

specimens were extended at a low rate to a predetermined stress, held for several minutes, unloaded, and subsequently reloaded to a higher stress; a long period of microstrain (microcreep) preceding gross yield was obtained at liquid nitrogen temperature, but not at room temperature.

To check the effect of temperature with the present loading procedure, specimens were tested at  $-80^{\circ}\text{C}$  ( $E-H$  in Table 1). All gave a greater drop in load on relaxation in the pre-yield region than at  $22^{\circ}\text{C}$ . Specimens  $G$  and  $H$  yielded during a period of straining, at stresses of 28 and 15 kg/mm<sup>2</sup>, and their behaviour differed from that in a conventional test at  $-80^{\circ}\text{C}$  (see Table 1: the normal upper and lower yield stresses were 34 and 24 kg/mm<sup>2</sup>). Specimens  $E$  and  $F$  gave similar behaviour to that at  $22^{\circ}\text{C}$ , with sudden yielding during relaxation at about the upper yield stress, and delay times of 36 and 126 sec; however, there was a slow fall in load before the sudden yielding, and the fall in load on yielding was not so abrupt as at  $22^{\circ}\text{C}$ . These results accord with the effects of temperature already noted, showing greater dislocation movement at  $-80^{\circ}\text{C}$  than at  $22^{\circ}\text{C}$ .

The present work shows that the yield behaviour of iron when loading at conventional strain-rates depends on the loading programme. In interpreting these or other delay time experiments it is necessary to consider not only the unlocking of dislocations, but also the possibility that the mechanism controlling yield is the multiplication of free dislocations.

The work described above has been carried out at the National Physical Laboratory, with the participation of Miss J. M. Hills.

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Received September 13, revised December 12, 1966.

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## CHEMISTRY

### A New Type of bis-(Acetylacetonato)metal(II) Polymer: the Trimer of bis-(Acetylacetonato) Zinc

THE versatility of acetylacetonate (acac) as a ligand is well documented<sup>1</sup>. It forms metal complexes of the following structural types: (1) normal chelate compounds<sup>2,3</sup>, (2) polynuclear bridged species<sup>4-6</sup>, (3)  $\gamma$ -carbon bonded complexes<sup>7,8</sup>, and (4) condensation products formed from complexes of the third category<sup>9</sup>. We report here the structure of  $[\text{Zn}(\text{acac})_2]_3$  which is an example of the second type with a new kind of stereochemistry in which zinc exhibits both five and six co-ordination.

Bullen, Mason and Pauling<sup>4</sup> inferred but could not prove a trimeric structure from preliminary cell measurements (now found to correspond to the non-standard monoclinic space group  $F2$ ). Recent measurements in this laboratory indicated possible space groups  $C2/m$ ,  $C2$  or  $Cm$ , with unit cell parameters of  $a=18.63$ ,  $b=8.437$ ,  $c=12.20$ , and  $\beta=112.68^{\circ}$ . The intensities of 1,928 reflexions were collected on a manual diffractometer; the Patterson synthesis unambiguously determined the space group as  $C2$ . The structure was solved by conventional Fourier and

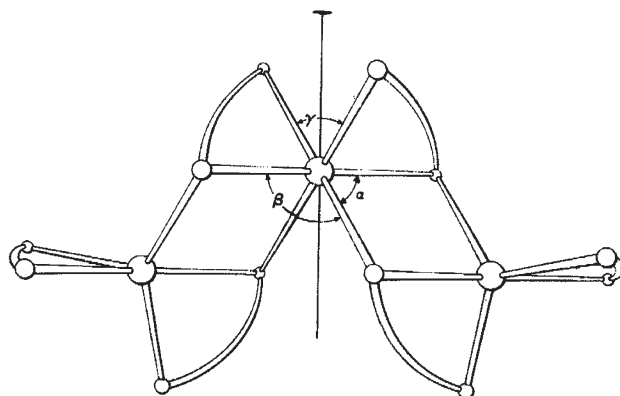


Fig. 1. Stereochemistry of  $\text{Zn}_3(\text{acac})_3$ . Carbon atoms of acetylacetonate ligands are omitted for clarity. The "octahedron" about the centre zinc atom is appreciably distorted. The main deviations from  $90^{\circ}$  angles are in those marked as  $\alpha$ ,  $\beta$  and  $\gamma$  on the sketch;  $\alpha=75.1^{\circ}$ ;  $\beta=105.8^{\circ}$ ;  $\gamma=101.7^{\circ}$ . Other angles are within  $4^{\circ}$  of  $90^{\circ}$ . The arrangement of oxygen atoms about the terminal zinc atoms approximates fairly closely (average deviation  $5^{\circ}$ ) to that for a trigonal bipyramid.

least squares techniques and has refined isotropically to a present reliability index,  $(\sum||F_c| - |F_0||)/\sum|F_0|$ , of 0.08.

The main features of the molecular structure are shown in Fig. 1. The crystallographic and molecular  $C_2$  axes are coincident and contain the central octahedrally co-ordinated zinc atom. The two terminal zinc atoms have a slightly distorted trigonal bipyramidal co-ordination. Unlike  $\text{Ni}_3(\text{acac})_6$  (ref. 4) and  $\text{Co}_4(\text{acac})_8$  (ref. 5),  $\text{Zn}_3(\text{acac})_6$  contains no acetylacetonate ligands with both oxygens serving as bridges. The relative stability of pentacoordinated zinc in this system is evidenced by the preferential formation of products of the type  $\text{Zn}(\text{acac})_2L$  over  $\text{Zn}(\text{acac})_2L_2$  complexes<sup>2,3,10</sup>. The presence of the central octahedrally co-ordinated zinc atom indicates, however, that the difference in stability is not large because otherwise one might expect a structure involving only five-co-ordinate zinc, such as the dimer of trigonal bipyramids reported for bis(*N*-methylsalicylaldiminato)zinc(II) (ref. 11). Thus, the tendency of  $M(\text{acac})_2$  molecules to form polymers can be said to result from the preference of the metal atoms for co-ordination numbers higher than 4, but not necessarily for a co-ordination number of 6. These polynuclear structures have been different in each of the three compounds so far structurally characterized (for  $M=\text{Ni}$ ,  $\text{Co}$ ,  $\text{Zn}$ ) and the structures are evidently quite sensitive to the stereochemical idiosyncrasies of the individual metal ions.

A detailed report of the results of this investigation will be submitted when further refinement, including absorption corrections and a weighting scheme, is complete. The work was supported by the U.S. National Science Foundation. One of us (R. E.) is a Union Carbide predoctoral fellow.

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Received December 12, 1966.

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