

## The Structure of Dichlorobis(pentane-2,4-dionato)rhenium(IV)

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ONE of the products obtained by the reaction of acetylacetonone and oxotrichlorobis(triphenylphosphine)rhenium(v) was claimed to be  $[\text{ReCl}_2(\text{C}_5\text{H}_7\text{O}_2)]$ .<sup>1</sup> A dimeric structure, which had two bridging acetylacetonate groups bonding through oxygen atoms, was suggested on the basis of molecular-weight determinations in solution, but no X-ray structural work has been reported so far.

We have determined the crystal structure of dichlorobis(pentane-2,4-dionato)rhenium(IV). Crystal data:  $\text{C}_{10}\text{H}_{14}\text{Cl}_2\text{O}_4\text{Re}$ ,  $M = 455.34$ , triclinic,  $a = 8.004 \pm 0.01$ ,  $b = 8.536 \pm 0.01$ ,  $c = 7.929 \pm 0.01$  Å,  $\alpha = 119^\circ 21' \pm 10'$ ,  $\beta = 92^\circ 18' \pm 10'$ ,  $\gamma = 56^\circ 23' \pm 10'$ ,  $U = 372.3$  Å<sup>3</sup>,  $D_m = 2.18 \pm 0.02$  (by flotation),  $Z = 1$ ,  $D_c = 2.03$ , space group  $P \bar{1}$  ( $C_i^1$ , No. 2).

Four layers perpendicular to  $[100]$  and five layers perpendicular to  $[\bar{1}21]$  were recorded with an integrating precession camera using Mo- $K_\alpha$  radiation and the intensities were estimated by means of a microdensitometer.

From Patterson projections down  $[100]$  and  $[\bar{1}21]$ , the positions of the heavier atoms (Re, Cl,

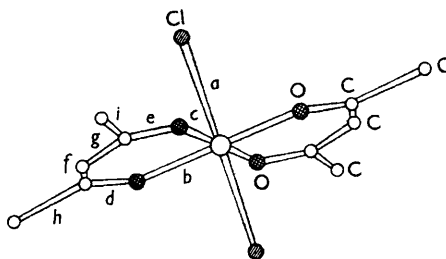


FIGURE. Structure of  $\text{Re}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  projected along the  $c$ -axis. The standard error for the Re-Cl distance is about 0.02 Å, for the Re-O distance about 0.05 Å, and for the other atom-atom distances about 0.1 Å.

$a = 2.33$ Å	$f = 1.53$ Å
$b = 2.04$	$g = 1.36$
$c = 2.13$	$h = 1.56$
$d = 1.32$	$i = 1.63$
$e = 1.31$	
$ab = 89.7$ ( $\pm 0.5$ )°	$dh = 133$ ( $\pm 1$ )°
$ac = 89.6$ ( $\pm 0.5$ )	$eg = 122.5$ ( $\pm 1$ )
$bc = 90.9$ ( $\pm 0.5$ )	$ei = 115$ ( $\pm 2$ )
$bd = 125$ ( $\pm 1$ )	$fg = 129$ ( $\pm 2$ )
$ce = 128$ ( $\pm 1$ )	$h = 122$ ( $\pm 2$ )
$df = 125$ ( $\pm 2$ )	$i = 122$ ( $\pm 2$ )

and O) were found and from the subsequent Fourier synthesis of electron density, the positions of all the other atoms (except hydrogen) were located. After preliminary Fourier refinement, co-ordinates and anisotropic temperature factors were refined by least-squares analysis to give a weighted reliability index of  $R = 8.8\%$  for 1044 independent nonzero reflections. Bond lengths in Å and angles are shown in the Figure. The rhenium atom, which is at the centre of symmetry, is surrounded by a slightly distorted octahedron of four oxygen atoms which form a plane containing the rhenium atom and two *trans*-chlorine atoms at a slightly longer distance. The  $\beta$ -diketone groups are bonded through the two oxygen atoms which is the commonest type of linkage in this kind of complex.<sup>2</sup>

The compound we examined was prepared in the same manner as that described previously.<sup>1</sup> We have no evidence for any dimer formation in

the solid state, the shortest rhenium-rhenium distance being 7.93 Å.

Further indirect evidence supports the monomer formulation. Mass-spectrographic examination showed that the highest-molecular-weight peaks were caused by  $\text{Re}(\text{acac})_2\text{Cl}_2^+$ ,  $\text{Re}(\text{acac})_2\text{Cl}^+$ , and  $\text{Re}(\text{acac})_2^+$  and no peaks were found which could be assigned to a fragment containing two rhenium atoms. Infrared-spectral measurements do not preclude the presence of a bridged dimers as suggested by Grove *et al.*<sup>1</sup> However, the infrared spectrum of the solid is very similar to those of copper and palladium acetylacetonates<sup>3</sup> and has no peaks in the region 1600–1700  $\text{cm}^{-1}$  where they have been found for other transition-metal compounds containing  $\beta$ -diketone groups bridging through the  $\gamma$ -carbonyl atom.<sup>4</sup>

We conclude that dichlorobis(pentane-2,4-dionato)rhenium(IV) is not dimeric in the solid state.

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<sup>1</sup> D. E. Grove, N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, 1965, 490.

<sup>2</sup> J. P. Fackler, *Progy. Inorg. Chem.*, 1963, 7, 361.

<sup>3</sup> K. Nakamoto, "Infra-red Spectra of Coordination Compounds," Wiley, New York, 1963, p. 219.

<sup>4</sup> D. Gibson, J. Lewis, and C. Oldham, *J. Chem. Soc. (A)*, 1967, 72.