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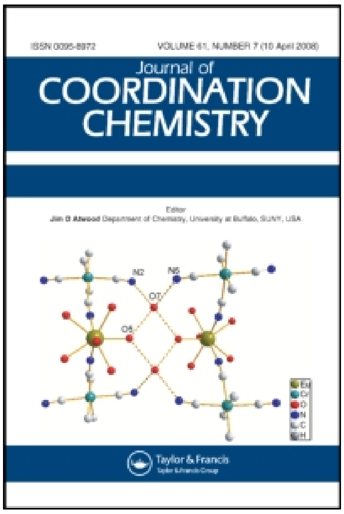

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
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THE STRUCTURE OF DICHLOROBIS-1, 10-PHENANTHROLINE MANGANESE(II)

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To cite this Article Malinowski, Tadeusz J. , Kravtsov, Victor Ch. , Simonov, Yurii A. , Lipkowski, Janusz and Bologa, Olga. A.(1996) 'THE STRUCTURE OF DICHLOROBIS-1, 10-PHENANTHROLINE MANGANESE(II)', Journal of Coordination Chemistry, 37: 1, 187 — 193

To link to this Article: DOI: 10.1080/00958979608023551

URL: http://dx.doi.org/10.1080/00958979608023551

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J. Coord. Chem., 1996, Vol 37, pp. 187–193
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THE STRUCTURE OF DICHLOROBIS-1, 10-PHENANTHROLINE MANGANESE(II)

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(Received February 14, 1995; in final form July 24, 1995)

The preparation and characterization of the title complex, [Mn(Phen)$_2$Cl$_2$] are reported. The crystal structure determination shows that the two 1,10-phenanthroline ligands and two Cl-atoms form the pyramidally distorted octahedron around Mn(II). The chemically equivalent ligands play a different structural role in this complex. Crystals of [Mn(Phen)$_2$Cl$_2$] are monoclinic, space group $P2_1/a$ with unit cell dimensions $a = 14.522(4)$, $b = 15.205(2)$, $c = 9.470(1)$Å, $\beta = 98.90(2)°$, $V = 2065.9(7)$Å^3, $Z = 4$. The structure was refined by a full-matrix least-squares procedure to $R = 0.043$ for 2783 observed reflections.

KEYWORDS: manganese(II), 1,10-phenanthroline, coordination polyhedron, X-ray crystal structure

INTRODUCTION

Coordination compounds of manganese have received interest because of the possibility to stabilize different oxidation numbers of Mn, to activate enzymes and take part in other biological processes[1] and their diverse application in catalysis. The mixed-valence binuclear complex[2] [(Phen)$_2$Mn(III)(μ-O)$_2$Mn(IV)(Phen)$_2$]$^{3+}$, where Phen = 1.10-phenathroline, is a model compound for Mn containing species occurring in photosynthesis.[3] The Phen is included as chelate ligand in various stable complexes in which Mn has different oxidation numbers. The Mn(I) complexes with Phen have been studied by X-ray structure determinations,[4–9] while structural information about Mn(II) compounds bearing the same ligand is quite restricted.[10,11] Crystal structure determination of the title compound

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[Mn(phen)$_2$Cl$_2$], **1** has been undertaken in order to elucidate the ligand coordination polyhedron.

EXPERIMENTAL

Preparation of [Mn(Phen)$_2$Cl$_2$]

The title compound was obtained from reaction between Phen and $MnCl_2 \cdot 6H_2O$ (two-to-one) in the presence of water. Crystals suitable for X-ray analysis were obtained directly from the preparation. *Anal.* Calcd. for $C_{24}H_{16}Cl_2MnN_4$ (%): C, 57.15; H, 3.38; N, 11.07. Found: C, 57.62; H, 3.35; N, 10.98%.

X-ray Crystallography

The yellow prismatic crystal was mounted in random orientation on the tip of a glass fibre with epoxy. Preliminary examination and data collection were performed on a KUMA four-circle diffractometer (graphite monochromator, MoK_α-radiation). The cell constants and orientation matrix were calculated from least-squares fitting of the setting angles for 63 reflections. Three control reflections, collected every 200 reflections, showed no significant trends. Crystal data and details of data collection together with structure refinement are summarized in Table 1. Intensity of data were corrected for LP factors. The absorption was not taken into account. The structure was solved by the heavy atom method. Non-H atoms were refined with anisotropic thermal parameters by a full-matrix least-squares procedure based on F^2. Hydrogen atoms were placed in idealized positions at 0.93 Å from corresponding C-atoms and only isotropic thermal parameters were refined for them. Neutral atom scattering factors with anomalous dispersion corrections were taken from ref. 12. All calculations were performed using the SHELXS-86[13] and SHELXL-93[14] program packages. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2. Selected bond distances and angles for *1* are listed in Table 3.

RESULTS AND DISCUSSION

A view of the complex with the numbering scheme is shown in Fig. 1, and Fig. 2 shows the packing of the molecules. The Mn(II) ion displays a distorted octahedral coordination with 1,10-phenanthroline ligands in a N,N-bidentate fashion and two Cl-atoms. The Phen ligands *A* (N(1A), N(2A),C(1A)-C(12A)) and *B* (N(1B), N(2B), C(1B)-C(12B)) are planar, the largest deviations from mean planes are 0.026(3) Å for C(3A) and 0.050(4) Å for C(2B) atoms, respectively. The Mn ion lies 0.317(3) Å from the ligand **A** mean plane and only 0.073(3) Å from the ligand **B**. The angle between the ligand-atom plane **A** and **B** is 89.49(6)°. It is necessary to note that the dihedral angles between these planes and plane **C** determined by Mn Cl(1) and Cl(2) differ (**AC** is 89.72(5)° and **B**/**C** is 75.51(4)°).

The metal-N(Phen) bond distances are equivalent when the *trans* ligands are the same[15,16] or these distances vary according to the electronegative character of the *trans*-ligand.[4,6] In the structure of **1** only two distances Mn(1)-N(1A) 2.295(3) Å and Mn(1)-N(2B) 2.294(3) Å are identical. Other bond distances Mn(1)-N(2A)

Table 1 Summary of crystal data, intensity collection and structural refinement for **1**.

Compound	$[Mn(Phen)_2Cl_2]$
Empirical formula	$C_{24}H_{16}Cl_2Mn\ N_4$
Formula weight	486.25
Temperature	293(2) K
Wavelength (Å)	0.71070
Crystal system	monoclinic
Space group	$P2_1/a$
a(Å)	14.522(4)
b(Å)	15.205(2)
c(Å)	9.470(1)
β(°)	98.90(2)
V(Å^3)	2065.9(7)
Z	4
$D_{calc.}$(g cm^{-3})	1.563
μ(cm^{-1})	9.18
F(000)	988
Crystal size (mm)	0.55 × 0.40 × 0.32
θ-range for data collection (°)	2.18 - 30.08
Index ranges	$-20 \leq h \leq 0,\ 0 \leq k \leq 21,\ -13 \leq l \leq 13$
Reflections collected	5098
Independent reflections	4944 [R(int) = 0.0328]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4944 /0/ 296
Goodness-of-fit on F^2	1.018
Final R indices for 2783 $F_{obs.}$ with [I>2σ(I)]	$R1^a = 0.0432$, $wR2^b = 0.1088$
R indices (all data)	$R1 = 0.1049$, $wR2 = 0.1395$
Largest diff. peak and hole (e Å^{-3})	0.533 and -0.501

[a] $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$.
[b] $wR2 = [\Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2]]^{0.5}$.
$w = 1/[\sigma^2(F^2) + (0.0713^*P)^2 + 0.3^*P]$, where $P = (\max(F_o^2,0) + 2^*F_c^2)/3$.

2.344(3) Å and Mn(1)-N(1B) 2.369(3) Å are longer due to the *trans* influence of the Cl anions. These two distances are not equal and the difference is significant (t_o = 5.9).[17] The distances Mn(1)-Cl(1) 2.451(1) Å and Mn(1)-Cl(2) 2.438(1) Å differ also (t_o = 9.2). Such distinctions between the lengths of chemical identical bonds were noted earlier in the structure of the 1,10-Phenanthroline bis(acetyl-acetonato) manganese(II) complex,[10] but the reason for this has not been explained. It can be

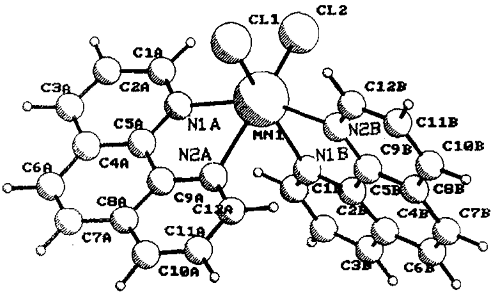

Figure 1 Molecular structure and numbering scheme for **1**.

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	*x/a*	*y/b*	*z/c*	U(eq)
Mn(1)	5487(1)	2709(1)	2454(1)	32(1)
Cl(1)	4233(1)	2838(1)	411(1)	47(1)
Cl(2)	6695(1)	3696(1)	1867(1)	47(1)
N(1A)	6174(2)	1467(2)	1715(3)	37(1)
N(2A)	4764(2)	1472(2)	3274(3)	37(1)
C(1A)	6859(3)	1467(3)	926(4)	47(1)
C(2A)	7152(3)	702(3)	288(4)	56(1)
C(3A)	6721(3)	-71(3)	472(4)	59(1)
C(4A)	6004(3)	-114(3)	1310(4)	50(1)
C(5A)	5752(2)	685(2)	1904(4)	38(1)
C(6A)	5521(4)	-904(3)	1572(5)	64(1)
C(7A)	4830(4)	-903(3)	2377(5)	62(1)
C(8A)	4547(3)	-106(2)	2998(4)	48(1)
C(9A)	4999(2)	690(2)	2740(4)	37(1)
C(10A)	3838(3)	-56(3)	3835(5)	56(1)
C(11A)	3596(3)	721(3)	4355(5)	55(1)
C(12A)	4076(3)	1476(3)	4050(4)	48(1)
N(1B)	6283(2)	2725(2)	4834(3)	36(1)
N(2B)	4684(2)	3583(2)	3820(3)	32(1)
C(1B)	7088(3)	2338(3)	5321(5)	46(1)
C(2B)	7526(3)	2395(3)	6742(5)	57(1)
C(3B)	7107(3)	2866(3)	7685(5)	56(1)
C(4B)	6259(3)	3292(2)	7230(4)	42(1)
C(5B)	5873(2)	3203(2)	5772(3)	34(1)
C(6B)	5772(3)	3807(3)	8153(4)	56(1)
C(7B)	4975(3)	4226(3)	7652(4)	53(1)
C(8B)	4569(3)	4167(2)	6166(4)	38(1)
C(9B)	5022(2)	3657(2)	5239(3)	31(1)
C(10B)	3751(3)	4613(3)	5581(4)	45(1)
C(11B)	3426(2)	4532(2)	4163(4)	42(1)
C(12B)	3911(2)	4015(2)	3309(4)	37(1)

supposed that differences in bond distances is connected with the electron configuration of the Mn(II) atom. The coordination polyhedron distortion is of pyramidal character. The N(1A), N(2A), N(2B) and Cl(2) atoms are situated in the equatorial plane and are roughly coplanar. The largest deviation from the mean plane is 0.041(3) Å for N(2A) atom. N(1B) and Cl(1) atoms are in apical positions. The bond distances Mn-N and Mn-Cl are shorter in the equatorial plane than for atoms in apical positions. The Mn ion is displaced from the equatorial mean plane by 0.253(3) Å in the direction of the Cl(1) anion.

The Phen ligands show no unusual features, the variation in the C-N and C-C lengths (Table 3) closely parallel in *A* and *B* and follow the pattern observed in other phenanthroline complexes. The N(1A)-Mn(1)-N(2A) and N(1B)-Mn(1)-N(2B) chelate angles equal 71.3(1)° and 70.9(1)° respectively, and are similar to those observed in Mn(II) Phen complexes.[10,11]

Two intramolecular contacts C(12B)...Cl(1) 3.368(4) Å and C(1A)...Cl(2) 3.521(4) Å are different. The first is shorter than the sum of van der Waals radii[18,19] Cl(1.75 Å) and C(1.75 Å), the second is a little longer. Perhaps these contacts are forced by the rigidity of the ligands and Mn(II) coordination polyhedron. However

Table 3 Bond lengths [Å] and angles [deg] for **1**.

Mn(1)-Cl(1)	2.451(1)	Mn(1)-N(2A)	2.344(3)
Mn(1)-Cl(2)	2.438(1)	Mn(1)-N(1B)	2.369(3)
Mn(1)-N(1A)	2.295(3)	Mn(1)-N(2B)	2.294(3)
N(1A)-C(1A)	1.334(5)	N(1B)-C(1B)	1.327(5)
N(1A)-C(5A)	1.361(5)	N(1B)-C(5B)	1.354(4)
N(2A)-C(12A)	1.329(5)	N(2B)-C(12B)	1.326(4)
N(2A)-C(9A)	1.355(5)	N(2B)-C(9B)	1.363(4)
C(1A)-C(2A)	1.406(6)	C(1B)-C(2B)	1.399(6)
C(2A)-C(3A)	1.357(7)	C(2B)-C(3B)	1.360(6)
C(3A)-C(4A)	1.405(6)	C(3B)-C(4B)	1.398(6)
C(4A)-C(5A)	1.411(5)	C(4B)-C(5B)	1.415(5)
C(4A)-C(6A)	1.432(6)	C(4B)-C(6B)	1.439(6)
C(5A)-C(9A)	1.446(5)	C(5B)-C(9B)	1.436(5)
C(6A)-C(7A)	1.350(7)	C(6B)-C(7B)	1.341(6)
C(7A)-C(8A)	1.433(6)	C(7B)-C(8B)	1.441(5)
C(8A)-C(10A)	1.396(6)	C(8B)-C(10B)	1.406(5)
C(8A)-C(9A)	1.416(5)	C(8B)-C(9B)	1.409(5)
C(10A)-C(11A)	1.348(6)	C(10B)-C(11B)	1.359(5)
C(11A)-C(12A)	1.396(6)	C(11B)-C(12B)	1.395(5)
Cl(1)-Mn(1)-Cl(2)	104.09(4)	Cl(2)-Mn(1)-N(2B)	102.62(8)
Cl(1)-Mn(1)-N(1A)	97.48(8)	N(1A)-Mn(1)-N(2A)	71.25(11)
Cl(1)-Mn(1)-N(2A)	90.57(8)	N(1A)-Mn(1)-N(1B)	97.34(10)
Cl(1)-Mn(1)-N(1B)	160.72(8)	N(1A)-Mn(1)-N(2B)	158.63(11)
Cl(1)-Mn(1)-N(2B)	91.06(7)	N(2A)-Mn(1)-N(1B)	82.59(10)
Cl(2)-Mn(1)-N(1A)	94.27(8)	N(2A)-Mn(1)-N(2B)	89.19(10)
Cl(2)-Mn(1)-N(2A)	160.82(8)	N(1B)-Mn(1)-N(2B)	70.93(10)
Cl(2)-Mn(1)-N(1B)	87.02(8)		
Mn(1)-N(1A)-C(1A)	124.6(3)	Mn(1)-N(1B)-C(1B)	126.9(3)
Mn(1)-N(1A)-C(5A)	116.9(2)	Mn(1)-N(1B)-C(5B)	115.5(2)
C(1A)-N(1A)-C(5A)	117.6(3)	C(1B)-N(1B)-C(5B)	117.7(3)
Mn(1)-N(2A)-C(9A)	115.4(2)	Mn(1)-N(2B)-C(9B)	117.9(2)
Mn(1)-N(2A)-C(12A)	126.3(3)	Mn(1)-N(2B)-C(12B)	123.8(2)
C(9A)-N(2A)-C(12A)	117.7(3)	C(9B)-N(2B)-C(12B)	118.3(3)
N(1A)-C(1A)-C(2A)	122.9(4)	N(1B)-C(1B)-C(2B)	123.5(4)
C(1A)-C(2A)-C(3A)	119.0(4)	C(1B)-C(2B)-C(3B)	118.8(4)
C(2A)-C(3A)-C(4A)	120.7(4)	C(2B)-C(3B)-C(4B)	120.3(4)
C(3A)-C(4A)-C(5A)	116.5(4)	C(3B)-C(4B)-C(5B)	117.0(4)
C(3A)-C(4A)-C(6A)	124.2(4)	C(3B)-C(4B)-C(6B)	123.9(4)
C(5A)-C(4A)-C(6A)	119.3(4)	C(5B)-C(4B)-C(6B)	119.1(4)
N(1A)-C(5A)-C(4A)	123.4(4)	N(1B)-C(5B)-C(4B)	122.9(3)
N(1A)-C(5A)-C(9A)	117.5(3)	N(1B)-C(5B)-C(9B)	118.0(3)
C(4A)-C(5A)-C(9A)	119.1(4)	C(4B)-C(5B)-C(9B)	119.1(3)
C(4A)-C(6A)-C(7A)	121.5(4)	C(4B)-C(6B)-C(7B)	121.5(3)
C(6A)-C(7A)-C(8A)	121.2(4)	C(6B)-C(7B)-C(8B)	121.1(4)
C(7A)-C(8A)-C(9A)	118.8(4)	C(7B)-C(8B)-C(9B)	118.8(4)
C(7A)-C(8A)-C(10A)	124.2(4)	C(7B)-C(8B)-C(10B)	123.3(4)
C(9A)-C(8A)-C(10A)	117.0(4)	C(9B)-C(8B)-C(10B)	117.9(3)
N(2A)-C(9A)-C(5A)	117.6(3)	N(2B)-C(9B)-C(5B)	117.7(3)
N(2A)-C(9A)-C(8A)	122.4(4)	N(2B)-C(9B)-C(8B)	121.9(3)
C(5A)-C(9A)-C(8A)	120.0(4)	C(5B)-C(9B)-C(8B)	120.4(3)
C(8A)-C(10A)-C(11A)	120.8(4)	C(8B)-C(10B)-C(11B)	119.3(3)
C(10A)-C(11A)-C(12A)	118.6(4)	C(10B)-C(11B)-C(12B)	119.7(4)
N(2A)-C(12A)-C(11A)	123.5(4)	N(2B)-C(12B)-C(11B)	122.9(3)

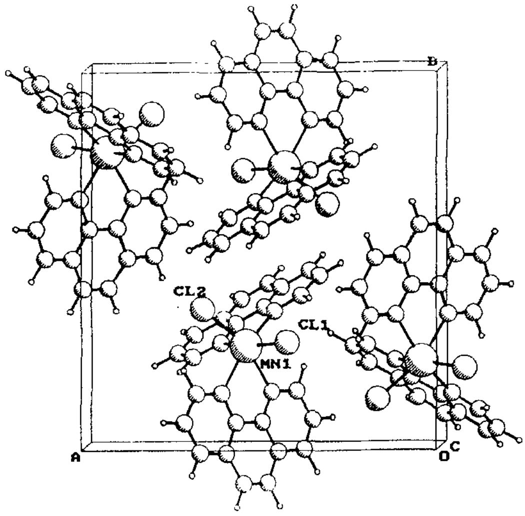

Figure 2 The molecular packing of **1**.

the corresponding H(C(12B))...Cl(1) 2.718(4) Å and H(C(1A))...Cl(2) 2.894(4) Å distances are in the range where C-H...Cl H-bond is possible[20] and may take part in stabilization of the complex. The angles are C(12B)-H...Cl(1) 127.7(1)° and C(1A)-H...Cl(2) 125.9(1)°

In conclusion the chemically equivalent ligands play somewhat different structural roles in this complex as shown by the ligand arrangement, bond distances in the coordination polyhedron and in the intramolecular contacts.

Fig. 2 shows the packing of the molecules. The molecules are held in the crystal by van der Waals forces. The closest intermolecular contacts are C(6A)...Cl(1)^{i}(1 -x, -y, -z) 3.537(4) Å, C(6B)...Cl(2)^{ii} (x,y,1 + z) 3.563(4) Å. Despite these contacts being a little longer than the sum of van der Waals radii of Cl and C, the corresponding H...Cl distances and C-H...Cl angles permit the existence of C-H...Cl intermolecular hydrogen bonds: H(C(6A))...Cl(1)^{i} 2.630(4) Å, H(C(6B))...Cl(2)^{ii} 2.648(4) Å. The angles C(6A)-H...Cl(1)^{i} 165.2(1)° and C(6B)-H...Cl(2)^{ii} 170.8(1)°. Other non-hydrogen contacts are longer than 3.6 Å.

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