Crystal Structure of a Molecular Complex of Acetylacetone with Manganese(II) Bromide, $MnBr_2(C_5H_8O_2)_2$

By SHIGETAKA KODA, SHUN'ICHIRO OOI, HISAO KUROYA,* YUKIO NAKAMURA, and SHINICHI KAWAGUCHI

(Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, Japan)

Summary The crystal structure of a molecular complex of acetylacetone with $MnBr_2$ has been determined by an *X*-ray diffraction analysis: the manganese and bromine atoms constitute an infinite chain $(MnBr_2)_\infty$ and two enolic acetylacetone molecules are linked to each metal atom as unidentate ligands, thus constructing the octahedral arrangement of $[MnBr_4O_2]$.

IN a previous communication a molecular complex of acetylacetone with cobalt(II) bromide, $CoBr_2(C_5H_8O_2)$, was reported by two of us.[1] By a similar direct reaction between anhydrous manganese(II) bromide and acetylacetone, pale-pink fluffy crystals of $MnBr_2(C_5H_8O_2)_2$ were obtained. Although $CoBr_2(C_5H_8O_2)$[1] and $[Ni(C_5H_8O_2)_3](ClO_4)_2$[2] show a strong i.r. band at 1705 and 1700 $cm.^{-1}$ respectively, indicating the co-ordination of a ketonic molecule of acetylacetone, the i.r. spectrum of the present complex exhibits C=O and C=C stretching bands at 1627 and 1564 cm^{-1} bearing a close resemblance to those of the enolic form of acetylacetone.[3] The effective magnetic moment of 6·14 B.M. confirms that this is a high-spin Mn^{II} complex. Recently a molecular adduct of acetylacetone with dioxobis(acetylacetonato)uranium(VI) was also suggested to contain the enolic molecule as a unidentate ligand.[4] In order to elucidate the novel mode of linkage of acetylacetone, a single-crystal *X*-ray analysis of the present complex was performed.

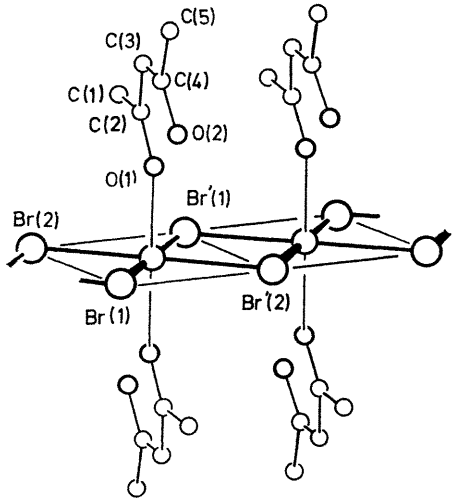

FIGURE. *Perspective drawing of the complex*

Needle-like crystals suitable for *X*-ray work were obtained by recrystallization of the compound from acetylacetone. Since they are highly sensitive to humidity, crystal specimens were sealed in thin-walled glass capillaries for use. Crystal data: monoclinic, $a = 3{\cdot}89$, $b = 15{\cdot}46$, $c = 12{\cdot}26$ Å, $\beta = 100{\cdot}1°$, $Z = 2$; $D_c = 1{\cdot}90$ g cm^{-3}, space group $P2_1/c$, $\mu = 151{\cdot}4$ cm^{-1} (for Cu-K_α). Intensities of 1169 independent reflections were estimated visually from multiple-film equi-inclination Weissenberg photographs taken around the *a*-axis with Cu-K_α radiation. The manganese atom lies on the centre of symmetry of the crystal lattice and the structure was solved by the conventional Patterson and Fourier methods. The positional and isotropic thermal parameters were refined by least-squares methods to an *R* factor of 0·159.

The perspective drawing of the complex is shown in the Figure. There are $(MnBr_2)_\infty$ chains elongated parallel to the *a*-axis. Each bromine atom bridges two adjacent manganese atoms with slightly different bond lengths; Mn–Br(1) = 2·681(3) Å and Mn–Br(2) = 2·710(3) Å. Br(1)–Mn–Br(2) and Br(1)–Mn–Br′(2) are 88(1)° and 92(1)°, respectively.

The acetylacetone molecule is planar, nearly bisecting the angle Br(1)–Mn–Br′(2). Of the two oxygen atoms, O(1) is co-ordinated to the metal atom with a bond length of 2·20(2) Å. Thus the acetylacetone acts as a unidentate ligand in the complex. Such a ligation scheme, as well as the i.r. data [ν(C=O) and ν(C=C)], indicates that the ligand molecule is in the enolic form.

The O–H group probably participates in intramolecular O–H · · · O hydrogen bonding as was found in the case of $UO_2(C_5H_7O_2)_2(C_5H_8O_2)$ mentioned above [O · · · O = 2·56(3) Å].

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[1] Y. Nakamura and S. Kawaguchi, *Chem. Comm.*, **1968**, 716.
[2] P. W. N. M. van Leeuwen, *Rec. Trav. chim.*, **1968**, **87**, 396.
[3] R. Mecke and E. Funck, *Z. Elektrochem.*, **1956**, **60**, 1124.
[4] J. M. Haigh and D. A. Thornton, *Inorg. Nuclear Chem. Letters*, **1970**, **6**, 231.