

## Coordination Behaviour of Mercury(II) towards Triazine-1-oxides

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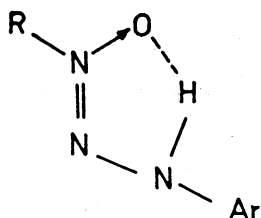
Mercury(II) chelates of monobasic bidentate/tridentate and dibasic tridentate/tetradentate triazine-1-oxides (TH, T'H & T''H<sub>2</sub>) conform to the stoichiometries (HgT<sub>2</sub>), (HgT<sub>2</sub>) and (HgT''). Four coordinate tetradral and six coordinate octahedral stereochemistries have been assigned to (HgT<sub>2</sub>) and (HgT<sub>2</sub>) chelates. Highly insoluble (HgT'') chelates with apparent coordination numbers three and four have also been obtained. In the case of apparent three coordination the extreme insolubility is due to polymerisation through  $\overset{|}{-C=O}$  oxygen instead of  $\overset{|}{-N\rightarrow O}$  oxygen. The quadridentate triazine-1-oxide ligand gives a cage like entrapped mercury(II) chelate. The attainment of six coordination is a consequence of the stereochemical requirements of the ligand donor groups of the *ortho*-substituents of  $\overset{3}{-N-Ar}$  group. The biocidal activity of triazine-1-oxide ligands and their mercury(II) derivatives has also been screened.

### INTRODUCTION

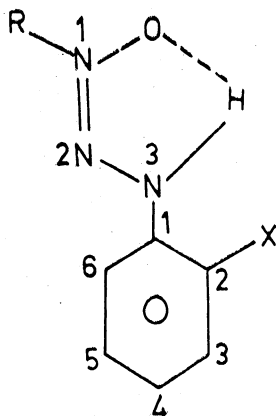
The coordination behaviour and uses as analytical reagent of triazine-1-oxides has been reviewed<sup>1</sup>. In continuation of our studies with these fascinating ligands, the coordination behaviour of mercury(II) has been examined. In its complexes, mercury(II) commonly shows coordination numbers from two coordinate linear to six coordinate octahedral geometry<sup>2</sup>. The perusal of chemical literature shows that higher coordination numbers are less common for divalent mercury although there are some reports of penta and hexa coordinate mercury(II)<sup>3</sup>. In the present communication we report the results of mercury(II) chelates of monobasic bidentate/tridentate and dibasic tridentate/quadridentate triazine-1-oxides (TH, T'H and T''H<sub>2</sub>). The ligands are represented by the general structures (I), (II), (III) and (IV) and the substituents in the aromatic ring are indicated by using prefixes *o*-, *m*-, *p*- which are counted with respect to the N-C (Ar) bond.

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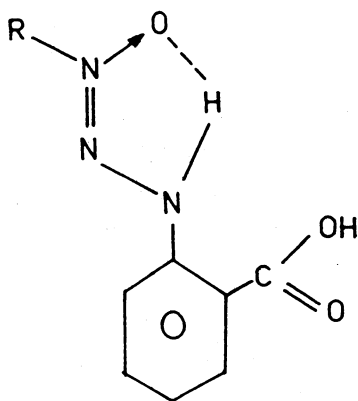
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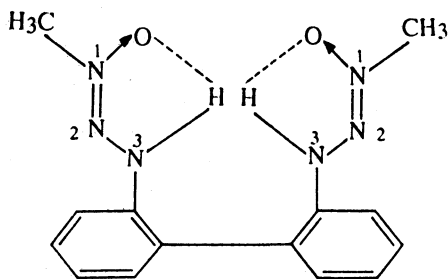
(I)

(X = OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, Cl, Br, I)

(II)



(III)



(IV)

R = alkyl, aryl or substituted aryl, Ar = aryl or o-substituted aryl, X = halogens/alkoxy

### EXPERIMENTAL

All chemicals used were of analytically pure grade unless otherwise specified. Triazine-1-oxides were synthesised by following published procedures<sup>4-6</sup>, that is, by coupling the diazonium salt solution with substituted hydroxylamine at 0°C using sodium acetate to control the acidity. Ligands were purified by recrystallisation from aqueous ethanol. Mercury(II) chelates were synthesised by straight-forward method of mixing the hot ethanolic solution of mercury(II) acetate (one drop of glacial acetic acid was added to make the solution clear) to hot alcoholic solution of the ligand in 1 : 1, 1 : 2 and 1 : 3 molar ratios. Mercury(II) chelates

were thrown down within a few minutes which were filtered hot, washed with hot ethanol and recrystallised from acetone.

## RESULTS AND DISCUSSION

Monobasic bidentate/tridentate triazene-1-oxides give chelates of the general formula  $[\text{HgT}_2]$  and  $[\text{HgT}'_2]$  irrespective of metal-ligand ratio while dibasic tridentate/quadridentate triazene-1-oxides give chelates of the type  $[\text{HgT}'']$  (Table 1).  $[\text{HgT}_2]$  and  $[\text{HgT}'_2]$  chelates are soluble in acetone, benzene and nitromethane. Conductivity measurements in nitromethane show that the non-electrolytic nature and molecular weights in freezing benzene give monomer values of mercury(II) chelates. Dibasic tridentate (3-*o*-carboxyphenyl-1-methyl triazene-1-oxidato) mercury(II),  $[\text{HgT}'']$  is highly insoluble in common organic solvents and could not allow the conductance and molecular weight determinations. Similar insoluble product was obtained with four coordinate biphenyl containing triazene-1-oxide (II). The extreme insolubility of the mercury(II) chelate indicates the polymeric nature of the compound in the first case and cage-like entrapped mercury(II) in the latter case. All attempts to react  $\text{HgT}_2$ ,  $\text{HgT}'_2$  and  $\text{HgT}''$  with dipyriddy/*o*-phenenthroline failed, showing reluctance on the part of mercury(II) to raise its coordination number.

Mercury(II) being a  $5d^{10}$  system has zero C.F.S.E. The coordination number and stereochemistry of mercury(II), therefore, cannot be dictated by C.F.S.E. and thus magnetic moment values and electronic spectra cannot throw any light on the coordination number and stereochemistry of Hg(II) chelates. In  $d^{10}$  system the coordination number and stereochemistry depends on minimum ligand-ligand repulsion, ionic size, electrostatic and covalent bonding forces<sup>7</sup>. The bidentate/tridentate nature of the ligands has been established from the study of I.R. spectra (Table 2).  $\overset{3}{\text{N}}\text{-H}$  band at  $3200\text{ cm}^{-1}$  completely disappears in metal chelates.  $\overset{1}{\text{N}}\text{-O}$  stretch at  $1300\text{ cm}^{-1}$  is considerably lowered to about  $1240\text{ cm}^{-1}$  due to  $\overset{1}{\text{N}}\text{-O}\rightarrow\text{M}$  electron drainage<sup>8</sup>, C=O band at  $1680\text{ cm}^{-1}$  is also lowered to  $1610\text{ cm}^{-1}$  in the case of [3-(*o*-carboxyphenyl)-1-methyl triazene-1-oxidato] mercury(II)<sup>8</sup>. These IR data clearly indicate that in the case of monobasic bidentate/tridentate triazene-1-oxide ligands both  $\overset{3}{\text{N}}$  and  $\overset{1}{\text{N}}\text{-O}$  oxygen act as donor groups. The tridentate nature of 3-(*o*-carboxyphenyl)-1-methyl triazene-1-oxide is proved due to lowering of C=O stretch besides absence of  $\overset{3}{\text{N}}\text{-H}$  and lowering of  $\overset{1}{\text{N}}\text{-O}$  bands. Tridentate nature of monobasic *ortho*-substituted chloro and methoxy triazene-1-oxides have been inferred indirectly by comparing the IR spectra of a well established compound bis[3-(*o*-chlorophenyl)-1-methyl triazene-1-oxidato] cobalt(II) through X-ray crystallographic studies<sup>8,9</sup>.

TABLE I  
 CHARACTERIZATION DATA OF REPRESENTATIVE MERCURY (II) CHELATES OF TRIAZINE-1-OXIDES (TH, T'H AND T''H<sub>2</sub>)  
 (TH: R = C<sub>6</sub>H<sub>5</sub>, Ar = C<sub>6</sub>H<sub>5</sub>; T'H: R = C<sub>6</sub>H<sub>5</sub>, Ar = C<sub>6</sub>H<sub>5</sub>; T''H<sub>2</sub>: R = C<sub>6</sub>H<sub>5</sub>, Ar = *o*-chlorophenyl; T'H<sub>2</sub>: R = C<sub>6</sub>H<sub>5</sub>, Ar = *o*-carboxyphenyl and R = CH<sub>3</sub>, Ar = biphenyl)

Complex	Colour	M.pt. (°C)	% Found (Calcd.)				cm <sup>2</sup> mole <sup>-1</sup>	Mol. wt. (Benzene)
			Hg	N	C	H		
HgT <sub>2</sub>	White	153	39.98 (40.06)	16.53 (16.78)	33.62 (33.56)	3.16 (3.19)	3.1	479.7 (500.6)
HgT' <sub>2</sub>	Yellow	131	35.31 (35.22)	14.61 (14.74)	37.32 (36.70)	4.36 (4.08)	2.0	552.0 (569.6)
HgT''	Yellow	175-76	49.87 (50.10)	10.87 (10.67)	24.71 (24.39)	2.30 (1.78)	—	—
HgT'' (Ar = biphenyl)	Yellow	185-86	39.76 (40.23)	16.62 (16.84)	33.21 (33.69)	2.45 (2.80)	—	—

TABLE 2  
 IMPORTANT I.R. BANDS ( $\text{cm}^{-1}$ ) OF TRIAZENE-1-OXIDES (TH, T'H and T''H<sub>2</sub>) AND  
 THEIR MERCURY(II) CHELATES

Ligand/Complex	R	Ar	$\nu_{\text{N-H}}$	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{Hg-N}}$	$\nu_{\text{Hg-O}}$
TH	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	3200 s	1290 m	-	-	-
HgT <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	-	1235 s	-	510 m	450 m
T'H	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> Cl(o)	3200 s	1300 m	-	-	-
HgT' <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> Cl(o)	-	1240 s	-	505 m	445 m
T''H <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> COOH(o)	3200 s	1295 m	1680 s	-	-
HgT''	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> COOH(o)	-	1235 s	1610 s	510 m	445 m
HgT''	CH <sub>3</sub>	Biphenyl	-	1240 s	-	510 m	450 m

s = sharp, m = medium.

The coordination number of mercury(II) in bis(monobasic bidentate triazene-1-oxidato) mercury(II) is four and the stereochemistry is tetrahedral for obvious reasons. In case of monobasic tridentate [3-(*o*-chloro/methoxyphenyl)-1-methyl/phenyl triazene-1-oxidato] mercury(II), the coordination number has been assigned to be six and the stereochemistry is distorted octahedron. This conclusion is based on the identical IR spectral bands of CoT'<sub>2</sub><sup>8,9</sup> and HgT'<sub>2</sub>. The coordination by *ortho*-substituent is due to the stereochemical disposition of the ligand donor groups. Since Hg(II) forms strong Hg-Cl bond, sometimes even giving the polymer structure, we assume the participation of the *ortho*-substituents in forming metal ligand bond. X-ray crystallographic study of CoT'<sub>2</sub><sup>8,9</sup> and study of models of HgT'<sub>2</sub> indicate severe distortion of the octahedron.

The apparent coordination number of mercury(II) in HgT'' is three. Although some three coordinate mercury(II) complexes are known<sup>10</sup> such compounds have been found to be the result of the steric requirements of the ligands rather than the preference for mercury(II) to give three coordinate complexes. The extreme insolubility of HgT'' in organic solvents indicated its polymeric nature. It is believed that mercury(II) acquires its usual four coordinate tetrahedral stereochemistry through polymerisation. There is  $\overset{1}{\text{N}}\rightarrow\text{O}$  oxygen as well as C=O oxygen available to act as a bridging atom. Bhattacharya and Ray<sup>5</sup> have argued in favour of C=O oxygen acting as a bridging atom in CuT'' based on magnetic moment values and some X-ray crystallographic evidences in similar type of complexes<sup>11</sup>. Since [CuT'']<sub>n</sub> and [HgT'']<sub>n</sub> have same stoichiometry as well as very similar IR spectra, it is believed that the C=O oxygen acts as a bridging atom.

Bridging through  $\overset{1}{\text{N}}\rightarrow\text{O}$  oxygen will lead to a strained four-membered ring while bridging through C=O oxygen will offer a strain-free 8-membered ring involving

the mercury (II) ions. Four membered ring is likely to be highly strained in tetrahedral geometry and is also likely to lead to subnormal magnetic moment in  $[\text{CuT}'' ]_n$  through super exchange<sup>12</sup>.  $[\text{CuT}'' ]_n$ , however, shows a normal magnetic moment of 1.85 B.M. A further support for bonding through  $\text{N}^1 \rightarrow \text{O}$  oxygen and  $\text{N}^3$ -atom is lent by identifying  $\text{Hg}-\text{O}$  stretch at  $445 \text{ cm}^{-1}$  and  $\text{Hg}-\text{N}$  at  $510 \text{ cm}^{-1}$ . Diphenyl containing triazine-1-oxide ligand giving chelate of the type  $\text{HgT}''$  fails to react with secondary ligands like dipy/*o*-phen. because of attainment of a very stable cage like entrapped mercury(II) ion. The reluctance on the part of mercury(II) to raise its coordination number through mixed ligand complex formation by dipyriddy/*o*-phenanthroline is due to its exceptionally high value of electron affinity (29.08 eV). Electron affinity value of an ion is the measure of its covalency. The greater the co-valent character of the metal ligand bond the smaller is the coordination number<sup>13</sup>. This is one of the most important factors favouring lower coordination number for mercury(II). Another line of argument explaining lower coordination numbers of mercury(II) is the  $d^9p$ ,  $d^9s$  and  $s-p$  separation energy values (14.7, 5.3 and 9.4 eV). Based on these energy differences Orgel<sup>14</sup> has invoked  $d$ - $s$  mixing in mercury(II) chelates and hence preference for lower coordination<sup>15</sup>.

### Method of Determination of Antibacterial Activity

Agar plate diffusion technique was employed for the determination of mercury(II) chelates antibacterial activity<sup>16</sup>. For this purpose filter paper (Whatman No. 41) discs (5 mm dia) saturated with the solution of test compounds (10 mg/ml in acetone) were placed on the nutrient agar plates (1.56% agar, 0.5% NaCl, 0.5% glucose and 2.5% pentone), all % being (w/v) in the pH range (6.5–7.0). After drying up the solvent each disc contained approximately 150 mg of the substance. The plates were incubated at the optimum growth temperature of  $37^\circ\text{C}$  and the zones of inhibition around the discs were measured after 24 hrs. All the experiments were carried out in duplicate. The results obtained show that monobasic/dibasic triazine-1-oxidato mercury(II) has far greater biocidal property compared to triazine-1-oxides and binary mercury(II) salts. Similar biocidal activity has been reported from this laboratory with organotin(IV) complexes of triazine-1-oxides.<sup>17</sup>

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