolecular network through C18—H18...Cl1^{vi} hydrogen bonds (Symmetry code: (vi) $-x, y - 1/2, -z + 1/2$) with C18...Cl1 distances of 3.463(2) Å (Table 3). The $\pi \cdots \pi$ stacking interactions (Janiak, 2000) has been observed only between aromatic rings from one of two 2,2'-bipyridine ligands.

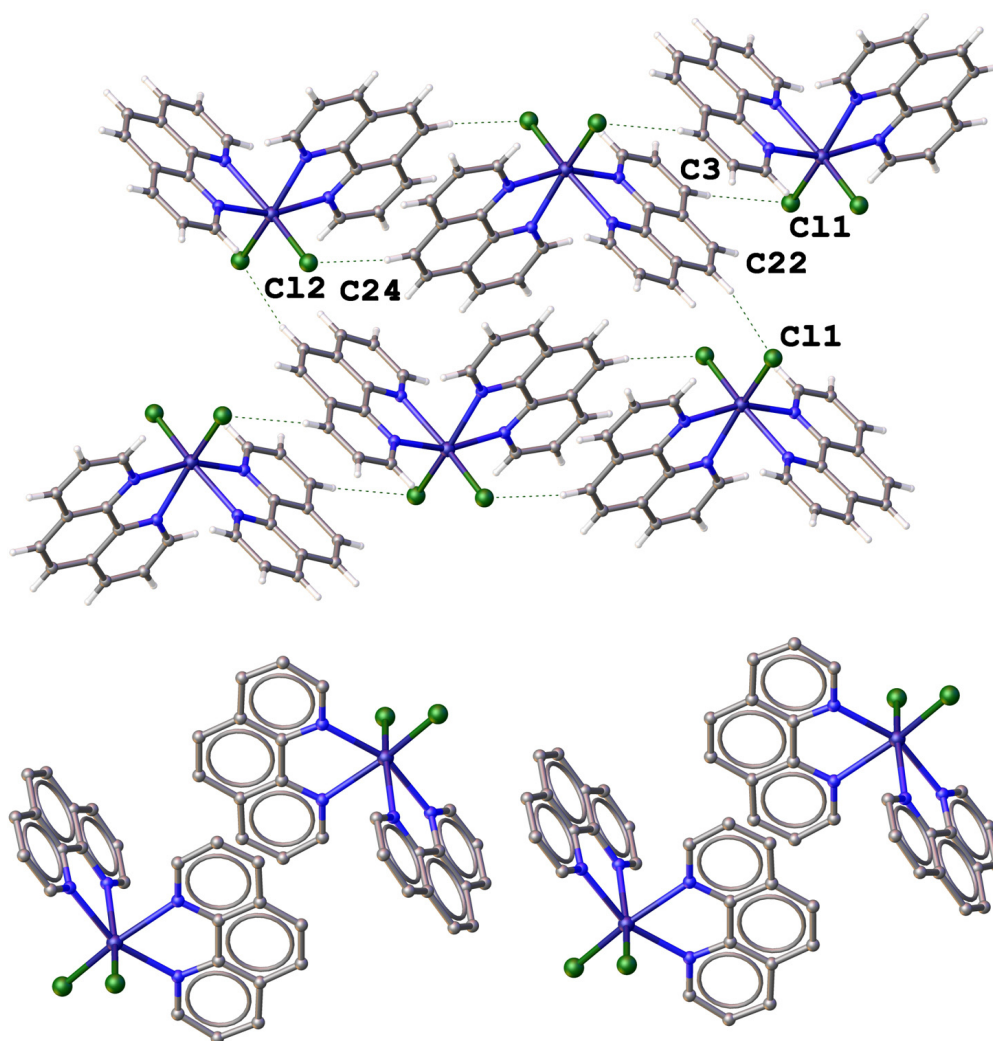
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Tab. 3. Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$ (Å)	$H \cdots A$ (Å)	$D \cdots A$ (Å)	$D-H \cdots A$ (°)
1				
C3—H3...Cl1 ⁱ	0.95	2.76	3.638(2)	154
C22—H22...Cl1 ⁱⁱ	0.95	2.62	3.552(2)	168
C24—H24...Cl2 ⁱⁱⁱ	0.95	2.60	3.725(2)	167
2				
C3—H3...Cl1 ^{iv}	0.95	2.79	3.618(2)	147
C7—H7...Cl1 ⁱⁱ	0.95	2.75	3.552(2)	142
C17—H17...Cl2 ^v	0.95	2.75	3.591(2)	148
C18—H18...Cl1 ^{vi}	0.95	2.69	3.463(2)	139

Symmetry codes: (i) $-x+2, -y+1, -z$; (ii) $x+1, y, z$; (iii) $-x+1, -y, -z$; (iv) $-x+1, -y+1, -z$; (v) $-x, -y, -z$; (vi) $-x, y-1/2, -z+1/2$.

**Fig. 3.** The C—H...Cl hydrogen bonds and $\pi \cdots \pi$ stacking interactions in crystal packing of **I**.

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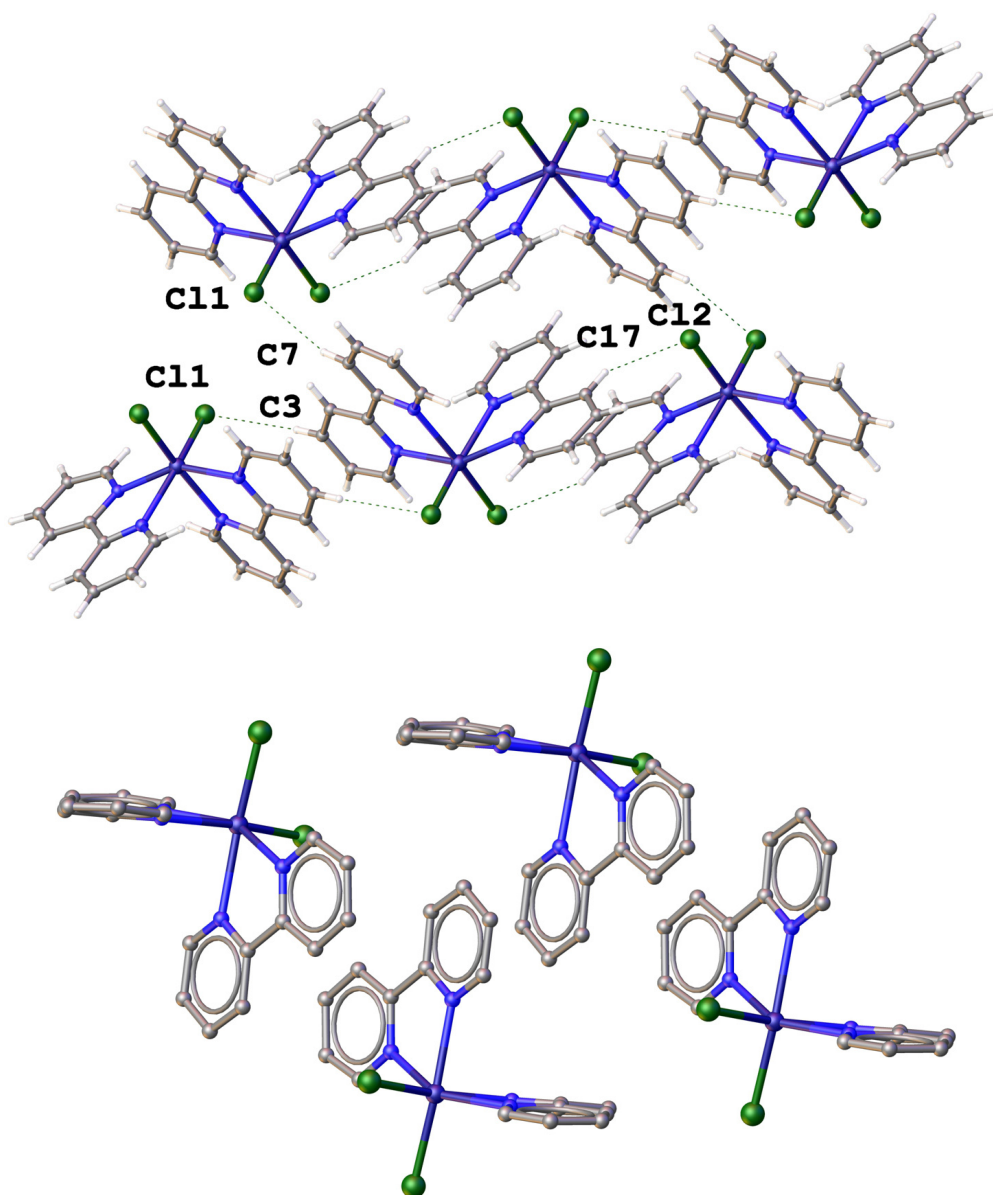


Fig. 4. C—H···Cl hydrogen bonds and π ··· π stacking interactions in crystal packing of II.

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