

Crystal Structure of Dichlorodiaquabis-(*p*-dimethylaminobenzaldehyde)manganese(II)

Veysel T. YILMAZ, Turan K. YAZICILAR, Halis ÖLMEZ

*Ondokuz Mayıs University, Faculty of Arts and Sciences
Chemistry Department, 55139 Kurupelit, Samsun - TURKEY*

R. Alan HOWIE

*Aberdeen University, Chemistry Department
Meston Walk, Aberdeen, AB9 2UE, UK*

Received 30.09.1997

The crystal structure of dichlorodiaquabis-(*p*-dimethylaminobenzaldehyde)manganese(II), $[\text{MnCl}_2(\text{OH}_2)_2(\text{C}_9\text{H}_{11}\text{NO})_2]$, was determined from X-ray intensity data. The structure consists of the isolated molecules of the complex. The central Mn atom in the complex is coordinated by two *p*-dimethylaminobenzaldehyde and two water molecules and also two chlorine atoms, resulting in a distorted octahedral environment. The same molecules or ions occupy *trans* positions. The crystal structure is stabilized by weak hydrogen bonds present between the isolated molecules.

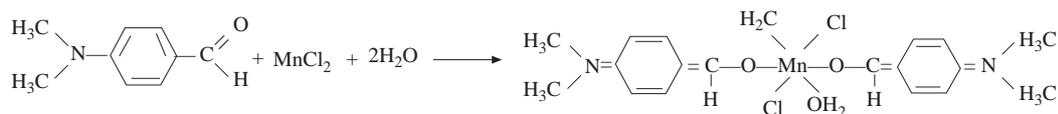
Introduction

p-dimethylaminobenzaldehyde (DMABA) reacts with various species to form molecular complexes^{1–8}. These complexes are used particularly in colorimetric determinations. Rosencrance and Jagodzinski⁹ first reported the synthesis and spectral characterization of the Zn(II) complex of DMABA. The crystal structure of hydrobromide salt¹⁰ and dichlorodiphenyl-tin(IV) complex¹¹ of DMABA were studied. Some transition metal complexes of this compound¹² were prepared for this study and we report the crystal structure of the Mn(II) complex of DMABA to illustrate the bonding of the ligand in the metal complexes.

Experimental

DMABA ($\text{C}_9\text{H}_{11}\text{NO}$) was purchased from Merck and recrystallized from water to remove any impurities present. MnCl_2 was the analytical reagent product used (Merck).

In the preparation of the complex, MnCl_2 was dissolved in absolute ethanol and a solution of DMABA in ethanol was added gradually to this solution. A colour change occurred during this process. The solution was allowed to crystallize at room temperature. The yellow-orange crystals of the complex were washed with acetone and dried in air. The reaction can be written as follows:



Single-crystal X-ray diffraction data were obtained from a suitable plate-needle crystal on a Nicolet P3 four-circle diffractometer with MoK α radiation and graphite monochromator at 298 K. The cell parameters were determined using 14 reflections in the range $8.6 < \theta < 10.1$. The RDNIC program¹³ was used for data reductions and SHELXS86¹⁴ and SHELX76¹⁵ for the structure solution and refinement, respectively. Refinement was by full-matrix least squares. Atomic-scattering factors were taken from Int. Tables for X-ray Crystallography¹⁶. Further details concerning data collection and refinement are given in Table 1. All non-H atoms were refined anisotropically. Aryl and methyl H atoms were refined isotropically in calculated positions with C-H = 0.95 Å. Aldehyde H was found in a difference map and refined isotropically according to standard methodology. H atoms in the water molecules were not determined. The molecular graphics were obtained using graphic programs^{17,18}. All computations were performed on the SUN SPARCServer (UNIX operating system) of the Computing Centre of the University of Aberdeen.

Table 1. Crystallographic data and refinement parameters for [MnCl₂(OH₂)₂(DMABA)₂]

Formula	C ₁₈ H ₂₂ N ₂ O ₄ MnCl ₂	Range of hkl	± 34; 0-10; 0-13
M _w	460.26	Scan type	$\theta/2\theta$
Crystal size(mm)	0.60 × 0.25 × 0.06	Scan speed(° min ⁻¹)	5.33-58.6
Crystal colour and habit	yellow-orange	2 θ max(°)	30
Crystal system	Monoclinic	Standard reflection	2
Lattice parameters		Max. intensity variation(%)	2.19
a(Å)	24.492(24)	No. of reflections measured	3268
b(Å)	8.609(7)	No. of reflections with F > 4 σ (F)	1398
c(Å)	9.814(12)	No. of refined parameters	136
α (°)	90	R	0.077
β (°)	96.89(9)	R _w	0.074
γ (°)	90	Weight scheme	1/(σ^2 F + 0.000893 × F ²)
V(Å ³)	2054(4)	Max Δ/σ	0.003
Space group	C2/c	$\rho_{\min} - \max(e\text{Å}^{-3})$	-0.62, 0.64
Z	4	GOF	1.8685
Dc(gcm ⁻¹)	1.488		
Reflection for lattice parameters			
number	14		
θ range(°)	8.6-10.1		
μ (cm ⁻¹)	9.04		
Temperature (K)	9.04		
Radiation, λ (Å)	Mo-K α 0.71073		

Results and Discussions

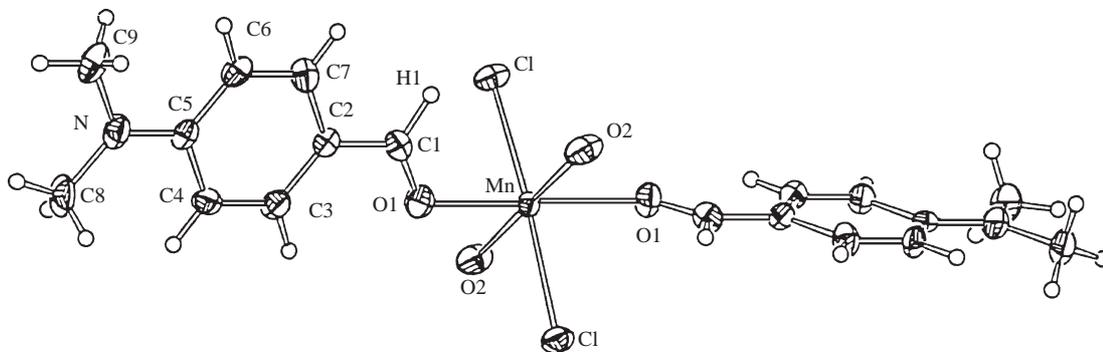
The molecular structure and unit-cell content of [MnCl₂(OH₂)₂(DMABA)₂] are illustrated in Figures 1 and 2, respectively. Atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are given in Table 2.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for the non-hydrogen atoms of $[\text{MnCl}_2(\text{OH}_2)_2(\text{DMABA})_2]$

	x/a	y/b	z/c	Ueq
Mn	0.5000	0.2328 (1)	0.2500	0.0238 (5)
Cl	0.5161 (1)	0.2508 (1)	0.5090 (2)	0.0381 (6)
O1	0.4107 (2)	0.2126 (1)	0.2636 (6)	0.0408 (18)
O2	0.5000	-0.0233 (1)	0.2500	0.046 (3)
O3	0.5000	0.4886 (1)	0.2500	0.044 (2)
N	0.1650 (3)	0.1003 (1)	0.4000 (7)	0.041 (2)
C1	0.3905 (3)	0.1226 (1)	0.3404 (8)	0.034 (2)
C2	0.3329 (3)	0.1139 (1)	0.3524 (7)	0.031 (2)
C3	0.2944 (3)	0.2093 (1)	0.2774 (8)	0.036 (2)
C4	0.2400 (3)	0.2076 (1)	0.2928 (8)	0.035 (2)
C5	0.2193 (3)	0.1031 (1)	0.3860 (7)	0.030 (2)
C6	0.2579 (3)	0.0048 (1)	0.4623 (8)	0.037 (2)
C7	0.3124 (3)	0.0109 (1)	0.4463 (8)	0.038 (2)
C8	0.1252 (3)	0.2037 (1)	0.3227 (10)	0.055 (3)
C9	0.1431 (4)	-0.0066 (1)	0.4953 (10)	0.052 (3)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 3 lists selected bond distances and angles. The lattice parameters given in Table 1 indicate that the complex has a monoclinic crystal structure and each unit cell contains four molecules of the complex. The structure consists of essentially isolated molecules. The bonding of DMABA through carbonyl oxygen, which is also evident in spectral data¹², is clearly shown in Figure 1.

**Figure 1.** A molecule of $[\text{MnCl}_2(\text{OH}_2)_2(\text{DMABA})_2]$ showing atom labels and 40 % probability ellipsoids for non-H atoms. H atoms are shown as spheres of arbitrary radius.

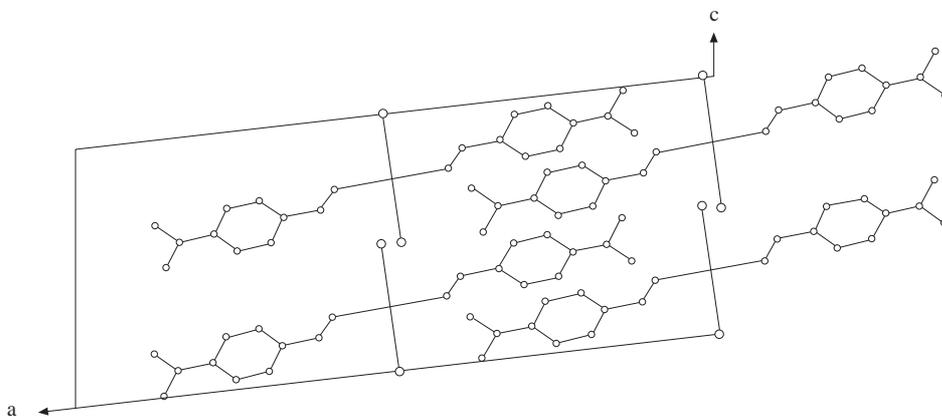
The molecule sits on 2-fold crystallographic axes passing through O2, O3 and Mn, and therefore has C_2 symmetry. The Mn(II) ion was octahedrally coordinated by two DMABA and two water molecules and two chlorine atoms occupying the *trans* positions. The interaxial angles (88.89 , 85.50 , 93.51°) in Table 3 indicate that Mn is in a slightly distorted octahedral environment. Figure 1 reveals that the DMABA molecules bonded to Mn occur in symmetry-related pairs but are twisted relative to one another with the result that the angle between the planes of the aromatic rings, $88^\circ C$ is very close to 90° . The DMABA shows almost complete planarity as a whole. The dihedral angles C8-N-C5-C6, C9-N-C5-C4 and O1-C1-C2-C7 were determined to be $178.9(7)^\circ$, $180.0(7)^\circ$ and $177.9(7)^\circ$, respectively.

Table 3. Selected bond lengths (Å) and angles (°) of $[\text{MnCl}_2(\text{OH}_2)_2(\text{DMABA})_2]$

Mn-Cl	2.5301(16)	O1-Mn-Cl	88.89(15)
Mn-O1	2.213(5)	O1-Mn-O2	85.50(18)
Mn-O2	2.204(7)	O2-Mn-Cl	93.51(12)
Mn-O3	2.202(7)	C1-O1-Mn	124.1(5)
C1-H1	1.04(6)	C1-C2-O1	123.9(5)
C1-O1	1.226(9)	N-C5-C4	120.6(7)
C1-C2	1.433(10)	C9-N-C5	122.6(7)
C5-N	1.353(9)	C1 ⁱⁱ -O2-C1 ⁱⁱⁱ	102.6(1)
C9-N	1.459(10)	C1-H1-O2	103(4)
C2-C3	1.393(10)		
C3-C4	1.358(10)		
C5-C4	1.419(10)		
C6-C7	1.364(10)		
C2-C7	1.413(10)		
O2...C1 ⁱⁱ	3.132(5)		
O2...C1 ⁱⁱⁱ	3.132(5)		
H1...O2	2.79(6)		
C1...O2	3.181(8)		

Symmetry operations:

- i. $1-x, y, 1/2-z$
- ii. $1-x, -y, 1-z$
- iii. $x, -y, z-1/2$

**Figure 2.** The unit cell of $[\text{MnCl}_2(\text{OH}_2)_2(\text{DMABA})_2]$ viewed from above b. Non-H atoms are shown as spheres of arbitrary radius increasing in the order Mn(thick), C, N, and O.

The length of Mn-carbonyl oxygen is 2.213 Å. The C-O bond length of the DMABA in the complex is 1.226 Å, which is significantly longer than that of the unreacted carbonyl group of the hydrobromide salt of the same ligand (1.184 Å)¹⁰. The loss of the double-bond character upon complexing resulted in the lengthening of the C-O bond and gave a partial double-bond character to the N-C5 bond (1.353 Å) when compared with N-C9 (1.459 Å) in the same molecule. The shortening of the N-C5 bond clearly shows that DMABA exhibits a quinonoid-like arrangement in the complex. The lengths of the C-C bonds in the benzene

ring of the complex ranged from 1.358 to 1.419 Å, the average value being 1.393 Å, which is somewhat different from those reported in the literature (1.375 Å)¹⁰. A comparison of the bond lengths of the benzene ring reveals some interesting results. The bond lengths of C3-C4 and C6-C7 are very similar and are significantly shorter than those of the others (C2-C3, C4-C5, C5-C6 and C2-C7). These observations also support the quinonoid-like structure of DMABA in the Mn(II) complex. X-ray studies of *p*-(dimethylamino)nitrobenzene showed that this type of molecule receive contributions from a quinonoid-type structure as indicated by decreased bond lengths¹⁹.

Because of the difficulty in determining the positions of H atoms in water molecules (O2), the intramolecular and intermolecular hydrogen bonding between the molecules was not clear. However, the distance between the aldehyde H and the water O2 (H1 ... O2 = 2.79(6) Å) suggests the existence of possible intramolecular hydrogen bonding. The intermolecular contacts between the water O and the C1 of the adjacent molecules (O2...C1ⁱⁱ and O2...C1ⁱⁱⁱ) are both 3.132(5) Å, which is indicative of such weak interactions. This interaction has the effect of connecting the molecules in 'step-ladder' chains running parallel to *c* (Fig. 2). It can be said that the crystal structure is stabilized by both weak hydrogen bonds and Van der Waals contacts.

Acknowledgement

The authors wish to thank Ondokuz Mays University for the financial support given to this project.

References

1. P. Byrom and J.H. Turnbull, **Talanta** **10**, 1217-21 (1963).
2. M. Pesez and A. Petit, **Bull. Soc. Chim. Fr.**, 122-128 (1947).
3. V.I. Rychkova and Y.I. Belskaya, **Energetik** **3**, 28-33 (1984). **Chem. Abstr.** **101**, 287 (1984).
4. H. Falter, K. Jayasimhulu and R.A. Day, **Analyt. Biochem.** **67**, 359-366 (1975).
5. A.A. Kulikov, M.K. Lukyanova and A.V. Nishlyuk, **Neftepererab. Neftekhim.** **9**, 31-32 (1988). **Chem. Abstr.** **109**, 184 (1988).
6. M.S. Kravchenko, A.V. Chernaya, L.V. Tokar and V.N. Kleshchevnikova, **Khim. Tekhnol. Vody** **10**, 126-129 (1988). **Chem. Abstr.** **109**, 317 (1988).
7. E. Sawicki and C.R. Sawicki, "**Aldehydes-Photometric Analysis**", Vols. 1 and 2, Academic Press, New York, 1975.
8. H.S. Rathore, A. Mohammad, F. Prakash and K. Kumari, **J. Chem. Sci.** **6**, 20-51 (1980). **Chem. Abstr.** **96**, 830 (1982).
9. J.G. Rosencrance and P.W. Jagodzinski, **Spectrochim. Acta**, **42A**, 869-879 (1986).
10. J.K. Dattagupta and N.N. Saha, **Acta Cryst.** **B29**, 1228 (1973).
11. C. Mahadevan, M. Seshasayee and A.S. Kothiwal, **Crys. Struct. Commun.** **11**, 1725-30 (1982). **Chem. Abstr.** **99**, 510 (1983).
12. T.K. Yazıcılar, V.T. Yılmaz and H. Ölmez, **Synth. React. Inorg. Met-Org. Chem.** **27**, 825-833 (1997).
13. R.A. Howie, "**RDNIC, Data Reduction Program for Nicolet P3 Diffractometer**", Univ. of Aberdeen, Scotland 1980.

14. G.M. Sheldrick, **Acta Cryst.** **A46**, 467 (1990).
15. G.M. Sheldrick, “**SHELX76, Program for Crystal Structure Determination**”, Univ. of Cambridge, England 1976.
16. “**International Tables for X-ray Crystallography**”, Vol.4, Kynoch Press, Birmingham, U.K., 1974.
17. P.D.G. Cradwick, PLOTAID, “**A Fortran Program for the Preparation of Molecular Drawings**”, Macaulay Land Use Research Inst., Aberdeen Scotland (1970).
18. P. McArdle, **J. Appl. Cryst.** **27**, 438 (1994).
19. T.C.W. Mak and J. Trotter, **Acta Cryst.** **18**, 68-74 (1965).