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### Dimercury(I)-Nitrogen Compounds and Other Addition Complexes of the Hg-Hg Ion

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## Dimercury(I)-Nitrogen Compounds and Other Addition Complexes of the $^+Hg-Hg^+$ Ion

The reaction between dimercury(I) salts and Lewis bases in polar solvents normally destroys the metal-metal bond of the  $^+Hg-Hg^+$  dimercury(I) ion. However, many stable dimercury(I) compounds with the bonding system  $E-Hg-Hg-E$  ( $E = N, P, As, Sb, O, S, Se, Sn$ ) have been described since 1958. The successful preparation of these dimercury(I) addition compounds is mainly due to the use of nonpolar solvents, the use of weak Lewis bases, and to the use of NH acidic nitrogen compounds. It is predicted that many more dimercury(I) compounds of this type can be formed.

### INTRODUCTION

The reaction of dimercury(I) with basic nitrogen compounds leads to insoluble black products originally considered as dimercury(I)-nitrogen compounds.<sup>1,2</sup> But upon x-ray examination it was found that, in addition to finely dispersed metallic mercury, only dimercury(II)-nitrogen compounds with four-coordinated nitrogen were present<sup>3-11</sup>:



The disproportionation reaction which occurs through splitting of the  $^+Hg-Hg^+$  metal-metal bond in the dimercury(I) salts with Lewis bases is driven by the precipitation of metallic mercury or by the formation of stable complexes of the dimercury(II) ion with the electron-pair donors. If the activity of mercury(II) is not decreased much by the Lewis bases, then the dimercury(I) ion will be stable with respect to disproportionation as can be seen from the standard potentials

$$\begin{aligned} Hg_2^{2+} &= Hg + Hg^{2+} \quad (E_0 = -0.115 \text{ V}) \\ K &= (Hg_2^{2+})/(Hg^{2+}) = 1.15 \times 10^{-2}. \end{aligned}$$

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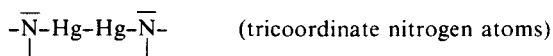
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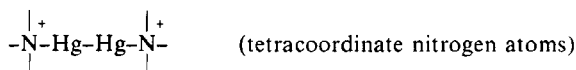
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For this reason stable dimercury(I)-nitrogen or other dimercury(I) addition compounds are only formed when the stability constants of the addition compounds in the two oxidation states are not too different. Since the complexes of dimercury(II) are normally more stable than those of dimercury(I), the disproportionation reaction is usually observed. The dimercury(I)-nitrogen compounds are only expected if the basicities of the nitrogen compounds are low.<sup>12</sup>

The following building blocks for dimercury(I)-nitrogen compounds are possible:



or



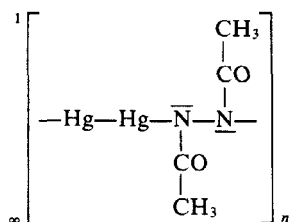
The first true dimercury(I)-nitrogen compound was obtained by the reaction of a NH acidic compound, diacetylhydrazine, with dimercury(I) nitrate in aqueous solution.<sup>13</sup> The dimercury(I) diacetylhydrazide,  $\text{Hg}_2[\text{N}_2(\text{COCH}_3)_2]$ , prepared in this manner belongs to the class of dimercury(I)-nitrogen compounds with tricoordinate nitrogen atoms;<sup>14</sup> compounds with tetracoordinate nitrogen atoms have since been obtained<sup>15,16</sup> by reaction of amines of lower basicity<sup>17</sup> with dimercury(I) salts.

The addition compounds of the  $\text{Hg}_2^{2+}$  ion with ligands containing donor atoms of the elements of the 4th, 5th and 6th main groups were only isolated a few years ago.<sup>18-24,46,56,57</sup>

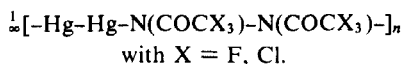
## DIMERCURY(I)-NITROGEN COMPOUNDS

### Compounds with Tricoordinate Nitrogen Atoms

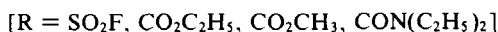
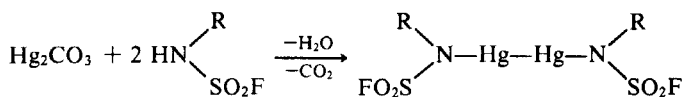
Investigations of the dimercuration of amides with mercury(II) salts in a molten state, which is accompanied by the bonding of mercury to nitrogen and carbon, led to the observation that the *N,N'*-diacetylhydrazide produced contained a small quantity of dimercury in the oxidation state  $1+$ .<sup>25</sup> Therefore, the dimercuration of *N,N'*-diacetylhydrazine with dimercury(I) salts was attempted under milder conditions. The orange-colored dimercury(I) diacetylhydrazide,  $\text{Hg}_2[\text{N}_2(\text{COCH}_3)_2]$ , forms an insoluble precipitate upon mixing aqueous solutions of diacetylhydrazine with dimercury(I) nitrate and adding  $\text{NaHCO}_3$  (Refs. 13,14):



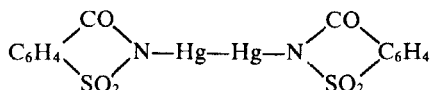
There also exist similar dimercury(I)–nitrogen compounds of the type



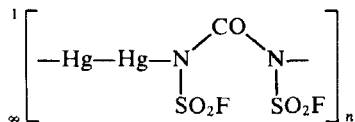
A series of other dimercury(I)–nitrogen compounds was obtained by the reaction of NH-acidic acylamides and hydrazides in benzene with freshly prepared (and dried) dimercury(I) carbonate in the dark<sup>14</sup>:



For bis(saccharine)dimercury(I)<sup>14</sup> we expect the group structure:



while for the dimercury(I) (*N,N'*-bis(fluorsulfonyl)ureide),<sup>14</sup> we expect either a chain or a ring structure, or both:

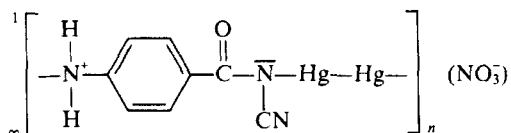


Aromatic sulfonyl and acylcyanamides react with dimercury(I) nitrate and form compounds with the composition<sup>26</sup>  $\text{Hg}_2\text{L}_2$  ( $\text{L} = \text{H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NCN}^-$ ,  $\text{C}_5\text{H}_4\text{N—SO}_2\text{NCN}^-$ ,  $\text{C}_5\text{H}_4\text{N—CONCN}^-$ ) with group structures.<sup>26</sup> The IR spectra do not allow one to decide whether the  $\text{Hg}_2^{2+}$  ion is bound to the amide group or to the nitrogen atom of the pyridine, which means that these compounds can have either tricoordinate or tetracoordinate nitrogen

TABLE I  
Structural data of dimercury(I)-nitrogen compounds

Compound	$d(\text{Hg}-\text{Hg}), \text{pm}$	$d(\text{Hg}-\text{N}), \text{pm}$	$\angle \text{Hg}-\text{Hg}-\text{N}$	Remarks	Reference
$\text{Hg}_2(1,4\text{-diazine})(\text{NO}_3)_2$	249.9(1)	255.5(2)	167.6°	Chain structure	50
$\text{Hg}_2(\text{quinoline})_2(\text{NO}_3)_2$	255.1(2)	217.8(4)	164.5°	Group structure	51
$\text{Hg}_2(3\text{-Cl-pyridine})_2(\text{ClO}_4)_2$	248.7(2)	221(2)	167.4°	Group structure	34
$\text{Hg}_2(1,8\text{-naphthyridine})_2(\text{ClO}_4)_2$	251.1(1)	278(1); 203(3)	128.2°; 174.4°	Group structure	35
$\text{Hg}_2(1,10\text{-phenanthroline})(\text{NO}_3)_2$	251.6(7)	248(4); 230(4)	136.7°; 78°	Phen coord. to one Hg	28
$\text{Hg}_2(4\text{-CN-pyridine})_2(\text{ClO}_4)_2$	249.8(2)	216(3)	176.0(7)°	Lig. bonded via py N	33
$\text{Hg}_2(\text{acridine})_2(\text{ClO}_4)_2$	251.77(5)	215.0(5)	180°	Group structure	37
$\text{Hg}_2(3\text{-aminopyridine})_2(\text{ClO}_4)_2$	251.1(1)	219(3); 225(3)	172°; 162°	Lig. bonded via py N	31
$\text{Hg}_2(\text{pyridine-3-sulfonate})$	249.4(1)	220.3(13)	165.6°	Lig. bonded via py N	32

atoms. Only the *p*-aminobenzoylcyanamidodimercury(I) nitrate has both tricoordinate and tetracoordinate nitrogen atoms in a chain structure<sup>26</sup>:

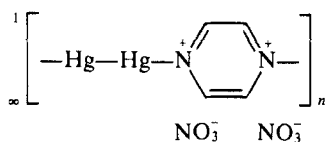


### Compounds with Tetracoordinate Nitrogen Atoms

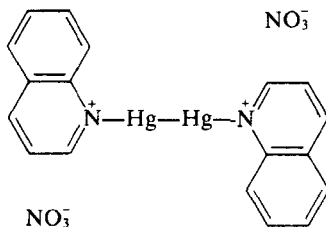
A dimercury(I)-nitrogen compound with tetracoordinate nitrogen atoms,  $\text{Hg}_2(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NO}_3)_2$ , was first described in 1966.<sup>27</sup> However, a later examination of this compound revealed that there were not only two but up to six molecules of aniline bound to one molecule of  $\text{Hg}_2(\text{NO}_3)_2$ .<sup>29</sup> The first x-ray structure determination of the addition compound of  $\text{Hg}_2(\text{NO}_3)_2$  with 1,10-phenanthroline was published in 1967.<sup>28</sup> In this compound,  $\text{Hg}_2(\text{phen})(\text{NO}_3)_2$ , one mercury atom of the  $\text{Hg}_2^{2+}$  ion is bonded to both nitrogen atoms of the phenanthroline, whereas the other mercury atom is coordinated to the oxygen atoms of the nitrate ion.

Addition compounds have been obtained from 1 mol of dimercury(I) nitrate with 2 mol of the following nitrogen compounds<sup>16</sup>: *p*-phenoxyaniline, 4-aminobiphenyl, 4-trifluoromethylaniline, 2-naphthylamine, quinoline, benzo(*f*)quinoline, acridine, 4-phenylpyridine; *o*-phenylenediamine and *p*-phenylenediamine yielded 1:1 addition compounds with  $\text{Hg}_2(\text{NO}_3)_2$ .

X-ray structure determinations have been performed on the addition compounds of  $\text{Hg}_2(\text{NO}_3)_2$  with 1,4-diazine (chain structure) (see Figures 1,2)<sup>50</sup>:



and with quinoline (group structure)<sup>51</sup>:



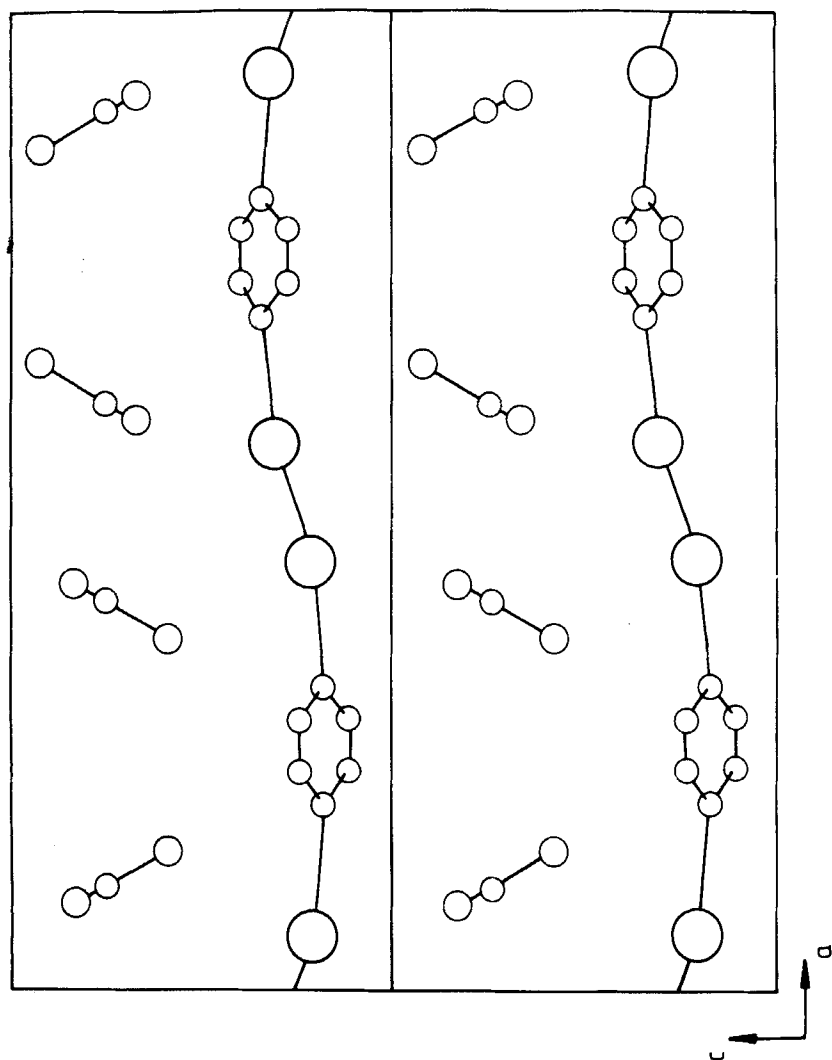


FIGURE 1 Graphic representation of two unit cells of the dimercury(I)-nitrogen addition compound  $\frac{1}{2}[\text{Hg}_2(\text{pyrazine})(\text{NO}_3)_2]$ .

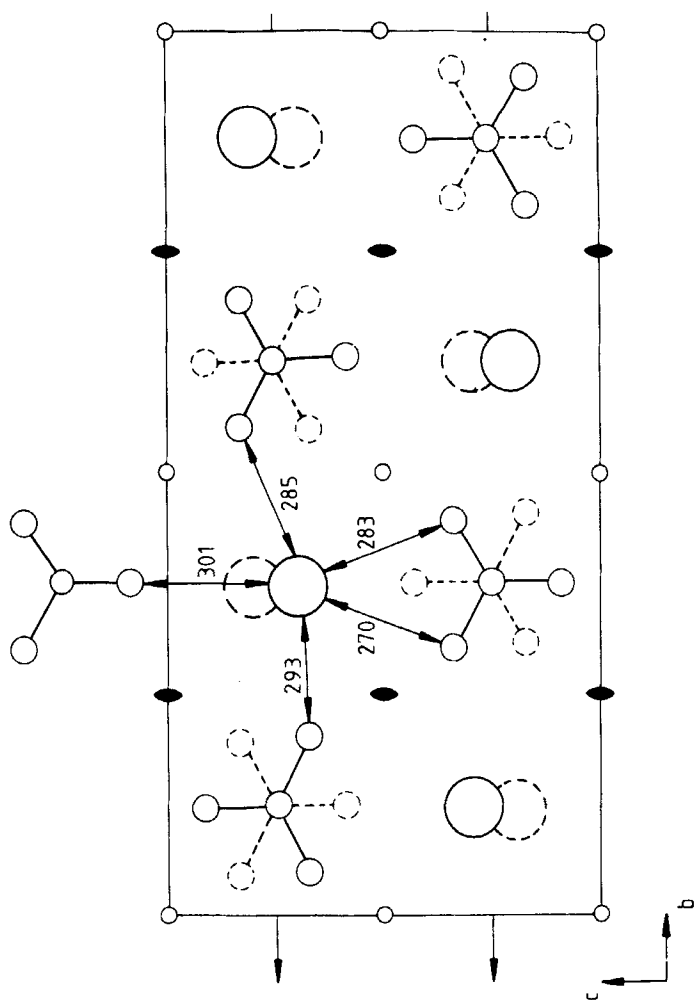
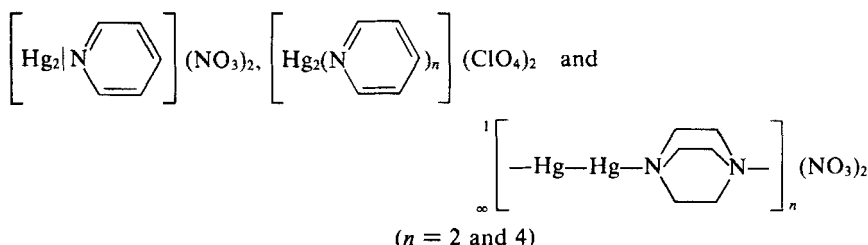


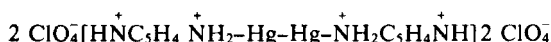
FIGURE 2 View along the chain direction in the structure of  $[\text{Hg}_2(\text{pyrazine})](\text{NO}_3)_2$ . Some interatomic distances (in pm) are shown.



Further addition compounds of  $\text{Hg}_2(\text{NO}_3)_2$  with aromatic amines<sup>29</sup> such as 1,10-phenanthroline, pyridazine, 2-pyrazinecarboxamide, 4-methylquinoline, 4-amino-4-methoxybenzoic sulfonamide, 4-fluoroaniline, 3-fluoroaniline and 2,5-difluoroaniline contain two molecules of the nitrogen compound and one molecule of  $\text{Hg}_2(\text{NO}_3)_2$ .<sup>29</sup> With 4-fluoroaniline there exists a compound containing four molecules of base per molecule of  $\text{Hg}_2(\text{NO}_3)_2$ .<sup>29</sup> Similar results were obtained in the synthesis of  $\text{Hg}_2(\text{NO}_3)_2$  and  $\text{Hg}_2(\text{ClO}_4)_2$  adducts with mono-, di-, and tri-substituted anilines, pyridine and 1,4-diazabicyclo(2.2.2)octane.<sup>30,52</sup> It is important to note that, in the synthesis of the adducts with pyridine and 1,4-diazabicyclo(2.2.2)octane, lowering the basicity of the nitrogen bases by the solvent has a critical influence upon the results:

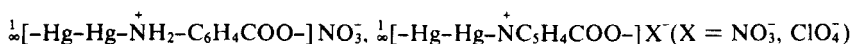


Adducts with  $\text{Hg}_2(\text{NO}_3)_2$  or  $\text{Hg}_2(\text{ClO}_4)_2$  are also formed by aminopyridine, trichloroacetamidopyridine and aminochloropyridine<sup>31</sup>; X-ray determination of the adduct between 3-aminopyridinium perchlorate and  $\text{Hg}(\text{ClO}_4)_2$  revealed the following structure<sup>31</sup>:



The  $\text{Hg}_2^{2+}$  ion is bound to the amino nitrogen but not to the pyridine nitrogen.

*p*-Aminobenzoic acid and nicotinic acid, respectively, form adducts with dimercury(I) salts with chain structures<sup>32</sup>:



Sulfanilic acid and pyridine-3-sulfonic acid form adducts with dimercury(I) salts with group structures.<sup>32</sup> X-ray examination of bis(pyridine-3-sulfonate) dimercury(I) dihydrate has shown that the  $\text{Hg}_2^{2+}$  ion is bound to the nitrogen atom of pyridine and not to an oxygen atom of the sulfur group. This compound is therefore an inner salt<sup>32</sup> (see Figure 3). In  $\text{Hg}_2(4\text{-CN-pyridine})_2(\text{ClO}_4)_2$ <sup>33</sup> and in  $\text{Hg}_2(3\text{-Cl-pyridine})_2(\text{ClO}_4)_2$ <sup>34</sup> the  $\text{Hg}_2^{2+}$  ion is also bound to

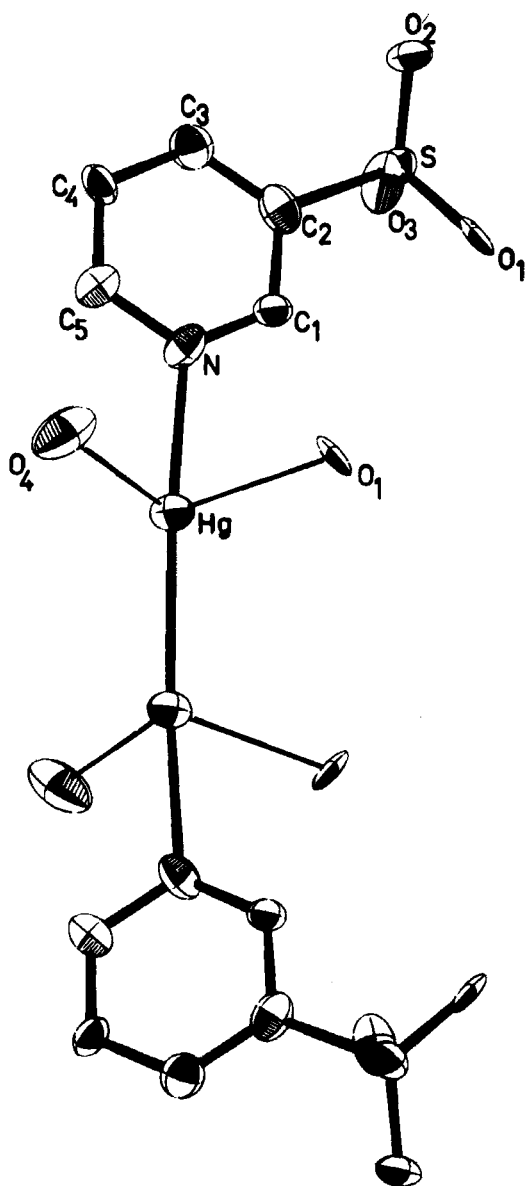


FIGURE 3 Structure of  $\text{Hg}_2(\text{pyridine-3-sulfonate})_2 \cdot 2\text{H}_2\text{O}$ .

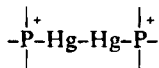
the nitrogen atom of pyridine. In the compound  $\text{Hg}_2(1,8\text{-naphthyridine})_2(\text{ClO}_4)_2$ <sup>34,35</sup> both nitrogen atoms are coordinated to the  $\text{Hg}_2^{2+}$  ion but with different bond lengths [ $\text{Hg}-\text{N} = 203(3)$  pm;  $\text{Hg}-\text{N} = 278(3)$  pm].

$\text{Hg}_2(\text{ClO}_4)_2$  sequentially coordinates two molecules of 2-chloropyridine, 5-nitroquinoline, quinoline, 2-picoline, 2-methylquinoline, 2,6-lutidine or 2,4,6-trimethylpyridine<sup>36</sup>; the structure of the addition complex  $\text{Hg}_2(\text{acridine})_2(\text{ClO}_4)_2$ <sup>37</sup> has been examined by x-ray methods.

Cyano carbon anions as the tricyanomethanide anion,  $\text{C}(\text{CN})_3^-$ , and the *p*-tricyanovinylphenyldicyanomethanide anion and some cyanopropenides (e.g., the 1,1,3,3-tetracyanopropenide anion) form addition compounds with the  $\text{Hg}_2^{2+}$  ion which show  $\text{Hg}-\text{Hg}-\text{N}$  bonding.<sup>48</sup> Even dianions as the 2-dicyanomethylene-1,1,3,3-tetracyanopropandiide form stable dimercury(I) compounds.<sup>48</sup>

## DIMERCURY(I)-PHOSPHORUS COMPOUNDS

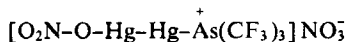
Until now it has not been possible to prepare compounds with the building blocks:



However results from NMR experiments suggest that, in liquid  $\text{SO}_2$  as a solvent,  $\text{PF}_3$  forms the cations  $(\text{Hg}_2\text{PF}_3)^{2+}$  or  $[\text{Hg}_2\text{P}(\text{CF}_3)(\text{C}_6\text{H}_5)_2]^{2+}$  with  $\text{P}(\text{CF}_3)(\text{C}_6\text{H}_5)$ .<sup>38</sup> It has so far not been possible to obtain real dimercury(I)-phosphorus compounds because of the disproportionation reactions.

## DIMERCURY(I)-ARSENIC COMPOUNDS

$\text{Hg}_2(\text{AsF}_6)_2$  seems to form a 1:1 adduct with  $\text{As}(\text{C}_6\text{H}_5)_3$  in liquid  $\text{SO}_2$ .<sup>38</sup> With  $\text{As}(\text{CF}_3)_3$ , a 1:1 adduct is formed with  $\text{Hg}_2(\text{NO}_3)_2$ .<sup>47</sup>



## DIMERCURY(I)-ANTIMONY COMPOUNDS

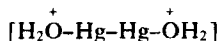
Triphenylstibine reacts with  $\text{Hg}_2(\text{AsF}_6)_2$  in liquid  $\text{SO}_2$  to form a 1:1 adduct.<sup>38</sup>

TABLE II  
Structural data of dimercury(I)-oxygen compounds

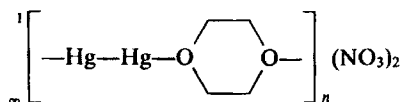
Compound	$d(\text{Hg}-\text{Hg}), \text{pm}$	$d(\text{Hg}-\text{O}), \text{pm}$	Remarks	Reference
$\text{Hg}_2(\text{OH})_2(\text{NO}_3)_2$	254(1)	215	$^+(\text{H}_2\text{O}-\text{Hg}-\text{Hg}-\text{OH}_2)^+$ cation	39-42
$\text{Hg}_2(\text{C}_3\text{H}_5\text{NO})_2(\text{ClO}_4)_2$	252.3(2)	219(2); 234(3); 243(3)	Dimeric group structure	43
$\text{Hg}_2((\text{C}_6\text{H}_5)_3\text{PO})_2(\text{ClO}_4)_2$	252.2(3)	229(2); 231(2); 243(2)	Group structure	44

## DIMERCURY(I)-OXYGEN COMPOUNDS

The dihydrates of some dimerccury(I) salts, e.g.,  $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  contain only the nearly linear ion<sup>39-42</sup>:



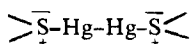
Saturated organic ethers, e.g., 1,4-dioxane or diethyleneglycol dimethyl ether, form crystalline adducts with the composition  $\text{Hg}_2(1,4\text{-dioxane})(\text{NO}_3)_2$ <sup>20</sup> or  $\text{Hg}_2(\text{diglyme})_2(\text{NO}_3)_2$ .<sup>20</sup> The adduct of  $\text{Hg}_2(\text{NO}_3)_2$  with 1,4-dioxane probably has a chain structure:



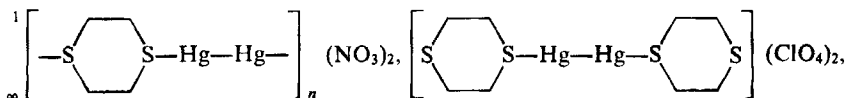
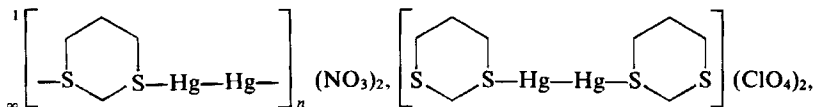
In  $\text{Hg}_2(\text{pyridine-oxide})_4(\text{ClO}_4)_2$ <sup>43</sup> three of the four pyridine oxide ligands build bridges with the neighboring dimeric units. With triphenylphosphine oxide one obtains adducts with  $\text{Hg}_2(\text{ClO}_4)_2$  which contain six molecules,<sup>44</sup> five molecules, or four molecules of the ligand.<sup>15</sup>

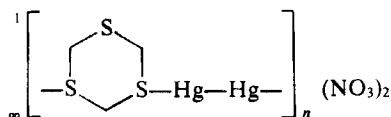
## DIMERCURY(I)-SULFUR COMPOUNDS

It was accepted for a long time that it was impossible to synthesize compounds with the building blocks:



There was only one compound known and it contained mercury(II) as well as dimerccury(I),  $\text{Hg}_2^{\text{I}}\text{Hg}_2^{\text{II}}\text{S}_2(\text{ClO}_4)_2$ .<sup>45</sup> The reaction of  $\text{Hg}_2(\text{NO}_3)_2$  or  $\text{Hg}_2(\text{ClO}_4)_2$  in methanol as a solvent with 1,3-dithiane, 1,4-dithiane or 1,3,5-trithiane leads to the following addition compounds<sup>18</sup>:





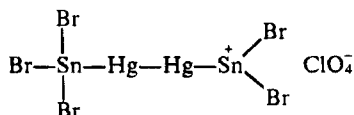
There is an x-ray structure determination of the 1,3-dithianedimercury(I) dinitrate<sup>18</sup>; the chains are connected like a helix as shown in Figure 4. Additional dimercury(I)-sulfur compounds were prepared by the reactions of dimercury(I) nitrate, perchlorate or hexafluorosilicate with the following sulfur-donor ligands in methanol solutions or in the two-phase water/benzene or methylene chloride system: 1,3-dithiolane, 2-phenyl-1,3-dithiolane, 2,2'-trimethylenebis(1,3-dithiolane), bis(benzylthiomethane) and dibenzylsulfide.<sup>19</sup> Polydentate sulfur-containing ligands with a neopentane framework form stable adducts with  $\text{Hg}_2(\text{NO}_3)_2$  or  $\text{Hg}_2(\text{ClO}_4)_2$ .<sup>22</sup> Using methanolic solutions of  $\text{Hg}_2(\text{NO}_3)_2$  it was possible to obtain stable adducts with the sulfur-donor ligands 2,2,4,4-tetrachloro-1,3-dithietane, *exo*-3,4,5-trithia-cyclo(5.2.1.0)decane,<sup>2,6</sup> 1,4-dimethyl-2,5,7-trithiabicyclo-1,3,5-trithiane and dibenzylsulfide.<sup>23</sup> In solutions of  $\text{Hg}_2(\text{AsF}_6)_2$  in liquid  $\text{SO}_2$  one obtains 1 : 1 adducts with  $(\text{C}_6\text{H}_5)_3\text{PS}$  or  $(p\text{-F-C}_6\text{H}_4)_2\text{PS}$ ,<sup>38</sup> which contain Hg-Hg-S bonds.

## DIMERCURY(I)-SELENIUM COMPOUNDS

Diphenylselenide does not form adducts with dimercury(II) salts; but reactions with dimercury(I) salts lead to stable adducts.<sup>21</sup> The x-ray structure of tetrakis(diphenylselenium)dimercury(I) diperchlorate<sup>21</sup> is shown in Figure 5. This adduct is polymorphic with two modifications (yellow and red)<sup>24</sup> with different Hg-Se distances and different Se-Hg-Hg angles (see Figure 6). It is possible to synthesize a 1 : 1 adduct between  $(\text{C}_6\text{H}_5)_3\text{PSe}$  and  $\text{Hg}_2(\text{AsF}_6)_2$  in liquid  $\text{SO}_2$  which also contains Hg-Hg-Se bonds.<sup>38</sup> Diphenyldiselenide also forms stable 1 : 1 adducts with  $\text{Hg}_2(\text{NO}_3)_2$  and  $\text{Hg}_2(\text{ClO}_4)_2$ .<sup>49</sup>

## DIMERCURY(I)-TIN(II) COMPOUNDS

The lone pair of electrons on tin in the oxidation state 2+ allows the addition of the  $\text{Hg}_2^{2+}$  ion without splitting the Hg-Hg bond.<sup>46</sup> The following compound



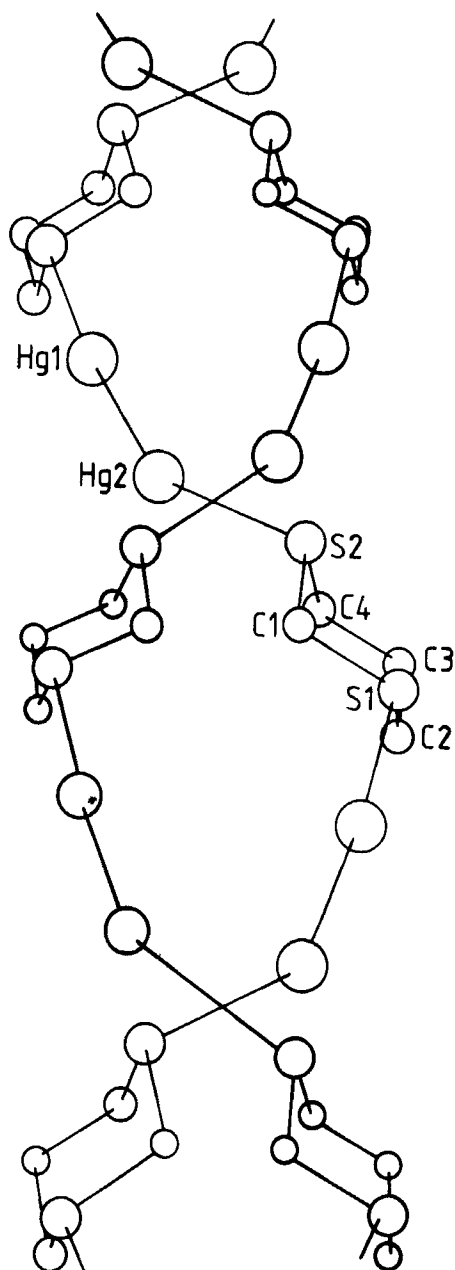


FIGURE 4 The helixlike packing of the  $[(C_4H_8S_2)-Hg-Hg-]$  chains in the structure of the dimercury(II)-sulfur compound  $\frac{1}{2}[Hg_2(1,3-dithiane)](NO_3)_2$ .

TABLE III  
Structural data of dimercury(I)-sulfur compounds

Compound	$d(\text{Hg-Hg})$ , pm	$d(\text{Hg-S})$ , pm	$\angle \text{Hg-Hg-S}$	Remarks	Reference
$\text{Hg}_2(1,3\text{-dithiane})(\text{NO}_3)_2$	252.69(14)	249.15(60)	174.05°	Chain structure	18

TABLE IV  
Structural data of dimercury(I)-selenium compounds

Compound	$d(\text{Hg-Hg})$ , pm	$d(\text{Hg-Se})$ , pm	$\angle \text{Hg-Hg-Se}$	Remarks	Reference
$\text{Hg}_2((\text{C}_6\text{H}_5)_2\text{Se})_4(\text{ClO}_4)_2$					
(a) Red modification	255.3(1)	265.3(2); 291.9(2)	152°; 104.4°	Group structure	24
(b) Yellow modification	255.8(1)	270.1(2); 280.2(2)	141°; 116.4°	Group structure	21



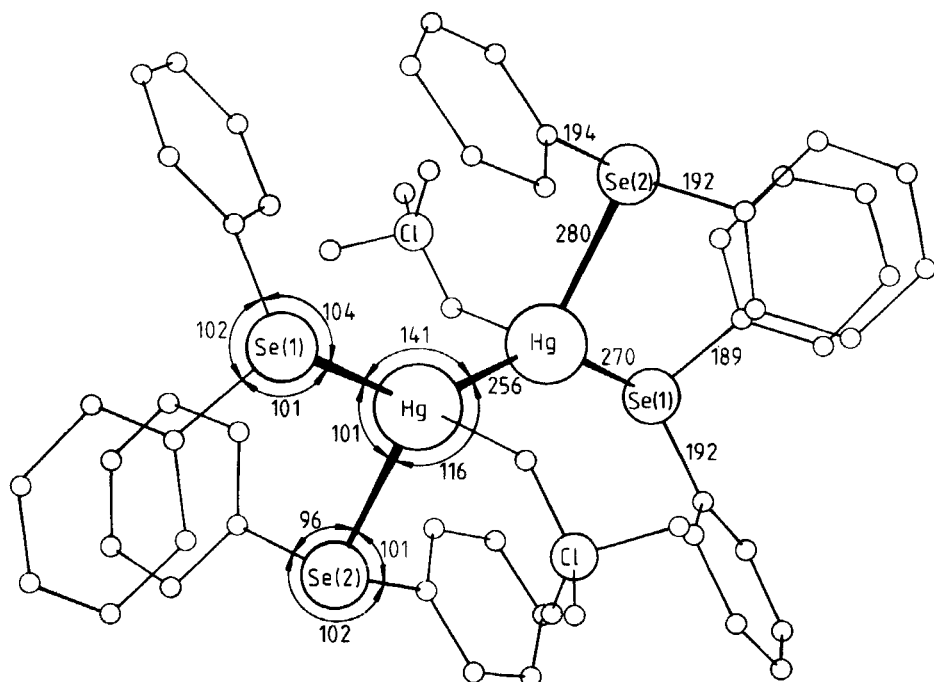
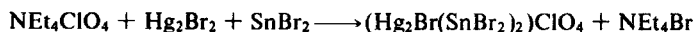


FIGURE 5 Atomic distances and bonding angles of the *yellow* modification of the dimercury(I)-selenium compound  $\text{Hg}_2[(\text{C}_6\text{H}_5)_2\text{Se}]_4(\text{ClO}_4)_2$ .

precipitates in molten  $\text{HgBr}_2$  at  $250^\circ\text{C}$  during the reaction



but it is impossible to isolate the orange precipitate without decomposition. By mass spectrometry  $\text{Hg}_2\text{Sn}_2\text{Br}^+$  and  $\text{Hg}_2\text{Sn}_2^+$  have been identified.<sup>46,57</sup>

## AROMATIC DIMERCURY(I) COMPLEXES

By using  $\text{Hg}_2(\text{AsF}_6)_2$  or  $\text{Hg}_2^{2+}$  salts a variety of aromatic compounds form  $\pi$  complexes in liquid  $\text{SO}_2$  which contain 1 mol of the aromatic compound.  $\text{Hg}_2(\text{PF}_6)_2$  forms 1:2 adducts with several aromatic compounds.<sup>53-55</sup> The adducts with carbazole, dibenzofuran, dibenzothiophene are probably  $\pi$  complexes, too.<sup>55</sup>

## SIGNIFICANCE OF THE OBSERVATIONS

About 10 years ago the existence of the dimercury(I) compounds described were considered improbable because the disproportionation reaction

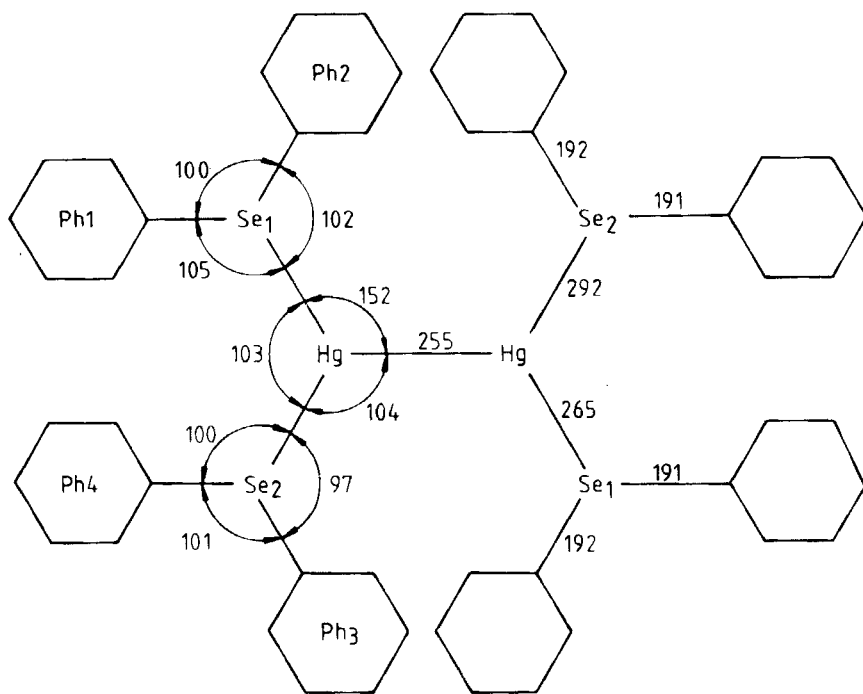


FIGURE 6 Atomic distances and bonding angles of the *red* modification of the dimercury(I)-selenium compound  $\text{Hg}_2[(\text{C}_6\text{H}_5)_2\text{Se}]_4(\text{ClO}_4)_2$ .

seemed to be preferred. Systematic weakening of the donor ability of the ligands in the addition compounds leads to preservation of the metal-metal bond, which is normally weakened by the population of antibonding molecular orbitals. Therefore, the research work described extends the knowledge of metal-metal bonds with  $\sigma$  character; the  $\text{Hg}_2^{2+}$  ion represents a typical example of this type of chemical bonding.

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