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NOTE

COMPLEXES OF ORGANOMETALLIC COMPOUNDS
XIX. DIMETHYLGOLD(III) OXINATE

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We have extended our studies on organometal complexes to the investigation of organogold(III) coordination chemistry, about which little is at present known[1]. The ligand 8-quinolinol was first selected because of the several recent investigations on the oxinates of organic derivatives of platinum, mercury, thallium, lead and tin (see refs. 2–7 and references quoted therein). This paper reports the preparation of dimethylgold(III) oxinate, and the determination of its osmometric, magnetic and spectroscopic behaviour.

The complex $(CH_3)_2Au(C_9H_6NO)$ was prepared according to the following procedure: 2 mmoles of $(CH_3)_2AuI$ (prepared and purified as elsewhere reported[8]) were dissolved in *ca.* 5 ml of acetone and a solution of C_9H_6NOH (8-quinolinol)(2 mmoles in 5 ml of acetone) was added. Neutralization by aqueous NaOH was followed by addition of water (*ca.* 20 ml) with stirring. The precipitated complex (yield 95–100%) was purified by dissolution in CH_3OH (*ca.* 10 ml) and by addition of H_2O (*ca.* 20 ml). The yellow needles obtained were dried under vacuum at room temperature to give material of m.p. 131°. (Found: C, 35.54; H, 3.20; Au, 52.28; N, 3.61; O, 4.19. $C_{11}H_{12}$-AuNO calcd.: C, 35.60; H, 3.26; Au, 53.06; N, 3.77; O, 4.31%.) The use of excess ligand in the synthesis did not alter the 1:1 composition.

The complex is slightly soluble in many organic solvents and insoluble in water; it is stable for at least several months as a solid state and in solution.

The solution chemistry of $(CH_3)_2Au(C_9H_6NO)$ was mainly investigated in methanol and benzene, which have been selected as examples of a polar coordinating solvent and a non-polar non-coordinating solvent, respectively.

The osmometry was carried out at 37° with a Mechrolab Osmometer Mod. 301 A, in the concentration range 4×10^{-3} to 1×10^{-2} *M*. The experimental molecular weight was 367 (benzene) and 380 (methanol), indicating that $(CH_3)_2Au(C_9H_6NO)$ is an undissociated monomer in both solvents.

The magnetic measurements were performed according to Gouy's method on the solid complex and on its 4×10^{-2} *M* methanol solutions. (No measurements could be made in benzene owing to insufficient solubility.) Since $(CH_3)_2Au(C_9H_6NO)$ is diamagnetic at the solid state and in methanol, four-coordinate Au^{III}, with a square planar configuration, can be assumed to be present in both phases.

The absorption and reflectance spectra of $(CH_3)_2Au(C_9H_6NO)$ were determined at 25° with Beckman DK-2A and DU spectrophotometers in the wavelength range 300 to 500 mμ. Three absorption bands were observed in solution, as for other organometal oxinates[4-7]. The most intense absorption band has its maximum at 420 mμ (ε 2.60×10^3) in benzene, and at 389 mμ (ε 2.73×10^3) in methanol. The reflectance spectrum of the solid shows a band with the maximum at 380–390 mμ. These data are fully consistent with the assumption that the ligand acts as a chelating bidentate base on the $(CH_3)_2Au^{III}$ moiety, in both solvent systems and at the solid state[4-7,9,10].

The blue shift of the absorption bands of $(CH_3)_2Au(C_9H_6NO)$, taking place when benzene is replaced by polar solvents, is noteworthy. The shift also occurs with the weaker absorption bands, which show maxima at 327 mμ (ε 1.16×10^3) and 342 mμ (ε 1.64×10^3) in benzene, and 318 mμ (ε 8.5×10^2) and 334 mμ (ε 1.02×10^3) in methanol. The addition of increasing amounts of methanol to benzene solutions of the complex causes a gradual blue shift of the absorption bands without isosbestic points; the maximum of the most intense band occurs at 395 mμ in 90% benzene+10% methanol (v/v). The absorption spectra in dimethyl sulfoxide and in methyl cyanide lie in between those in benzene and methanol; the maximum of the most intense absorption band is at 404 mμ in both solvents, the absorptivity being of the same order as that in methanol and benzene. It seems then likely that the blue shift is to be ascribed to a solvent effect on the $\pi^* \leftarrow \pi$ transition of the ligand[9].

Summarizing, we believe that the configuration of $(CH_3)_2Au(C_9H_6NO)$ is square-planar, in which the four sp^2d hybrid orbitals of the gold(III) atom are employed to bind two carbon atoms of the methyl groups (which must be in a *cis* configuration) and the N and O atoms of the oxinate anion. Obviously, the possibility of further coordination on gold(III) is not excluded.

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