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CRYSTAL STRUCTURE OF TRIMERIC BIS(ACETYLACETONATO)MANGANESE(II)

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The crystal structure of $Mn(acac)_2$ has been determined by using three-dimensional X-ray counter data. The unit cell contains a formula unit of $Mn_3(acac)_6$, a centrosymmetric trimer, with the Mn-Mn distance of 3.108(2) Å. Each manganese atom is coordinated by six oxygen atoms of the ligands: the terminal manganese atom is in a distorted trigonal prism and the central atom in a trigonal antiprism.

The crystal structures of anhydrous acetylacetonates of the divalent nickel,1) cobalt,2) zinc,3) and iron4) metals have been studied but that of manganese has been remained undetermined until now. Graddon and Mockler5) made molecular weight determinations and concluded that the manganese compound is trimeric in hydrocarbon solvents, and they assumed that the structure of the manganese compound in the solid phase is similar to that of the nickel compound. We now report the crystal and molecular structure of bis(acetylacetonato)manganese(II).

The anhydrous bis(acetylacetonato)manganese(II) was prepared as pale yellow crystals from the dihydrate by repeated sublimation. The crystal belongs to the triclinic system, space group $P\bar{1}$, with one trimer in the unit cell of a=11.680(6), b=8.429(3), c=10.975(5) Å, α=106.24(4), β=119.54(4), and γ=65.10(3)°. The crystal of 0.5 x 0.4 x 0.4 mm^3 was selected and 2565 independent reflections were collected using an automatic four-circle diffractometer with monochromated MoKα radiation. The structure was solved by the heavy-atom method and refined by a block-diagonal least-squares procedure to R=0.052.

Bis(acetylacetonato)manganese(II) was found to be trimeric and centrosymmetric. The molecular structure is illustrated in Fig. 1. Each of manganese atoms is surrounded by six oxygen atoms of the ligand molecules, and one of the oxygen atoms

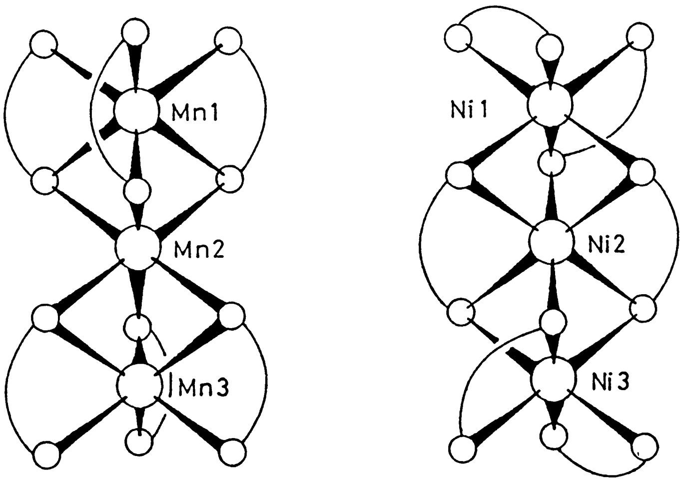

Fig. 1.
A schematic drawing comparing the coordination of the metals in $Mn_3(acac)_6$ and $Ni_3(acac)_6$

of each ligand bridges two metal atoms. The coordination geometry of the terminal metal is described as a distorted trigonal prism, while that of the central metal as a trigonal antiprism, i.e., a distorted octahedron. Both prisms share a common trigonal face and the Mn-Mn distance is 3.108(2) Å. The arrangement of oxygen atoms in this trimer is different from that of the nickel compound, where the oxygen atoms coordinate octahedrally. Weighted mean values of Mn-O distances are grouped as follows: Mn1-O(non-bridging)=2.098(4) Å; Mn1-O(bridging)=2.246(15) Å; Mn2-O(bridging)=2.171(6) Å. Each of the three ligands is planar and the interplanar angles are 119.3, 119.4, and 121.2°. The structures of the ligands are similar: weighted mean values of the selected molecular parameters are as follows: O(non-bridging)-C=1.250(8) Å; O(bridging)-C=1.279(5) Å; Mn1-O(non-bridging)-C=135.4(7)°; Mn1-O(bridging)-C=130.5(6)°. These values show the unsymmetrical structure of the ligand due to the characteristic mode of its coordination. This provides remarkable contrast to many other metal acetylacetonates,$^{6)}$ where the structures of the ligands are well symmetrized.

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