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# The Crystal and Molecular Structure of Bis(acetylacetonato)manganese(II) Dihydrate

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The crystal and molecular structure of bis(acetylacetonato)manganese(II) dihydrate, $Mn(C_5H_7O_2)_2 \cdot 2H_2O$, has been determined from three-dimentional X-ray diffraction data. The compound has a center of symmetry. The octahedral arrangement of the ligand atoms about the central manganese atom is distorted; the Mn–O(1) and Mn–O(2) distances are 2.129 and 2.150 Å ,respectively, the Mn–O($H_2O$) distance is 2.267 Å. The metal atom lies 0.561 Å out of the least-squares plane of the chelate ring. The chelate is isostructural with the cobalt, nickel, and magnesium analogues.

The molecular structures of the acetylacetonato complexes of some bivalent first transition metals were studied by gaseous electron-diffraction method by one of us (S. S.).[1] The complexes take the coordination number four in a gaseous state, but usually six in a solid state because of polymerization of the chelate or addition of solvent molecules. The purpose of the present study is to find the difference between the molecular structures in the two phases.

The crystal structure of $Mn(C_5H_7O_2)_2 \cdot 2H_2O$ has been reported recently by Montgomery and Lingafelter.[2] However, we were not aware of this when we started this work. Montgomery and Lingafelter determined the structure using 588 independent reflections recorded on Weissenberg photographs which were taken with Fe$K\alpha$ radiation and intensities of which were measured with the aid of a photometer. Comparison of their results with ours showed a good agreement between the two independent determinations.

## Experimental

The crystals of bis(acetylacetonato)manganese(II) dihydrate were prepared by standard procedure.[3] The unit cell dimensions and the space group were determined from Weissenberg and rotation photographs using Cu$K\alpha$ radiation ($\lambda=1.5418$ Å). It is monoclinic with two molecules in a unit cell of the dimensions, $a=11.17$, $b=5.42$, $c=11.32$ Å and $\beta=106.2°$, and the space group is $P2_1/c$ (No. 14) which is required from the systematic absence for $0k0$ when $k$ is odd and for $h0l$ when $l$ is odd. The calculated density is 1.46 g cm$^{-3}$. A needle-shaped crystal selected carefully was used for intensity measurements. Three-dimensional intensity data were recorded on equi-inclination Weissenberg photographs taken with Cu$K\alpha$ radiation by means of the multiple film technique at room temperature. The intensities of 1202 independent reflections from $h0l$ to $h4l$ were measured visually by the use of a scale consisting of spots obtained from a selected reflection with different exposure times. All intensities were used in a least-squares calculation. Corrections for Lorentz and polarization factors were made in the usual way, while those for absorption and extinction were neglected.

## Structure Determination

Since the compound $Mn(C_5H_7O_2)_2 \cdot 2H_2O$ has a center of symmetry, the manganese atom was placed at the origin of the unit cell. The two-dimensional coordinates of the five carbon and three oxygen atoms were obtained approximately from the sharpened ($B=4.0$ Å$^2$) Patterson projection, $P(u,w)$. Successive Fourier syntheses refined the positional parameters of the light atoms on the same plane and gave the orientation of the molecular framework. At this stage, calculated structure factors gave a discrepancy factor, $R_1=\sum||F_o|-|F_c||/\sum|F_o|$, of 0.218 for $h0l$ reflection, assuming an isotropic temperature parameter of 3.0 Å$^2$ for all atoms.

The three-dimensional structure which was used as the input for a least-squares calculation was assumed as follows: The acetylacetone ring takes a planar form, and the bond lengths and bond angles are equal to the average values which were estimated by Lingafelter[4] from the structures of many other acetylacetonate complexes.

The positional and the isotropic thermal para-

1) S. Shibata, Proceedings of the 10th International Conference on Coordination Chemistry (1967), p. 82.

2) H. Montgomery and E. C. Lingafelter, *Acta Crystallogr.*, **B24**, 1127 (1968).

3) R. G. Charles, "Inorganic Syntheses," Vol. 6, p. 164 (1960).

4) E. C. Lingafelter, *Coordin. Chem. Rev.*, **1**, 151 (1966).

meters were refined by a least-squares procedure with block-diagonal matrix approximation. Computations were carried out by means of a HITAC 5020E computor using a program by T. Ashida.

In the refinement procedure, the function to be minimized was $\sum w(|F_o|-|F_c|)^2$ and the weights, $w$, were unity for $F_o \geqq 0.5$ and zero for $F_o < 0.5$. All of the observed data including zero reflections were used in the calculation. The atomic scattering factors of manganese, oxygen and carbon atoms were taken from International Tables for X-ray Crystallography.[5] Correction for anomalous scattering of manganese atom was neglected.

Five iterations of the refinement gave a discrepancy factor $R_1$ of 0.139 and the isotropic temperature factors were obtained for each atom. It was noticeable that the isotropic temperature factors for the two methyl carbon atoms, C(1) and C(5), and the oxygen atom of water, O(3), are considerably large.

Refinement with a consideration of anisotropic temperature factors was carried out five cycles with the use of the same program and gave a smaller discrepancy factor $R_1$ of 0.093 for non-zero reflections. Anisotropic temperature factors were expressed as

$$\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{13}hl)\right]$$

The final atomic coordinates with their estimated standard deviations and the anisotropic temperature factors are listed in Tables 1 and 2, respectively. The observed and the calculated structure factors are tabulated in Table 3.*1

## Discussion

According to preliminary results from an electron-diffraction experiment,[1] gaseous bis(acetylacetonato)manganese(II) takes planar form and the distance between manganese and oxygen atoms is 2.28 Å. However, the present study showed that the chelate in a crystal takes distorted octahedron and the average length of the corresponding bond is 2.14 Å. A comparison between them will be made when a conclusive result of electron-diffraction is obtained.

Table 1. The final atomic coordinates and their estimated standard deviations ($\times 10^4$)

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Mn | 0 | 0 | 0 |
| O(1) | 1538 (5) | −2281 (14) | 963 (6) |
| O(2) | 1249 (6) | 1553 (14) | − 915 (5) |
| O(3) | 613 (7) | 3021 (16) | 1426 (6) |
| C(1) | 3604 (9) | −3365 (23) | 2028 (8) |
| C(2) | 2702 (7) | −1775 (19) | 1107 (7) |
| C(3) | 3145 (8) | 119 (21) | 499 (8) |
| C(4) | 2434 (8) | 1669 (20) | − 471 (8) |
| C(5) | 3093 (10) | 3643 (25) | −1004 (9) |

The average dimension of a manganese acetylacetonate ring is shown in Fig. 1. Each manganese atom is surrounded by six coordinated oxygen atoms. Four of the coordination sites are occupied by the two bidentate acetylacetone groups and two

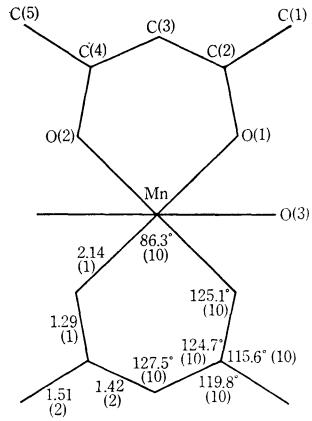


Fig. 1. The average dimensions of $Mn(C_5H_7O_2)_2 \cdot 2H_2O$.

Table 2. Anisotropic temperature factors and their estimated standard deviations ($\times 10^4$)

| | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Mn | 31 (1) | 168 (9) | 36 (1) | −10 (7) | 16 (2) | 25 (7) |
| O(1) | 36 (5) | 145 (31) | 49 (5) | −10 (19) | 16 (8) | 48 (20) |
| O(2) | 42 (5) | 196 (32) | 37 (5) | −48 (21) | 14 (8) | 17 (21) |
| O(3) | 83 (7) | 248 (39) | 33 (5) | −43 (26) | 15 (10) | −51 (22) |
| C(1) | 59 (9) | 243 (54) | 33 (7) | 105 (34) | −11 (12) | 53 (31) |
| C(2) | 33 (7) | 145 (47) | 27 (6) | 33 (26) | 6 (10) | −51 (25) |
| C(3) | 60 (8) | 84 (43) | 39 (7) | −26 (32) | 23 (11) | − 5 (30) |
| C(4) | 56 (8) | 126 (46) | 36 (7) | − 9 (29) | 54 (12) | −36 (28) |
| C(5) | 75 (10) | 326 (56) | 39 (7) | −132 (39) | 66 (14) | 1 (35) |

5) "International Tables for X-ray Crystallography," Vol. III, Birmingham, Kynoch Press (1962), p. 202.

*1 The $F_o$–$F_c$ table is kept as Document No. 7004 at the office of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥250 for photoprints. Payment may be made by check or money order payable to: Chemical Society of Japan.

are occupied by the water molecules. The average distance of the Mn–O($C_5H_7O_2$) is much shorter than that of Mn–O($H_2O$), 2.267 Å, by 0.130 Å. However, in the crystal structure of $Zn(C_5H_7O_2)_2 \cdot H_2O$,[6] there is no considerable difference between the Zn–O($C_5H_7O_2$) distance and the Zn–O($H_2O$); the average distance is $2.02 \pm 0.02$ Å.

The O–O separation in an acetylacetonate ring is 2.926 Å. Lingafelter[4] pointed out that the O–O distance of the acetylacetonate chelate ring decreases with the increase in an oxidation number of a metal, and the above result seems to be an additional proof to this rule.

The structure of $Mn(C_5H_7O_2)_2 \cdot 2H_2O$ is essentially the same as the structures of the corresponding cobalt,[7] nickel[8] and magnesium analogues.[9] Morosin found that in these metal acetylacetonates the metal is displaced out of the least-squares plane formed by the chelate ring OCCCO. In the present work a similar displacement was observed. The sum of the interior angles of the ring was 539.9°, although 540° must be required for planarity. Therefore the chelate ring is planar within experimental errors, and the least-squares plane has the equation $-0.2845X+0.6796Y+0.7287Z=-0.5611$ (referred to the monoclinic coordinates). The distance from the manganese atom to this ligand plane was 0.561 Å, in contrast to the corresponding distance in $Mn(C_5H_7O_2)_3$, 0.12 Å.[10] The decrement may be due to steric hindrance among the chelate frames which are considerably flexible. Deviations of the light atoms from the least-squares plane are as follows:

| | | | | | |
|---|---|---|---|---|---|
| O(1) | 0.027 | O(2) | −0.019 | C(1) | −0.151 |
| C(2) | −0.039 | C(3) | 0.017 | C(4) | 0.014 |
| C(5) | 0.092 | O(3) | 2.655 Å | | |

Table 4. Intramolecular bond lengths and angles

Bond lengths (Å)

| | | |
|---|---|---|
| Mn | O(1) | 2.150 (7) |
| Mn | O(2) | 2.129 (8) |
| Mn | O(3) | 2.267 (8) |
| C(1) | C(2) | 1.504 (16) |
| C(4) | C(5) | 1.515 (17) |
| C(2) | C(3) | 1.401 (16) |
| C(3) | C(4) | 1.434 (16) |
| O(1) | O(2) | 2.926 (11) |
| O(1) | O(3) | 3.146 (11) |
| O(2) | O(3) | 3.035 (11) |
| O(1) | C(2) | 1.294 (13) |
| O(2) | C(4) | 1.280 (13) |

Bond angles* (°)

| | | | |
|---|---|---|---|
| O(1) | Mn | O(2) | 86.3 |
| Mn | O(1) | C(2) | 125.1 |
| Mn | O(2) | C(4) | 125.1 |
| O(1) | Mn | O(3) | 90.8 |
| O(2) | Mn | O(3) | 87.3 |
| O(1) | C(2) | C(1) | 114.9 |
| C(2) | C(3) | C(4) | 127.5 |
| C(3) | C(4) | C(5) | 119.5 |
| O(1) | C(2) | C(3) | 125.1 |
| O(2) | C(4) | C(3) | 124.3 |
| C(1) | C(2) | C(3) | 120.0 |
| O(2) | C(4) | C(5) | 116.3 |

* Average error is 1°.

Both of the methyl groups exist significantly out of the chelate plane. The chelate ring is folded by 21° about the O(1)–O(2) axis. The intramolecular bond lengths and angles are listed in Table 4.

The intermolecular distance between O(3) $(x,y,z)$ and O(2) $(x, 0.5-y, 0.5+z)$ and between O(2) $(-x, -y, -z)$ and O(3)$(-x, -0.5+y, 0.5-z)$ are 2.867 Å. The lengths may indicate the presence of the intermolecular hydrogen bonds between neighbouring oxygen atoms related by the twofold screw axis. Other intermolecular distances can be explained reasonably by the assumption that they are in van der Waals contact.

6) H. Montgomery and E. C. Lingafelter, *Acta Crystallogr.*, **16**, 748 (1963).
7) G. J. Bullen, *ibid.*, **12**, 703 (1959).
8) H. Montgomery and E. C. Lingafelter, *ibid.*, **17**, 1481 (1964).
9) B. Morosin, *ibid.*, **22**, 316 (1967).
10) B. Morosin and J. R. Brathovde, *ibid.*, **17**, 705 (1964).