[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MINNESOTA]

Coördination Compounds of Mercury. I

BY THOMAS D. O'BRIEN

Mercury exhibits a coördination number of 3 in such groups as $HgCl_3^-$ and a coördination number of 4 in $[Hg(CN)_4]^{-2}$ and $[HgCl_4]^{-2}$. Whereas this same type of ion exists for zinc and cadmium, the latter two elements also exhibit a coördination number of 6. The present study was undertaken to attempt to determine whether mercury also has a stable coördination number of 6.

There are several reports[1] of compound formation between ethylenediamine (en = ethylenediamine) and mercuric chloride, but the results are generally qualitative and usually contradictory. Sinha and Ray[2] report the preparation of $Hg\,py_6(ClO_4)_2$ in which the mercury seems to be 6-coördinate.

Experimental

The ethylenediamine was dehydrated according to the method of Putnam and Kobe[3] and the fraction boiling at 117° collected.

en $(HgCl_2)_2$.—Ten milliliters of a solution containing 3.0 g. (0.05 mole) of ethylenediamine was slowly added with stirring to 200 ml. of a solution containing 27.16 g. (0.1 mole) of mercuric chloride. After standing for two hours the precipitate was filtered and washed with water. The precipitate was then treated with a solution containing 0.2 mole of hydrochloric acid and allowed to stand, with intermittent stirring, for one hour. The very small amount of undissolved residue was filtered and to the clear filtrate was added a solution containing 0.1 mole of ethylenediamine. After standing two hours the precipitate was filtered and the above procedure repeated. The final precipitate was washed with successive portions of water, methanol, acetone and ether and then dried at 100° for two minutes. Prolonged heating at 100° causes decomposition.

Anal. Calcd. for en $(HgCl_2)_2$.: Hg, 66.5; Cl, 23.5. Found: Hg, 66.0; Cl, 23.3.

en $HgCl_2$.—Same procedure followed as described above except a 1:1 molar ratio of base to salt used.

Anal. Calcd. for en $HgCl_2$: Hg, 60.5; Cl, 21.4. Found: Hg, 60.2; Cl, 21.4.

The white precipitate of en $HgCl_2$ was dissolved in aqueous ethylenediamine and the solution was allowed to evaporate slowly at room temperature. The crystals that formed were washed with ether and dried to constant weight at 100°.

Anal. Calcd.: Cl, 21.4. Found: Cl, 21.3.

$Hg\,en_2\,SO_4$ and $[Hg\,en_2\,(H_2O)_2]SO_4$.—Mercuric sulfate was dissolved in excess ethylenediamine and the solution was allowed to evaporate slowly in a covered Petri dish. The large crystals that formed were removed, washed once with anhydrous ether and blotted well between layers of filter paper.

Anal. Calcd. $[Hg\,en_2\,(H_2O)_2]SO_4$: Hg, 44.3; SO_4, 21.2. Found: Hg, 44.5; SO_4, 21.3.

The above compound is efflorescent, slowly losing water to the atmosphere at room temperature. When heated at 100° to constant weight (ten to twelve hours) or when dried over concentrated sulfuric acid the theoretical amount of water (7.98%) is lost, and stable $[Hg\,en_2]SO_4$ results. Prolonged heating of this compound causes a slow decomposition.

Anal. Calcd. $Hg\,en_2\,SO_4$: Hg, 48.2; SO_4, 23.0. Found: Hg, 48.2; SO_4, 23.3.

$(en\,2H)_2HgCl_6$.—Some en $HgCl_2$ was dissolved in the smallest volume of *N* hydrochloric acid solution. To the clear solution was added an equal volume of concentrated hydrochloric acid. The crystals which formed were filtered and then redissolved in the smallest volume of water. Concentrated hydrochloric acid was again added and the crystals which formed were again filtered, redissolved and reprecipitated. After the final filtration the precipitate was washed with methanol, then acetone, and finally ether, then dried in an oven for three minutes at 100°. Longer drying causes no decomposition.

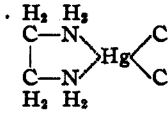
Anal. Calcd. $(en\,2H)_2HgCl_6$: Hg, 37.3; Cl, 39.6; N, 10.42. Found: Hg, 37.2; Cl, 39.6; N, 10.44.

Cryoscopic Measurements.—The conventional freezing point lowering apparatus was used with a Beckman thermometer. When 0.238 g. of $(en\,2H)_2HgCl_6$ was dissolved in 46.2 g. of water a freezing point lowering of 0.121° was observed. When 0.416 g. of the salt was dissolved in 45.6 g. of water a freezing point depression of 0.210° was observed.

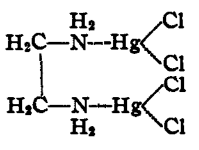
Refractive Index.—To 100.00 cc. of a 0.1 *M* solution of mercuric chloride there was added 0.90 g. (0.015 mole) of ethylenediamine. The solution was shaken at intervals while digesting for one hour. A small portion of this was filtered and the refractive index of the clear filtrate determined on a Bausch and Lomb refractometer. The above procedure was repeated with separate solutions using increasing amounts of ethylenediamine. The refractive index values of portions of the mixtures were determined after standing for twenty-four hours, and five days, with no change in value. All values are averages of at least six different readings.

Discussion of Results

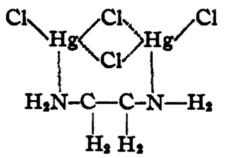
Results of the present study show that both en $HgCl_2$ (I) and en $(HgCl_2)_2$ (II) exist. A possible structure of (I) is shown in which the mercury is 4-coördinate. Two immediately apparent possible structures for (II) are:



(I)



and



(IIa) (IIb)

The mercury has a coördination number of three, in IIa and the mercury is 4-coördinate in IIb, the chloride bridges being analogous to those in the polymeric halides of aluminum and gold.

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(1) (a) Schering, German Patent 12,095 (1901); (b) Siemssen, *Chem. Ztg.*, **36**, 214 (1912); (c) Ray and Dhar, *Trans. Chem. Soc.*, **103**, 3 (1913); (d) Tranke and Loewe, *Ber.*, **47**, 1908 (1914).

(2) Sinha and Ray, *J. Indian Chem. Soc.*, **20**, 32 (1943).

(3) Putnam and Kobe, *Trans. Electrochem. Soc.*, **74**, 610 (1938).

Both (I) and (II) are soluble in an excess of ethylenediamine. All attempts to isolate the soluble complex failed, because any solid substance separated from the solution evolved ethylenediamine to give (I). With the analogous sulfate, however, crystalline bis(aquo)bis(ethylenediamine)mercury(II) sulfate was isolated. This compound decomposed slowly at room temperature, and rapidly at 100°, to give the stable Hg en_2 SO_4.

The simple possibilities for the soluble ethylenediamine mercury chloride salt are (1) [Hg en_2 Cl_2,] (2) [Hg en_2 $(H_2O)_2$]Cl_2, and (3) [Hg en_3]Cl_2 (III), with the last one being favored because of the break in the refractive index curve (Fig. 1) at a 3:1 ratio of ethylenediamine to mercuric chloride. The break at the 1:2 ratio probably corresponds to the complete formation of (I). As more ethylenediamine is added it reacts completely with insoluble (I) to form equally insoluble (II), causing no change in the refractive index, which is the value for the pure solvent (for water, n_{28} 1.3321). The refractive index of the corresponding sulfate could not be determined because of the formation of insoluble basic salts when mercuric sulfate is put in water.

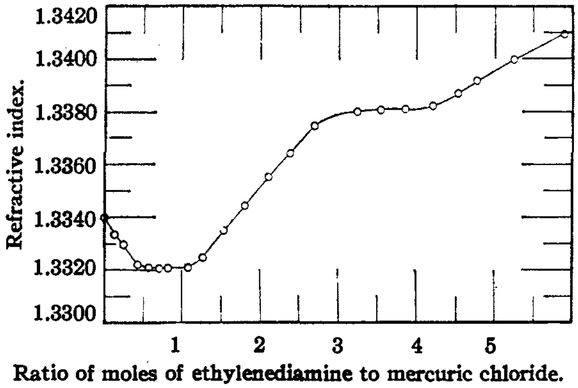

Fig. 1.—Change of refractive index of solution of ethylenediamine and mercuric chloride as concentration of ethylenediamine is increased.

Treatment of (I), (II) or (III) with an excess of concentrated hydrochloric acid produces a white crystalline substance, only slightly soluble in an excess of hydrochloric acid but easily soluble in water. The formula (en $2H)_2[HgCl_6]$ (IV) is assigned to the compound in accordance with the analogous copper salt.[4] Cryoscopic measurements indicate that when dissolved in water, (IV) completely dissociates into 2(en 2H+), 4 Cl^- and $HgCl_2$ (only very slightly dissociated). Using 1.86 as the freezing point constant of water, the two observed lowerings of 0.121° and 0.120° correspond to 6.8 and 6.7 particles, respectively, per mole of salt.

Any highly soluble chloride will cause the precipitation of (IV). Saturated solutions of copper, lithium, and cadmium chlorides when added to an aqueous solution of (IV) cause precipitation of the bis(ethylenediamine)hexachloromercury salt and not the metal hexachloromercury salt.

That the mercury to chloride bonds are more ionic than covalent is further supported by the non-availability of possible bonding orbitals for six coördination. Kimball[5] gives the following possibilities: d^2sp^3, d^4sp, d^5p, d^3p^3, d^3sp^2, d^5s and d^4p^2. As the 5d orbitals in mercury are filled, and as it is extremely doubtful if the 6d orbitals are available for covalent bonding, it appears as if the Hg–Cl bonds must be largely ionic in character.

Summary

1. The existence of Hg en Cl_2 and en$(HgCl_3)_2$ has been demonstrated.

2. The results indicate that mercury probably has a coördination number of 6 in the compound (en $2H)_2[HgCl_6]$ and that the [Hg en_2 $(H_2O)_2]^{+2}$, ion probably exists in solution, wherein the mercury is also 6-coördinate.

3. The new compounds Hg en_2 SO_4 and Hg en_2 $(H_2O)_2SO_4$ have been prepared.

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[4] Jonassen, Crumpler and O'Brien, THIS JOURNAL, 67, 1709 (1945).

[5] Kimball, *J. Chem. Phys.*, 8, 188 (1940).