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Oxochloromolybdenum(V) Tetraphenylporphyrin: O=Mo(TPP)Cl. Synthesis and Structure

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Recently there has been an increasing interest in the chemistry of molybdenum porphyrins. Several methods of preparation of these compounds using a molybdenum complex in a high-temperature boiling solvent were reported [1–7]. However, apart for the case of extremely severe reaction conditions, the yields are low or the reaction incomplete.

We wish to report here a novel synthesis and the full characterization of oxochloromolybdenum(V) tetraphenylporphyrin: O=Mo(TPP)Cl. This compound, which is a versatile intermediate in the coordination chemistry of molybdenum porphyrins, was obtained in good yield by a modification of Fleischer's method [1, 2]. It was identified by elemental analysis and I.R. spectroscopy.

The I.R. spectra exhibit two very intense bands, one at 937 cm^{-1} (KBr pellet or Nujol mull) assigned to the Mo=O stretch and the other at 242 cm^{-1} (Aerosil pellet) possibly attributed to the Mo–Cl stretch. The visible spectra in CH_2Cl_2 showed four absorptions at 678 nm ($\epsilon \times 10^{-3} = 9.2$), 632 (8.4), 504 (41), 420 (shoulder) and is significantly different from that reported for O=Mo(TPP)Cl·HCl which exhibits two extra absorption maxima at 448 and 382 nm [1, 2].

The magnetic susceptibility was determined by the Faraday method using $HgCo(NCS)_4$ as a standard. The effective magnetic moment was found to be: μ_{eff}^{corr} = 1.75 B.M. (273 K), 1.72 (77 K) which is consistent with a d^1 molybdenum(V) complex.

Crystals of tetragonal-pyramidal shape were obtained by slow evaporation of a solution in CH_2Cl_2 and subjected to X-ray crystal structure analysis.

Crystal Data

The crystals are tetragonal, space group I4/m, a = 13.469(3) Å, c = 9.852(2) Å with two molecules in the unit cell. 488 independent reflexions having $I > 2\sigma(I)$, $2\theta < 82°$ were collected on a Nonius CAD-4 automatic diffractometer with Zr filtered MoKα radiation and a graphite monochromator, using the ω–2θ scan mode. The structure was solved by the heavy-atom method and refined by full matrix least-squares computation using anisotropic thermal parameters for all but the H, O and Cl atoms. The final conventional R(R_w) was 0.0552 (0.0406).

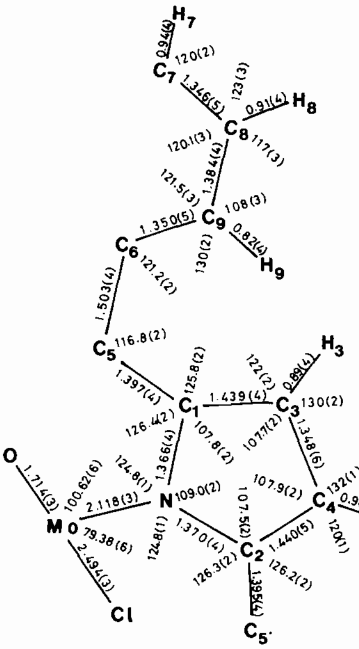

Figure 1. Asymmetric unit of the complex.

Figure 1 depicts the asymmetric unit of the complex (to which the C(5)' atom has been added). The Mo–N distance is 2.118(3) Å and the molybdenum atom is displaced 0.390(2) Å out of the mean plane of the porphyrin nitrogen, towards the oxo ligand. Bond parameters of the core are in good agreement with those reported for some metalloporphyrins which also present the same disordered I4/m structure [8]. The Mo–O distance is 1.714(3) Å close to that in $(O{=}Mo(TPP))_2O$: 1.707(3) Å [9]. The Mo–Cl distance is 2.494(3) Å longer than the sum of the covalent radii of Mo and Cl atoms (*i.e.* 2.29 Å). Hence, this bond has an ionic character (sum of the ionic radii of Mo^{5+} and Cl^- = 2.46 Å). In the case of $MoCl_2(TPP)$ the Mo–Cl(1) and Mo–Cl(2) distances are respectively 2.347(4) and 2.276(4) Å [10].

In conclusion we suggest that the present complex is better formulated as a cationic compound $[O{=}Mo(TPP)]^+Cl^-$.

Experimental

H_2TPP (6.24 g, 10 mmol) and $Mo(CO)_6$ (13.2 g, 50 mmol) were refluxed under argon over a period of two hours in a mixture of anhydrous and oxygen-free decalin (400 ml) and octane (100 ml). A dark blue cristalline precipitate was collected by suction filtration and thoroughly washed with pentane. The excess of $Mo(CO)_6$ was removed by sublimation (80 °C under 0.1 mm Hg) and the product then chromatographed over alumina ("Aluminium oxide 90 active Merck", activity grade 1, 500 g). Elution with ethanol-free CH_2Cl_2 and evaporation of the deep-brown effluent produced the emerald-green cristalline O=Mo(TPP)Cl which was dried under vacuum at 100 °C for several hours (4.83 g, 63.5%). *Anal.* Calcd. for $C_{44}H_{28}ClMoN_4O$: C: 69.53; H: 3.71; Cl: 4.66; Mo: 12.62; N: 7.37. Found: C: 69.14; H: 3.76; Cl: 4.73; Mo: 12.3; N: 7.36.

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