

## Synthesis and Crystal Structure of Mn(II) Complex with 2,9-Bis(*n*-2',5'-diazahptanyl)-1,10-phenanthroline

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A new complex  $[\text{MnL}][\text{MnCl}_4] \cdot 0.5\text{C}_2\text{H}_5\text{OH}$ , of which L represents 2,9-bis(*n*-2',5'-diazahptanyl)-1,10-phenanthroline, has been synthesized and structurally determined by X-ray diffraction analysis. It crystallizes in the monoclinic system, space group P2(1)/c, with  $a = 13.676(4) \text{ \AA}$ ,  $b = 11.255(4) \text{ \AA}$ ,  $c = 20.153(7) \text{ \AA}$ ,  $\beta = 105.101(5)^\circ$ ,  $M_r = 655.25$ ,  $V = 2995.0(17) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.453 \text{ Mg/m}^3$ ,  $\mu = 1.225 \text{ mm}^{-1}$  and final  $R = 0.0466$ . The complex consists of one  $[\text{MnL}]^{2+}$  cations, one  $[\text{MnCl}_4]^{2-}$  anion and half alcohol molecule. The Mn(II) ion is coordinated by six nitrogen atoms of the ligand, in which the two nitrogen from the phenanthroline and the two from the imine groups near the phenanthroline are in the equatorial plane while the two from the imine groups at the end of both arms in the axial positions. Hydrogen bonds are formed between the chlorine ions of  $\text{MnCl}_4^{2-}$  and the adjacent hydrogen atoms of imine group.

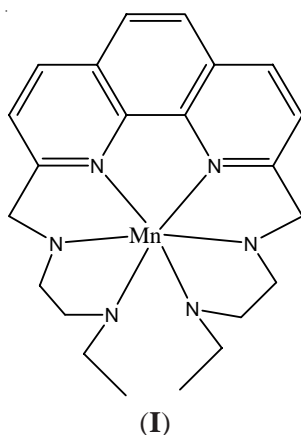
**Key Words:** Synthesis, Crystal structure, Mn(II) complex, 2,9-Bis(*n*-2',5'-diazahptanyl)-1,10-phenanthroline.

### INTRODUCTION

The polypyridine ligands, *e.g.* 2,2'-bipyridine, 1,10-phenanthroline, *etc.* continue to attract much research interest, especially because of their rich redox chemistry and photochemistry<sup>1,2</sup>. Most of the work on phenanthroline derivatives has been prompted by the intense interest in their catalytic, redox, photoredox properties, biological activity, complexation activity and novel supermolecular chemistry<sup>3-9</sup>. Phenanthroline derivatives containing amine groups are potential ligands containing both soft and hard sites. The binding capacity of transition-metal ions with these ligands allows their coordination chemistry to encompass a variety of geometries and oxidation states with reactivity ranging from biological systems to organometal-

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lic chemistry. The synthesis of the Mn(II), Zn(II) complexes with N,N'-diisopropyl-1,10-phenanthroline-2,9-dimethanamine and their crystal structure has been reported previously<sup>10</sup>. As a continuation of our investigation, herein the synthesis of a new multidentate ligand 2,9-bis(*n*-2',5'-diazheptanyl)-1,10-phenanthroline and its crystal structure of Mn(II) complex (**I**) is reported.



### EXPERIMENTAL

Elemental analyses were performed on a Perkin Elmer 24°C elemental analyzer. IR spectra were obtained as KBr disks on a Nicolet 170 SX FT-IR spectrometer. <sup>1</sup>H NMR spectra were recorded with Varian UNITY-plus 400 MHz spectrometer. D<sub>2</sub>O was used as a solvent with trace amounts of the reference 3-trimethyl-silyl-1-propanesulfonic acid, sodium salt (DSS).

2,9-dimethyl-1,10-phenanthroline was purchased from Fluka. Other chemicals used were of analytical reagent grade. The ligand 2,9-bis(*n*-2',5'-diazheptanyl)-1,10-phenanthroline was prepared by the reaction of 1,10-phenanthroline-2,9-dicarboxaldehyde<sup>11</sup> and *n*-1,4-diazahexane by reported procedure<sup>12</sup>.

A solution of MnCl<sub>2</sub>·4H<sub>2</sub>O (0.0396 g, 0.2 mmol) in CH<sub>3</sub>CH<sub>2</sub>OH (10 mL) was added dropwise to an ethanol solution (2 mL) of L·4HCl·3H<sub>2</sub>O (0.058 g, 0.1 mmol) and NaOH (0.016 g, 0.4 mmol). A pale-yellow crystal of the complex suitable for X-ray analysis was obtained by slow diffusion of Et<sub>2</sub>O vapor into the solution, yield 0.049 g, 75%. Anal. Calcd. (%) for C<sub>23</sub>H<sub>35</sub>Cl<sub>4</sub>Mn<sub>2</sub>N<sub>6</sub>O<sub>0.50</sub>: C, 42.1; H, 5.3; N, 12.8. Found (%): C, 42.5; H, 5.0; N, 13.0. IR: ν(NH) 3437, 3234, 1502, ν(phen) 1593, 1387, 858, ν(ClO<sub>4</sub><sup>-</sup>) 1107, 651 cm<sup>-1</sup>.

Determination of the unit cell and data collection was performed on a Bruker Smart 1000X diffractometer using graphite monochromated MoK<sub>α</sub> radiation (λ = 0.71037 Å) at 298 ± 2 K with crystal size 0.25 × 0.20 × 0.20

mm<sup>3</sup>. A total of 12355 reflections including 5417 independent with  $I > 2\sigma(I)$  were collected by  $\theta$ - $2\omega$  scan technique in the range  $2.09 \leq \theta \leq 25.24^\circ$ . The structure was solved using direct methods in SHELXS-97<sup>13</sup> and refined using a full-matrix least-square procedure on  $F^2$  in SHELXL-97<sup>14</sup>. Further details of the structure analysis are given in Table-1. Selected bond lengths, angles and positional parameters are presented in Tables 2 and 3, respectively.

TABLE-1  
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR  
[ML][MnCl<sub>4</sub>].0.5C<sub>2</sub>H<sub>5</sub>OH

Empirical formula	C <sub>23</sub> H <sub>35</sub> Cl <sub>4</sub> N <sub>6</sub> O <sub>0.50</sub> Mn <sub>2</sub>
Formula weight	655.25
Temperature (K)	293 ± 2
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions (Å or °)	a = 13.676(4) b = 11.255(4), β = 105.101(5) c = 20.153(7)
Volume (Å <sup>3</sup> )	2995.0(17)
Z, Calculated density (Mg/m <sup>3</sup> )	4, 1.453
Absorption coefficient (mm <sup>-1</sup> )	1.225
F(000)	1348
Crystal size (mm)	0.25 × 0.20 × 0.20
θ range for data collection (°)	2.09 to 25.24
Limiting indices(h, k, l)	-11,16; -13,12; -24,23
Reflections collected/unique	12355/5417
Completeness to θ = 25.03°	99.8 %
Max. and min transmission	0.7917 and 0.7493
Data/restraints/parameters	5417/2/334
Goodness-of-fit on F <sup>2</sup>	1.015
Final R indices [I > 2σ(I)]	R1 = 0.0466, wR2 = 0.1237
R indices (all data)	R1 = 0.0985, wR2 = 0.1452
Largest diff. peak and hole (e. Å <sup>-3</sup> )	0.668 and -0.372

TABLE-2  
BOND LENGTHS (Å) AND ANGLES (°) FOR [MnL][MnCl<sub>4</sub>].0.5C<sub>2</sub>H<sub>5</sub>OH

Mn(1)-N(6)	2.261(4)	Mn(1)-N(3)	2.320(4)
Mn(1)-N(1)	2.292(4)	Mn(1)-N(5)	2.430(4)
Mn(1)-N(4)	2.308(4)	Mn(1)-N(2)	2.454(4)
N(6)-Mn(1)-N(1)	164.94(14)	N(1)-Mn(1)-N(5)	104.80(16)
N(6)-Mn(1)-N(4)	95.84(13)	N(4)-Mn(1)-N(5)	69.94(13)
N(1)-Mn(1)-N(4)	98.82(14)	N(3)-Mn(1)-N(5)	139.00(13)
N(6)-Mn(1)-N(3)	97.74(13)	N(6)-Mn(1)-N(2)	94.19(14)
N(1)-Mn(1)-N(3)	90.46(15)	N(1)-Mn(1)-N(2)	76.91(15)
N(4)-Mn(1)-N(3)	70.24(13)	N(4)-Mn(1)-N(2)	139.01(14)
N(6)-Mn(1)-N(5)	77.07(14)	N(3)-Mn(1)-N(2)	69.07(13)
N(5)-Mn(1)-N(2)	150.96(13)		

TABLE-3  
 ATOMIC COORDINATES ( $\times 10^4$ ) AND EQUIVALENT ISOTROPIC  
 DISPLACEMENT PARAMETERS ( $\text{\AA}^2 \times 10^3$ )

Atom	x	y	z	U(eq)
Mn(1)	3205(1)	2607(1)	804(1)	32(1)
Mn(2)	6656(1)	2581(1)	1630(1)	38(1)
Cl(1)	5172(1)	3800(1)	1452(1)	47(1)
Cl(2)	6357(1)	838(1)	2204(1)	66(1)
Cl(3)	6706(1)	2039(1)	498(1)	55(1)
Cl(4)	8127(1)	3580(2)	2235(1)	72(1)
N(1)	3041(3)	4369(4)	216(2)	51(1)
N(2)	4139(3)	2244(4)	-63(2)	43(1)
N(3)	2186(3)	1666(3)	-153(2)	31(1)
N(4)	1574(3)	2447(3)	920(2)	33(1)
N(5)	3162(3)	3152(4)	1963(2)	40(1)
N(6)	3802(3)	960(3)	1419(2)	35(1)
C(1)	1998(7)	5613(7)	712(5)	136(4)
C(2)	2068(6)	5042(7)	74(5)	105(3)
C(3)	3294(5)	4154(6)	-448(3)	69(2)
C(4)	4229(4)	3428(5)	-364(3)	59(2)
C(5)	3655(4)	1349(5)	-575(3)	44(1)
C(6)	2531(4)	1242(4)	-659(2)	36(1)
C(7)	1882(4)	710(4)	-1244(2)	43(1)
C(8)	869(4)	651(5)	-1302(3)	49(1)
C(9)	474(4)	1098(4)	-773(2)	38(1)
C(10)	1174(3)	1584(4)	-201(2)	30(1)
C(11)	-585(4)	1064(5)	-765(3)	50(1)
C(12)	-897(4)	1487(5)	-226(3)	50(1)
C(13)	-180(3)	1950(4)	372(3)	39(1)
C(14)	849(3)	2005(4)	377(2)	31(1)
C(15)	-447(4)	2365(5)	968(3)	47(1)
C(16)	287(4)	2785(5)	1512(3)	49(1)
C(17)	1313(4)	2812(4)	1472(3)	38(1)
C(18)	2129(4)	3304(5)	2056(3)	48(1)
C(19)	3750(4)	2213(5)	2398(3)	52(2)
C(20)	3492(4)	984(5)	2073(3)	49(1)
C(21)	3520(4)	-176(5)	1042(3)	55(2)
C(22)	3912(5)	-1304(5)	1428(3)	71(2)
C(23)	1074(12)	3810(10)	8008(8)	111(6)
C(24)	197(9)	3890(11)	8260(6)	56(4)
O(1)	-569(10)	4079(10)	7815(6)	173(7)

## RESULTS AND DISCUSSION

The complex consists of [MnL]<sup>2+</sup> cation, [MnCl<sub>4</sub>]<sup>2-</sup> anions and half alcohol molecule. The perspective view of [MnL]<sup>2+</sup> with the numbering scheme is given in Fig. 1. The Mn(II) ion is coordinated by six nitrogen

atoms of the ligand and the coordination geometry can be described as a distorted octahedron arrangement: N(2), N(3), N(4) and N(5) in the equatorial plane [N(4)-Mn(1)-N(3) 70.24(13)°; N(4)-Mn(1)-N(5) 69.94(13)°; N(5)-Mn(1)-N(2) 150.96(13)°; N(2)-Mn(1)-N(3) 69.07(13)°], N(1) and N(6) in the axial positions [N(6)-Mn(1)-N(1) 164.94(14)°]. The Mn-N bond lengths are from 2.261(4) to 2.454(4) Å, which are in the normal range. All Mn-N bond lengths can be classified into three groups: Mn(1)-N(1) [2.292(4) Å] and Mn(1)-N(6) [2.261(4) Å]; Mn(1)-N(3) [2.320(4) Å] and Mn(1)-N(4) [2.308(4) Å]; Mn(1)-N(2) [2.454(4) Å] and Mn(1)-N(5) [2.430(4) Å]. In the first group, the nitrogen atoms are in the axial positions coming from the imine groups at the end of both arms and the bond lengths are the shortest. In the second group, the nitrogen atoms are in the equatorial plane from the phenanthroline ring and the bond lengths are moderate. In the third group, compared with the first group, the nitrogen atoms are in the equatorial plane from the imine group near the phenanthroline ring and the bond lengths are larger. This difference is probably resulted from the larger geometric tension of the two five-membered rings in the equatorial plane involving the nitrogen near the phenanthroline (the average angle of N-Mn-N 70°) than the two ones in the axial positions (the average angle of N-Mn-N 77°) because of the simultaneous formation of three adjacent five-membered rings in the equatorial plane.

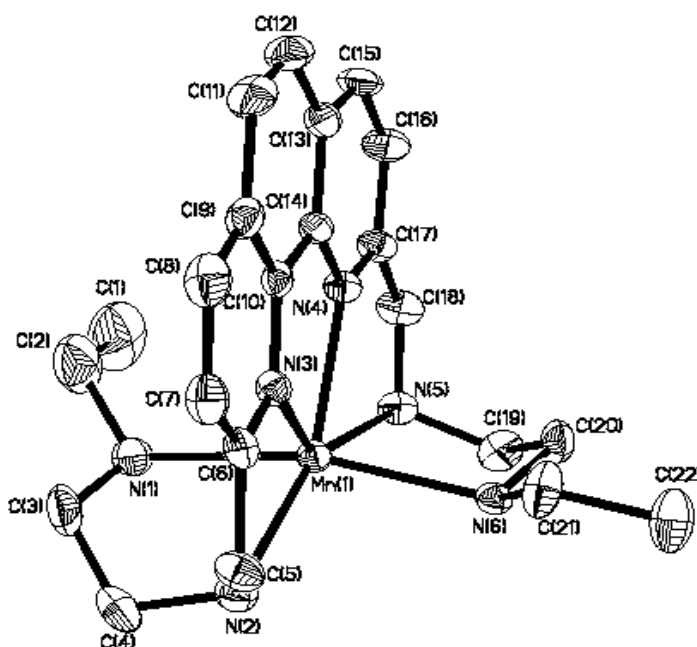


Fig. 1. View of  $[\text{MnL}]^{2+}$  with the numbering scheme adopted

Different from *N,N'*-diisopropyl-1,10-phenanthroline-2,9-dimethanamine<sup>10</sup>, the four nitrogen atoms from both arms of this ligand simultaneously coordinate with the same Mn(II) ion. This may be attributed to the cooperative effect that, for this hexadentate ligand, the coordination of nitrogen from the imine groups at the end of both arms in the axial positions favours the coordination of nitrogen from the imine groups near the phenanthroline ring in the equatorial plane while the effect of the former tetradentate ligand is absent.

Fig. 2 is a packing diagram of the complex. Hydrogen bonds are formed between the chlorine ions of  $[MnCl_4]^{2-}$  and the adjacent hydrogen atoms of imine group.

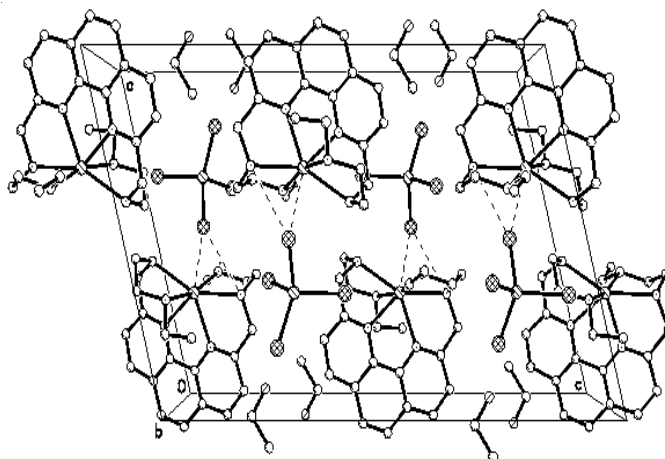


Fig. 2. Packing diagram for  $[MnL][MnCl_4] \cdot 0.5C_2H_5OH$

Although, we attempted to get binuclear complex of the ligand by changing the ratio of the metal ion to the ligand, we only obtained the mononuclear complex. The excess Mn(II) ions are combined with  $Cl^-$  ions forming  $[MnCl_4]^{2-}$  anions, as a result of the strong complexation ability of the symmetrical hexadentate ligand and spherical coordination surroundings of Mn(II) ions.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication No. CCDC- 219814. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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