Molecular Structure of Dimethyl(2,4-pentanedionato)gold(III)

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A gas-phase electron diffraction study of dimethyl(2,4-pentanedionato)gold(III) indicates a square-planar structure with r_a(Au–O) = 2.085(7), r_a(Au–C) = 2.054(5) Å, angle OAuO 90.9(6)°, and CAuC 92.7(24)°, as well as the normal parameters of an acetylacetone ligand.

Laser chemical vapour deposition (l.c.v.d.)[1] has been reported for a number of metals. Metal β-diketonates are a class of complexes that thermally and photochemically decompose to high-purity metals.[2] Baum and Jones[3,4] have found that dimethyl(2,4-pentanedionato)gold(III), [AuMe$_2$(acac)], which was prepared by the method of Brain and Gibson[5] is an excellent source for gold deposition. Therefore, it is very interesting to detect the existence of [AuMe$_2$(acac)] in the gas phase and determine its molecular structure. The ability of β-diketonates to co-ordinate to metals through either the central carbon atom or the two oxygen atoms is well documented[6] and the presence of different structures in the solid and gas phases is possible.

Experimental

The complex [AuMe$_2$(acac)] was prepared according to the literature procedure and purified by sequential sublimation to yield white crystalline needles. Electron diffraction photographs were taken using an r^3 sector on Kodak Electron-Image plates at camera distances of 143.93 and 293.79 mm. Exposure times were 50 and 20 s for the short and long camera distances, respectively, with an electron-beam current of 0.6 μA. The sample was vaporized at 377 K through a high-temperature nozzle. The accelerating voltage was 40 kV and the wavelength was determined from the diffraction patterns of thallium(I) chloride. The optical densities of the plates were measured by use of a digital microphotometer.[7]

Scattering intensities were levelled by the theoretical background obtained from the elastic and inelastic scattering factors of Schäfer *et al.*[8] and Cromer and Mann,[9] respectively. The molecular intensities are shown in Figure 1 and the radial distribution function in Figure 2.

The molecular structure (Figure 3) was determined by a least-squares analysis of the molecular intensities. A structure in which the β-diketone ligand co-ordinates to the metal through the C$_r$ atom was excluded. A tetrahedral configuration around the central atom was also excluded in the preliminary analysis. The following assumptions were made in the least-squares refinement: the configuration around the gold is planar and the whole molecule has C_{2v} symmetry, the methyl groups have local C_{3v} symmetry, the C–H bond is eclipsed with respect to the C=O bond, r(C$_m$–H) = 1.10, r(C$_r$–H) = 1.08 Å, and angle CC$_m$H 109.5°.

Results and Discussion

The parameters listed in the Table were obtained from the least-squares calculations. The mean amplitudes of vibration, l, not listed were calculated using the force constants from the spectroscopic study.[10]

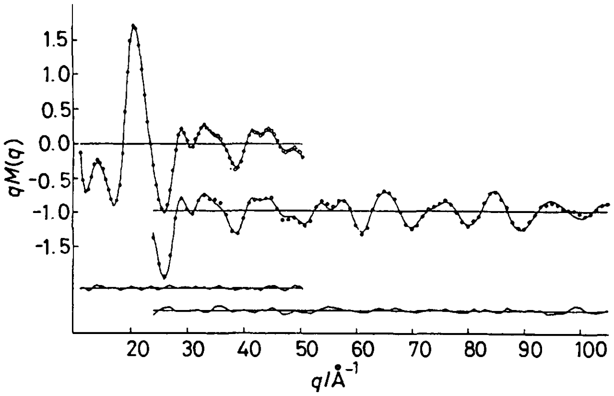

Figure 1. Molecular intensities for gaseous dimethyl(2,4-pentanedionato)gold(III); long and short camera distance data. The dots represent the experimental points and the solid curves the theoretical intensities. The lower curves show the residuals; $q = \frac{40}{\lambda} \sin \frac{\theta}{2}$, for wavelength λ and scattering angle θ.

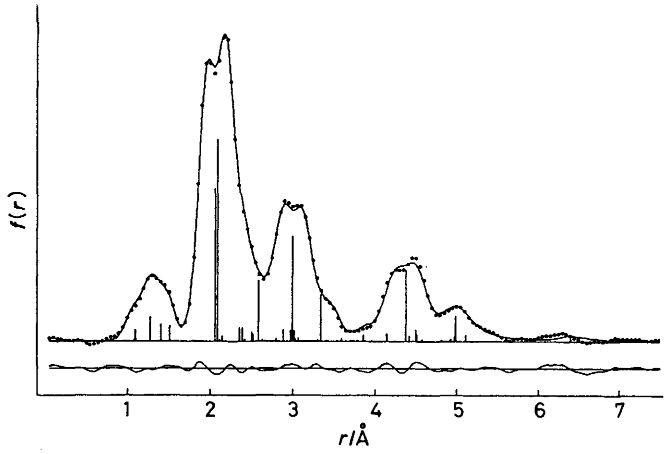

Figure 2. Radial distribution curves for gaseous dimethyl(2,4-pentanedionato)gold(III). The dots represent the experimental curve and the solid line the theoretical curve. The lower curve shows the difference and the vertical bars represent the bond distances and their scattering powers

Gaseous [AuMe$_2$(acac)] is monomeric and the metal is co-ordinated to two oxygen and two carbon atoms in a square-planar configuration, as expected for gold(III) complexes. The

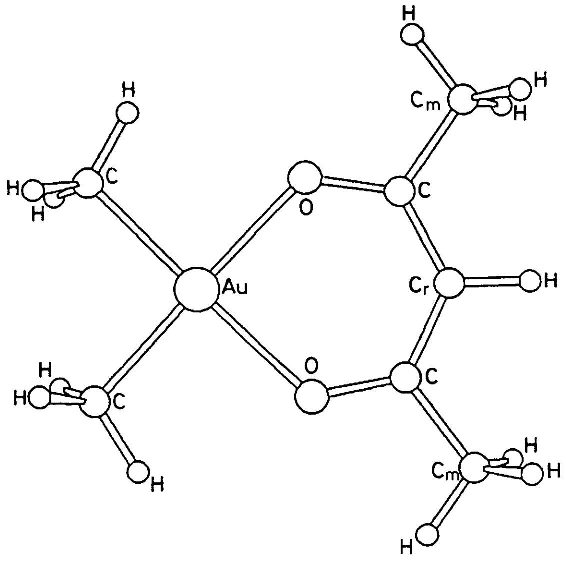

Figure 3. Molecular model of dimethyl(2,4-pentanedionato)gold(III)

Table. Molecular parameters from the least-squares refinement for gaseous dimethyl(2,4-pentanedionato)gold(III)

	r_a/Å		Angle/°		l/Å
Au–O	2.085(7)	OAuO	90.9(6)	Au–O	0.094(10)
C–O	1.273(4)	CC_rC	127.8(9)	Au···C	0.071(5)
$C–C_r$	1.403(5)	C_rCC_m	118.7(6)	$Au \cdots C_r$	0.092(18)
$C–C_m$	1.508(7)	CAuC	92.7(24)	$Au \cdots C_m$	0.099(13)
Au–C	2.054(5)	AuCH	106.4(17)	Au–C	0.057(3)
C–H	1.092(11)				

Values in parentheses are the limits of error in the last digit.

structure of the β-diketone ligand is normal since the *r*(C–O), $r(C–C_r)$, $r(C–C_m)$, angle CC_rC, and C_rC_mO are very similar to the values observed for other β-diketonate complexes.[11] The Au–C bond distance is very close to the mean value of 2.06 Å reported for dimethylgold(III) hydroxide[12] and appears to be covalent since the covalent distance is estimated to be 2.02 and 2.05 Å by using 1.25[13] and 1.28 Å,[14] respectively, as the atomic radii of square-planar gold. On the other hand, the Au–O distance is larger than the Au–C distance in spite of the smaller oxygen covalent radii[15] (0.66 Å for oxygen and 0.77 Å for carbon). It is also much larger than the calculated covalent values of 1.91[13] and 1.94 Å[14] and thus not so covalent as reported for several β-diketone complexes in the gas phase.[16]

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