

Structure of the Manganese (V) Complex- $\text{Mn}\cdot\mathbf{3}/\mathbf{2}(\mu\text{-DHBQ})\cdot\mathbf{4H}_2\mathbf{O}\cdot\mathbf{2Cl}$

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Abstract: The novel complex of Mn(V): $\text{Mn}\cdot\mathbf{3}/\mathbf{2}(\mu\text{-DHBQ})\cdot\mathbf{4H}_2\mathbf{O}\cdot\mathbf{2Cl}$ (where, H_2DHBQ = 2,5-dihydroxyl-1,4-benzoquinone) was synthesized and its crystal structure has been determined by X-ray diffraction. The complex belongs to trigonal system with space group P3(#147), $a=1.415(2)$ nm, $c=0.6552(4)$ nm, $V=1.1371(7)$ nm³, $Z=2$, $D_x=1.183$ g/cm³, $\mu=7.37$ cm⁻¹, $F(000)=408.00$, $R=0.041$, $R_w=0.046$.

Keywords: Manganese (V), crystal structure, bridging ligand, 2,5-dihydroxyl-1,4- benzoquinone.

Few compounds with Mn in the +5 oxidation state were structurally characterized so far. C.L.Hill¹ first determined the crystal structure of the Mn (V) complex: **NMnTpMPP-Nitriodotrtrakis** (p-methoxyphenyl) porphinnato-manganese (V). The papers^{2,3} reported several novel manganese(V) and (VI) complexes. Recent publications have been established that the coordination compounds of high valent manganese display many interesting features. They show ability to undergo intramolecular interligand or metal-ligand electron transfer reaction, especially on the nature of the biological unit responsible for water oxidation/oxygen evolution in the photosynthetic apparatus of green plants and cyanobacteria^{4,5}. In this paper we synthesized and determined the novel complex of manganese (V): $\text{Mn}\cdot\mathbf{3}/\mathbf{2}(\mu\text{-DHBQ})\cdot\mathbf{4H}_2\mathbf{O}\cdot\mathbf{2Cl}$

Experimental

2,5-dihydroxyl-1,4-benzoquinone was prepared and purified as reported previously⁶. The ligand H_2DHBQ was dissolved in H₂O diluted EtOH ($V_{\text{H}_2\text{O}} : V_{\text{EtOH}} = 2:1$), and then adjusted pH=9 with NaOH; MnAc₂ was dissolved in H₂O. The single crystals grew by allowing two solutions to diffuse slowly in the H-tube at room temperature. The red prismatic single crystals of the title complex suitable to X-ray diffraction were obtained for 15 days. Anal. Fond.(%): C 26.58, H 2.80, Calc.for (%) $\text{Mn}\cdot\mathbf{3}/\mathbf{2}(\mu\text{-DHBQ})\cdot\mathbf{4H}_2\mathbf{O}\cdot\mathbf{2Cl}$, C 26.69, H 2.74.

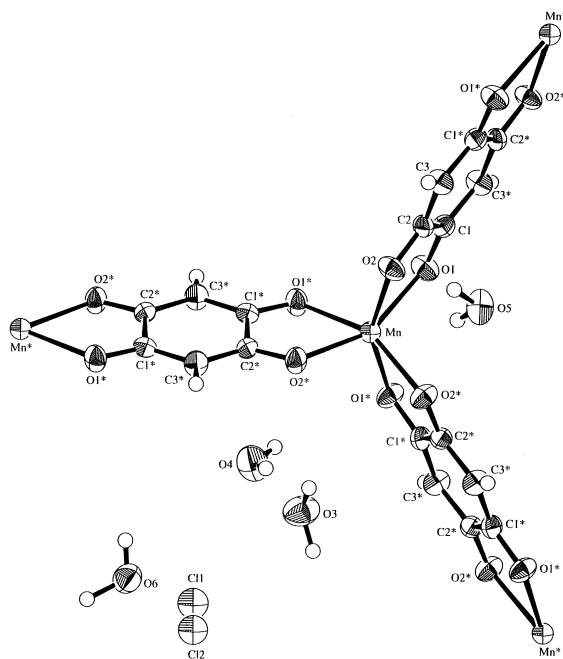
The single crystal $\text{Mn}\cdot\mathbf{3}/\mathbf{2}(\mu\text{-DHBQ})\cdot\mathbf{4H}_2\mathbf{O}\cdot\mathbf{2Cl}$ having approximate dimensions of $0.20 \times 0.20 \times 0.30$ mm³ was mounted on a glass fiber. All measurements were determined on a Rigaku AFC7R CAD₄ diffractometer with graphite monochromated

Mok α radiation ($\lambda = 0.071069$ nm). The data were collected at a temperature of 20 ± 1 ° C using the scan technique to a maximum value of 54.9° . A total of 2009 reflections were collected, 1747 were unique ($R_{int}=0.036$), of which 975 reflections were considered as observed [$I>3(I)$] and used for the structure determination. Usual Lp and empirical absorption correction were applied. The structure was solved by the Patterson method followed by Fourier synthesis, structure refinement was carried out by full-matrix least-square procedures using the teXsan program package [teXsan: Crystal structure analysis package, Molecular structure Corporation (1985 & 1992)]. H atoms were located in a difference Fourier maps. Anisotropic refinement including all the non-H atoms converged to an agreement factors, and the final deviation factors are $R=0.041$, $R_w=0.046$. Crystal Data: $M_r=405.02$, $a=1.415(2)$ nm, $c=0.6552(4)$ nm, $V=1.1373(7)$ nm³, $Z=2$, $D_x=1.183$ g/cm³, $F(000)=408.00$, $\mu = 7.37$ cm⁻¹, $S=1.28$, $(\Delta \rho)_{min}=-0.32$ e/A³, $(\Delta \rho)_{max}=0.28$ e/A³.

Results and Discussion

The strongest peak at 338 nm which belongs to $\pi \rightarrow \pi^*$ is considered to be the peak of $O=C-C=C-O$ conjugated structure transitions of ligand **DHBQ**²⁻, but in the free ligand **H₂DHBQ** this absorption peak appears at 285nm. $\nu_{C=O}$ in the free ligand **H₂DHBQ** appear at 1620 cm⁻¹, but they appear 1630 cm⁻¹ with a wide band and weak absorption peak in the complex according to the IR spectra of the free ligand **H₂DHBQ** and the complex. Final atomic coordinates and equivalent temperature for all atoms are given in the **Table I**. Bond distances and angles are listed in the **Table II**. The crystal structure of **Mn•3/2(μ -DHBQ)•4H₂O•2Cl** is shown in **Figure I**.

Figure I. Molecular Structure of **Mn•3/2(μ -DHBQ)•4H₂O•2Cl**



**Structure of the Manganese (V) Complex-
Mn₃/2(μ-DHBQ)•4H₂O•2Cl**

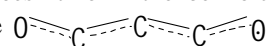
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Table I. Atomic coordinates and equivalent isotropic temperature factors (Å²) of all atoms

Atoms	x	y	z	Beq
Mn	0.6667	0.3333	0.5002(2)	2.33(1)
Cl1	1.0000	0.0000	1.0000	3.69(5)
Cl2	1.0000	0.0000	0.5000	3.39(5)
O1	0.5639(2)	0.3724(2)	0.6870(4)	2.86(6)
O2	0.6278(2)	0.4363(2)	0.3139(4)	2.81(6)
O3	0.7949(3)	0.1136(3)	0.3167(5)	4.96(8)
O4	0.8886(3)	0.2063(3)	0.6862(4)	4.92(8)
O5	0.4586(2)	0.2289(2)	0.9998(4)	3.72(7)
O6	1.1258(2)	0.1255(2)	0.7515(4)	4.01(7)
C1	0.5294(3)	0.4320(3)	0.6094(5)	2.31(7)
C2	0.5682(3)	0.4704(3)	0.3912(5)	2.17(7)
C3	0.5372(3)	0.5370(3)	0.2935(5)	2.63(8)
H1	0.5595	0.5590	0.1615	4.8211
H2	0.7810	0.1540	0.2160	4.8211
H3	0.7720	0.0370	0.3040	4.8211
H4	0.8640	0.1960	0.5750	4.8211
H5	0.8470	0.2030	0.7990	4.8211
H6	0.5080	0.2890	0.9170	4.8211
H7	0.5010	0.2190	1.0989	4.8211
H8	1.1300	0.1900	0.7646	4.8211
H9	1.2020	0.1320	0.7130	4.8211

Table II. Bond distances (nm) and relevant bond angles (°)

Mn-O1	0.2174(3)	Mn-O2	0.2172(3)	O1-C1	0.1273(4)	O2-C2	0.1268(4)				
C1-C2	0.1530(4)	C2-C3	0.1380(5)	O3-H3	0.097	O4-H4	0.079	O4-H5	0.093		
O3-H2	0.096	O5-H6	0.095	O5-H7	0.094	O6-H8	0.089	O6-H9	0.107	C3-H1	0.092
Nonbond distance (nm)				Bond angle (°)							
Cl1-Cl2	0.328	Cl1-O6	0.2411(3)	Cl2-O6	0.2424(3)	O1-Mn-O2	73.69(9)	Mn-O1-Cl	118.1(2)		
O1-O5	0.2742(3)	O2-O5	0.2743(3)	O3-O4	0.2757(4)	O1-Cl-C2	114.8(3)	C2-C1-C3	120.0(3)		
O3-O5	0.2770(4)	O3-O6	0.2861(4)	O4-O5	0.2766(4)	O2-C2-C1	115.3(3)	C1-C2-C3	119.7(3)		
O4-O6	0.2854(5)										

The central atom **Mn (V)** is six-coordinate from three different bidentate ligands **DHBQ²⁻**. The coordination geometry around **Mn (V)** atom is octahedron structure due to six same coordination oxygen atoms. The average bond distance of Mn-O is 0.2173 nm. The ligand **DHBQ²⁻** plays the role of the molecular bridging ligand, and respectively connects two **Mn (V)** atoms to form a smallest unit of six **Mn (V)** atoms. The molecular bridging ligand **DHBQ²⁻** can coordinate with most transition metal ions, but those complex crystal structure haven't been reported so far. According to **Table II**. The bond distance C1-C2 is 0.1530 nm, which belongs to the single bond distance. It indicates that the whole ligand **DHBQ²⁻** doesn't form the benzoic ring conjugated structure, there exists the resonance structure . Therefore, the coordination form of **DHBQ²⁻** can be represented by the style of **Figure I**, which is similar to the result of the **Rh₄(μ-CA)₂(cod)₄ complex** (CA=chloranilate anion; Cod=cycloocta-1, 5-diene)⁷.

The cell unit of the hexagram structure containing six **Mn (V)** atoms is shown in **Figure III**, and the smallest unit hexagram extends three-dimension netlike skeleton. In

the unit of hexagram structure there contains a larger cavity which holds six Cl^{-1} ions and twelve H_2O , which don't arrange in the style of intimate package, and they interact with each other by Van der waals force or hydrogen bonds. So the intensity of crystal is 1.18 g/cm^3 , which is unique for metal-transition complexes.

Figure II. The coordination scheme of Mn (V) and DHBQ²⁻

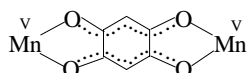
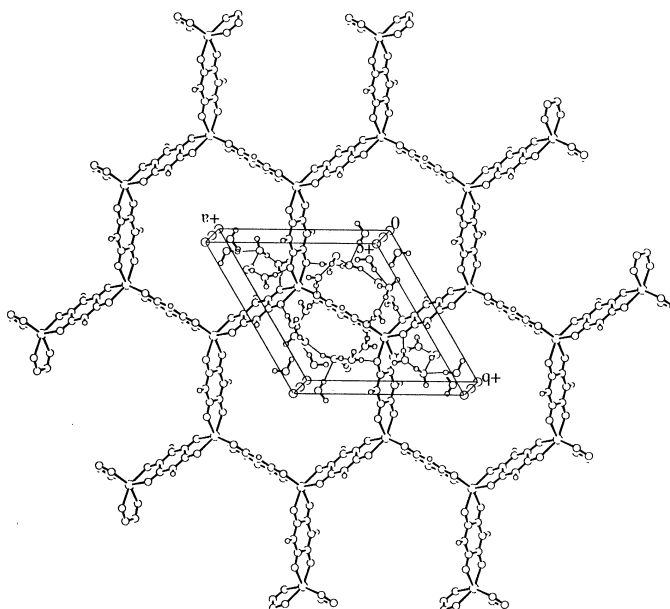


Figure III. The hexagram structure of $\text{Mn}\cdot\frac{3}{2}(\mu\text{-DHBQ})\cdot 4\text{H}_2\text{O}\cdot 2\text{Cl}$



Acknowledgments

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