

Mercury–Oxygen Distances in Complexes of Mercuric Chloride

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AZOXYANISOLE forms a 1:1 adduct with mercuric chloride. The crystals from acetone are monoclinic, space group $P2/c$, with four units of $C_{14}H_{14}N_2O_3HgCl_2 \cdot \frac{1}{2}[Me_2CO]$ in a cell of dimensions $a = 20.94$, $b = 3.993$, $c = 24.95$ Å, $\beta = 122^\circ 0'$. After Fourier and least-squares refinement of the crystal structure the value of R over 2,809 independent reflexions is 13.3%. The mercury atom is in an almost undistorted mercuric chloride molecule with $d(Hg-Cl) = 2.282$, 2.285 Å, $\angle ClHgCl = 175^\circ$; the octahedral environment of

the mercury atom is completed by the oxygen atom of the azoxy-group at 2.60 Å and by three chlorine atoms of neighbouring molecules at 3.10, 3.15, and 3.18 Å.

Quinoline *N*-oxide forms a 1:1 adduct with mercuric chloride. The crystals are orthorhombic, space group $Pna2_1$, with four units of $C_9H_7NOHgCl_2$ in a cell of dimensions $a = 14.57$, $b = 17.91$, $c = 3.987$ Å. Fourier and least-squares refinement of the crystal structure reduced the value of R to 12.5% over 1,078 independent reflexions.

The mercury atom is octahedrally co-ordinated by two close chlorine atoms at 2.299 and 2.304 Å with $\angle \text{ClHgCl} = 174^\circ$, two oxygen atoms at 2.56 and 2.61 Å, and two chlorine atoms of neighbouring molecules at 3.12 and 3.35 Å.

In the 1:2 adduct between mercuric chloride and triphenylarsine oxide the mercury atom is in a distorted tetrahedral environment with $d(\text{Hg}-\text{O}) = 2.32, 2.37 \text{ \AA}$, $d(\text{Hg}-\text{Cl}) = 2.32, 2.33 \text{ \AA}$, $\angle \text{ClHgCl} = 147^\circ$.¹ Though detailed molecular parameters have not been determined, the corresponding complex involving triphenylphosphine oxide is isomorphous with the arsenic complex² and thus has a similar molecular structure. In the 1:1 adduct between mercuric chloride and triphenylarsine oxide, oxygen-bridging enables the mercury atom to have a distorted tetrahedral environment in which $d(\text{Hg}-\text{O}) = 2.47 \text{ \AA}$.³ The higher metal co-ordination number, the smaller distortion of the HgCl_2 molecule, and the longer Hg-O distances in the complexes with the NO-containing ligands indicate that the NO residue is

a poorer electron donor than the AsO or PO residue. This difference can reasonably be correlated with the marked difference in electronegativity between nitrogen on the one hand and phosphorus and arsenic on the other.

In the 1:1 adduct between mercuric chloride and cyclohexane-1,4-dione⁴ the mercury atom, situated on a two-fold axis, is octahedrally co-ordinated by two chlorine atoms at 2.30 Å, two oxygen atoms at 2.79 Å, and two chlorine atoms at 3.25 Å. The Hg-O distance is distinctly longer than that obtained with the NO-containing ligands. The greater electron-donor capacity of the N-O function, relative to that of the C-O function, can be associated with the importance of the ionic form X^+-O^- in azoxy- and N-oxide derivatives and the relatively small contribution of such an ionic form to the electronic structure of the unconjugated carbonyl group.

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¹ C.-I. Brändén, *Acta Chem. Scand.*, 1963, **17**, 1363.

² C.-I. Brändén, *Arkiv Kemi*, 1964, **22**, 501.

³ C.-I. Brändén, *Arkiv Kemi*, 1964, **22**, 485.

⁴ P. Groth and O. Hassel, *Acta Chem. Scand.*, 1964, **18**, 1327.