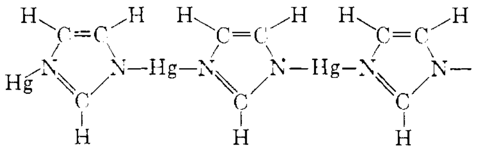

with one positive charge per polymer unit. A similar substance $Hg(C_3H_3N_2)Cl$ has been reported.[15] The structure proposed above is similar to that which occurs in $Hg(NH_2)Br$[16] and $Hg(NH_2)Cl$.[17]

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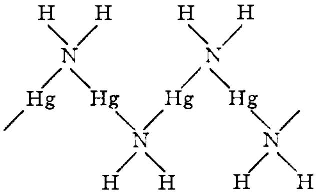
[15] K. Böttcher, *Chem. Zentralblatt*, **102**, II, 2757 (1931).

[16] L. Nijssen and W. N. Lipscomb, *Acta Cryst.*, **5**, 604 (1952).

[17] W. N. Lipscomb, *ibid.*, **4**, 266 (1951).



Acknowledgments.—Mr. Tetsuo Yamane designed and developed the cell and potentiometric techniques which we have used. We have profited also from his advice and criticism regarding other features of this research. We are grateful to the AEC for support of this work via the contract AT-(11-1)-188.

PASADENA, CALIFORNIA

[CONTRIBUTION NO. 2522 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA]

Complexes of Mercury(I) with Polyphosphate and Dicarboxylate Anions and Mercury (II) Pyrophosphate Complexes[1]

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It has been discovered that mercurous mercury forms complexes with pyrophosphate, tripolyphosphate, oxalate, α-dimethylmalonate and succinate. These complexes are stable toward disproportionation to mercury(II) complexes and mercury. If L^{-q} is the anion, the principal complexes are $Hg_2L_2^{-2q+2}$ and $Hg_2L(OH)^{-q+1}$. The formation constants determined from the potential of a mercury–mercurous electrode in ligand solutions are: $Hg_2(P_2O_7)_2^{-6}$, $(2.4 \pm 0.6)10^{12}$ M^{-2}; $Hg_2(OH)P_2O_7^{-3}$, $(4.4 \pm 0.6)10^{15}$ M^{-2}; $Hg_2(P_3O_{10})_2^{-8}$, $(1.7 \pm 0.3)10^{11}$; $Hg_2(OH)P_3O_{10}^{-4}$, $(1.0 \pm 0.2)10^{15}$; $Hg_2(C_2O_4)_2^{-2}$, $(9.5 \pm 0.2)10^{6}$; $Hg_2(OH)C_2O_4^{-1}$, $(1.1 \pm 0.2)10^{13}$; $Hg_2[(CH_3)_2C(CO_2)_2]_2^{-2}$, $(3.3 \pm 0.6)10^{7}$; $Hg_2(OH)[(CH_3)_2C(CO_2)_2]^{-1}$, $(3.8 \pm 0.5)10^{13}$; $Hg_2[(CH_2)_2(CO_2)_2]_2^{-2}$, $(1.9 \pm 0.3)10^{7}$; $Hg_2(OH)[(CH_2)_2(CO_2)_2]^{-1}$, $(2.8 \pm 0.6)10^{13}$. (The ionic strength was 0.75 M ($NaNO_3$), except for oxalate and succinate, where it was 2.5 M ($NaNO_3$).) The mercurous compounds have a characteristic ultraviolet spectrum. Theory and experiment agree that mercurous complexes of ligands (such as NH_3 and CN^-) which form strong covalent bonds to mercury are unstable toward disproportionation to give mercuric complexes but "ionic" chelating ligands can form stable mercurous complexes. The mercury(II) pyrophosphate complex was studied from the potential of a Pt electrode in Hg_2^{I}, Hg^{II}, pyrophosphate solutions at pH 7–10. The principal species is $Hg(OH)(P_2O_7)^{-3}$, with a formation constant of $(2.8 \pm 0.6)10^{17}$ M^{-2}.

The equilibrium constant for the formation of mercurous ion from elementary mercury and mercuric ion is 130 in 0.5 M $NaClO_4$.[2]

$$Hg + Hg^{++} = Hg_2^{++}, K = \frac{(Hg_2^{++})}{(Hg^{++})} = 130 \quad (1)$$

The equilibrium is readily reversible. When a complexing ligand is added to a mercurous solution, the usual reaction that occurs is disproportionation of the mercurous ion to give elementary mercury and a complexed mercuric ion. This occurs, for example, with the complexing ligands, CN^- and NH_3. It is due to the relatively greater stability of the mercuric complexes. The same situation occurs for many insoluble compounds. Thus, mercurous ion is unstable in basic solutions and in the presence of sulfide ion. Compounds such as "mercurous sulfide" or "mercurous oxide" reported in the past have been shown to be a mixture of mercury and the corresponding mercuric compound.[3,4]

The general impression conveyed by textbooks and by the chemical literature is that there are no known stable complexes of mercurous ion. Sillén and co-workers have suggested, on the basis of potentiometric evidence, that there are weak complexes of Hg_2^{++} formed by nitrate, sulfate and perchlorate anions, with formation constants of: 2.5 M^{-1} ($Hg_2NO_3^+$), 0.5 M^{-2} ($Hg_2(NO_3)_2$), 20 M^{-1} (Hg_2SO_4), 250 M^{-2} ($Hg_2(SO_4)_2^{-2}$) and 0.9 M^{-1} ($Hg_2ClO_4^+$).[2,5] This presumably is mainly ion-pair association. It is also possible that the assumption of constant activity coefficients at constant ionic strength is not sufficiently reliable to enable one to identify such weak complexes with certainty by potentiometric experiments.

However some time ago, Stromeyer[6] and then Brand[7] reported that when sodium pyrophosphate solution is added to a mercurous solution, a white precipitate forms and then redissolves in excess of the reagent, which suggests the formation of a strong, stable complex.

We have confirmed and extended these observations and have now found that mercurous ion forms stable complexes with pyrophosphate (Py^{-4}), tripolyphosphate (Tp^{-5}), oxalate (Ox^{-2}), α-di-

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[1] Presented at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

[2] S. Hietanen and L. G. Sillén, *Arkiv Kemi*, **10**, 103 (1956).

[3] R. Fricke and P. Ackermann, *Z. anorg. Chem.*, **211**, 233 (1933).

[4] W. N. Lipscomb, THIS JOURNAL, **73**, 1015 (1951).

[5] G. Infeldt and L. G. Sillén, *Svensk kem. Tidskr.*, **58**, 104 (1946).

[6] F. Stromeyer, *Schweigger's Journal*, **58**, 130 (1830); as reported in J. W. Mellor "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Longman, Greens & Co., London, 1923, p. 1003.

[7] Brand, *Z. anal. Chem.*, **28**, 592 (1889).

methylmalonate (Ma^{-2}) and succinate (Su^{-2}) anions. For all these cases, the presence of Hg(I) in the solutions can be shown by the quantitative precipitation of Hg_2Cl_2 upon addition of NaCl solution and also by the characteristic ultraviolet spectrum of mercurous (see later). The Hg(I) complexes can be formed by mixing Hg(II)-ligand solutions with elementary mercury, showing that the Hg(I) complexes are stable to disproportionation.[8]

Experimental

Materials.—Mercuric nitrate was prepared by dissolving HgO in HNO_3 and was standardized by titration against KCNS with ferric ion as indicator.[9]

Mercurous nitrate solutions were prepared by shaking together for one hour Hg, $Hg_2(NO_3)_2$ and HNO_3. The reagent was standardized gravimetrically by precipitation of the chloride and also by the brom phenol blue method.[10]

J. T. Baker reagent grade $Na_4P_2O_6 \cdot 10H_2O$ was used. Sodium tripolyphosphate, $Na_5P_3O_{10} \cdot 6H_2O$, was obtained from technical grade sodium tripolyphosphate as described by Watters, *et al.*[11]

Allied Chemical & Dye Corporation $K_2C_2O_4 \cdot H_2O$ was used as a source of potassium oxalate. Potassium malonate was prepared from the technical malonic acid as described by Bailar.[12] Dimethylmalonic acid from K. & K. (Kuthe and Kuthe) Laboratories was used as supplied. Matheson reagent grade sodium succinate was recrystallized twice from water.

Potentiometric Method.—The cell was made up with a Beckman saturated calomel electrode, a J-type mercury electrode in which the mercury surface could be renewed by overflow and a salt bridge (0.75 *M* $NaNO_3$). There were provisions for titrating in reagents and for maintaining a nitrogen atmosphere. A magnetic stirrer was used. The cell was in a water-bath at 27.4 ± 0.1°. The e.m.f.'s were measured with a Leeds and Northrup type K-2 potentiometer and a 0.01 μamp. per mm. galvanometer; *p*H measurements were made with a Beckman GS *p*H Meter and a Beckman General Purpose Glass Electrode. In all cases, a stable potential was established almost instantly after addition of a reagent.

All optical measurements were made with a Cary Model 11 Spectrophotometer at room temperature. A hydrogen lamp and quartz cells with a path length of 1.00 cm. were used.

The potentiometric measurements were made at 27.4 ± 0.1°, and in most cases at an ionic strength of 0.75 *M* adjusted with $NaNO_3$. Due to low solubilities of mercurous oxalate and mercurous succinate salts, an ionic strength of 2.5 *M*, adjusted with $NaNO_3$, was used in both cases.

Results

Analysis.—The experimental data indicate the necessity of considering the equilibria

$$Hg_2^{++} + 2L^{-q} = Hg_2L_2^{-2q+2} \qquad K_2 \qquad (2)$$

$$Hg_2^{++} + OH^- + L^- = Hg_2(OH)L^{-q+1} \qquad K_1 \qquad (3)$$

The potential of the mercury electrode with respect to the reference electrode is given by

$$E = E^0 + 29.7 \log (Hg_2^{++}) \qquad (4)$$

with E^0 *vs.* s.c.e. = 539 mv. at 27.4°.

From stoichiometric considerations we obtain for the total mercurous ion concentration[13]

$$(\Sigma Hg_2^I) = (Hg_2^{++}) + (Hg_2(OH)L^{-q+1}) + (Hg_2L_2^{-2q+2}) \qquad (5)$$

and with the equations for the formation constants, the relation that results is

$$\frac{(\Sigma Hg_2^I)}{(Hg_2^{++})} - 1 = K_1(OH^-)(L^{-q}) + K_2(L^{-q})^2 \qquad (6)$$

$$\left(\frac{(\Sigma Hg_2^I)}{(Hg_2^{++})} - 1\right) \Big/ (L^{-q}) = K_1(OH^-) + K_2(L^{-q}) \qquad (7)$$

The total mercurous concentration, (ΣHg_2^1), is of course known. The free mercurous ion concentration, (Hg_2^{++}), is calculated from the observed potential by equation 4. Usually, the ligand concentration was much larger than the total mercurous concentration; where necessary, corrections for the amount of ligand complexed were made by a successive approximations procedure. Corrections for the hydrogen ion equilibria of the ligands were also made as discussed below.

Since the determination of formation constants involves the concentrations of unprotonated ligands as they exist in solution, effective *pK*'s were measured by *p*H titration curves for the media used in the complexing experiments. The results are displayed in Table I. Since the alkali metals form complexes with pyrophosphate and tripolyphosphate ions,[14] the values given in Table I differ from those determined in media where the supporting electrolyte contains tetraalkylammonium cations. The results in Table I, of course, are appropriate values for the analysis of our complexing data.

TABLE I

pK'S OF LIGANDS STUDIED

Pyrophosphate	$pK_4 = 8.00^a$
	$pK_3 = 5.68^a$
Tripolyphosphate	$pK_5 = 7.58^b$
	$pK_4 = 5.29^b$

	Oxalate[c]	α-Dimethylmalonate	Succinate
pK_2	3.66	5.48	5.20
pK_1	1.62	2.88	3.85

[a] $pK_4 = 8.93$ and $pK_3 = 6.13$ for $\mu = 1.0$ *M* $(CH_3)_4NCl$.[14]
[b] $pK_5 = 8.81$ and $pK_4 = 5.83$ for $\mu = 1.0$ *M* $(CH_3)_4NCl$.[11]
[c] $\mu = 2.5$ *M* $NaNO_3$; all other data for 0.75 *M* $NaNO_3$.

Mercury(I) and Mercury(II) Pyrophosphate Complexes.—Figure 1 is a plot of the function on the left-hand side of equation 7 *vs.* molar concentration of $P_2O_7^{-4}$ at a given *p*H. (The concentration of $P_2O_7^{-4}$ was calculated from the total pyrophosphate concentration, using the acid constants of Table I and making the necessary small corrections for the amount complexed.) Equation 7 predicts an intercept of $K_1(OH^-)$ and a slope of K_2. At low *p*H (<9), the intercepts increase with increasing *p*H and the slopes are constant, as expected from equation 7. However at high *p*H and low pyrophosphate concentrations, the plots curve upwards as the Py^{-4} concentration decreases. We believe that this behavior is due to the disproportionation of mercurous salts to mercuric oxide and mercury

$$Hg_2^I \longrightarrow HgO + Hg$$

The standard potential of the Hg,HgO electrode is[15]

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[8] A preliminary announcement of these results has appeared: THIS JOURNAL, **81**, 4438 (1959).

[9] I. M. Kolthoff and J. J. Lingane, *ibid.*, **57**, 2377 (1935).

[10] W. Pugh, *J. Chem. Soc.*, 1824 (1937).

[11] J. Watters, E. D. Loughran and S. M. Lambert, THIS JOURNAL, **78**, 4855 (1956).

[12] W. B. Schaap, H. A. Laitinen and J. C. Bailar, *ibid.*, **76**, 5868 (1954).

[13] We should also include $Hg_2(OH)^+$ with a formation constant of 10^9 M^{-1} (L. G. Sillén, W. Forsling and S. Hietanen, *Acta Chem. Scand.*, **6**, 901 (1952)) but its concentration is negligible compared to $Hg_2(OH)L$ and Hg_2L_2.

[14] J. I. Watters, S. M. Lambert and E. D. Loughran, THIS JOURNAL, **79**, 3651, 4262 (1957).

[15] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952.

$$Hg + 2H_2O = (HgO)_c + 2H^+ + 2e^-, E^0 = 931 \text{ mv.}$$

$$E\,(vs.\ \text{s.c.e.}) = 690 + 59.5 \log (H^+) \quad (8)$$

The solubility of HgO is $2.25 \cdot 10^{-4}$ M,[15] so in solutions where the mercury concentration is less than $2.25 \cdot 10^{-4}$ M, mercury will be present in solution as HgO if the potential is more positive than that given by the equation

$$E = 690 + 29.75 \log \frac{(\Sigma Hg)}{2.25 \cdot 10^{-4}} + 59.5 \log (H^+) \quad (9)$$

The data in Fig. 1 which do not conform to equation 7 were all for potentials either more positive or only slightly less positive than calculated from equation 9. However, at high pyrophosphate concentrations at pH 9.55, the expected behavior from equation 7 with reasonable values of K_1 and K_2 is observed.

In summary of this point, the situation at high pH appears to be that at low pyrophosphate concentration, there is disproportionation according to the equation

$$Hg_2^I(OH)Py^{-3} + OH^- = HgO + Hg + Py^{-4} + H_2O \quad (10)$$

and the observed potential is close to that of the Hg,HgO electrode. At higher Py concentration, reaction 10 proceeds to the left and the mercurous hydroxy pyrophosphate anion is present. It is remarkable that the mercuric oxide formed at low Py is not lost by adsorption on the walls and that reaction 10 is quantitatively reversed at high Py.

The results obtained for the slopes and intercepts, and hence for K_1 and K_2 of equation 7, are given in Table II. For reasons to be explained shortly, we now refer to K_1' rather than K_1.

TABLE II

SLOPE (K_2) AND INTERCEPT ($K_1'/(OH^-)$) FROM FIG. 1

pH	$K_1' \cdot 10^{-15}$ (M^{-2})	$K_2 \cdot 10^{-12}$ (M^{-2})
7.12		2.70
7.45		2.84
8.34	5.95	2.10
8.39	5.90	1.95
8.83	7.20	2.80
8.90	6.90	(2.40)[a]
9.55	15.2	3.70[b]
Av.	$(6.5 \pm 0.7)10^{15}$	$(2.4 \pm 0.6)10^{12}$

[a] Only one pyrophosphate concentration, slope assumed.
[b] Slope and intercept from high pyrophosphate concentration only; results not included in averaging.

It is worthwhile to report explicitly that the Nernst law behavior as regards Hg_2^{++} concentration was observed both at high and low pH (for points where the potentials showed that HgO was not present). These data are shown in Table III.

TABLE III

VALIDITY OF THE NERNST LAW

(Σ Py) = 0.020 F

	pH = 7.12		pH = 8.90	
(Σ Hg_2^I)$\cdot 10^5$ F	E (obsd.), mv.	E (calcd.), mv.	E (obsd.), mv.	E (calcd.), mv.
0.951	167.8		106.0	
1.89	176.5	176.7	115.2	114.9
3.84	186.5	185.8	124.6	124.0
5.75	192.3[a]	191.2	129.9[a]	129.2
9.35	198.8[a]	197.4	137.0[a]	135.5

[a] Corrections were made due to a slight change in pH.

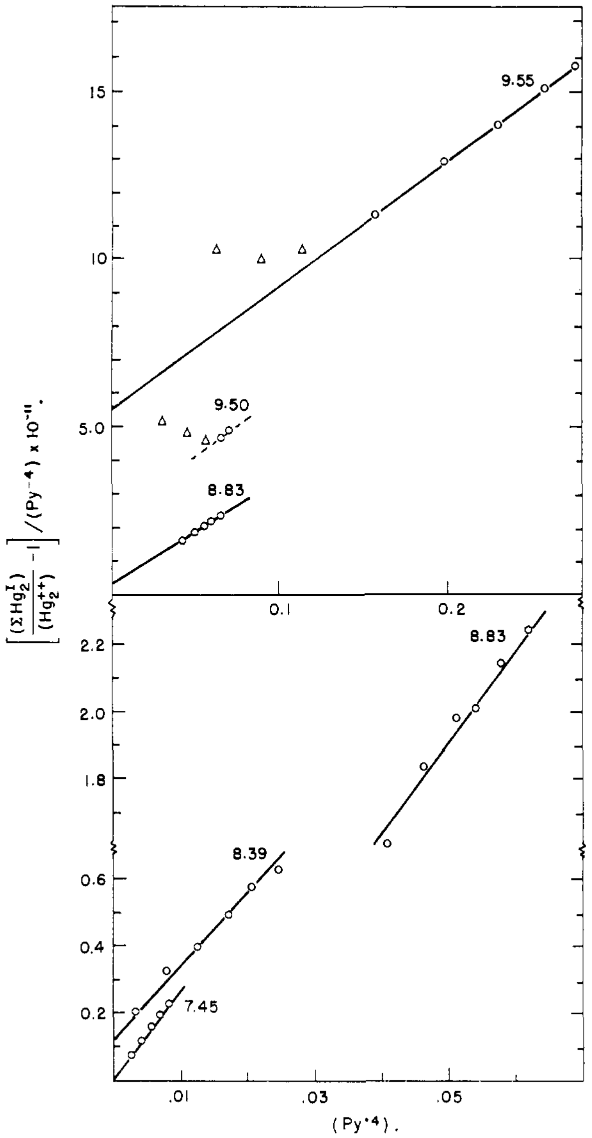


Fig. 1.—Plot of equation 7 at different pH's for the determination of K_1 = intercept/(OH^-) and K_2 = slope; (ΣHg_2^{++}) ≈ $1 \times 10^{-5} - 1 \times 10^{-4}$ F; (ΣPy) ≈ 0.004–0.3 F; △ refers to the points obtained from the potentials either more positive or only slightly less positive than that of an Hg, HgO electrode. Note the change in horizontal scale for the upper half of the figure.

Mercury(II) pyrophosphate complexes were studied from the potential of a Pt electrode in a Hg_2^{++}, Hg^{++} pyrophosphate solution.

The potential of the mercurous–mercuric couple with respect to the reference electrode is given by

$$E = E^0 + 59.5 \log (Hg^{++})/(Hg_2^{++})^{1/2} \quad (11)$$

with E^0 = 637 mv. (vs. s.c.e.) at 27.4°.

Substituting (Hg_2^{++}) as a function of K_1 and K_2, the equation results

$$\log (Hg^{++}) = \frac{E - E_0}{59.5} + \frac{1}{2}\log (\Sigma Hg_2^I) - \frac{1}{2}\log [K_1(OH^-)(Py^{-4}) + K_2(Py^{-4})^2]$$

The ratio $[(\Sigma Hg^{II})/(Hg^{++})]/(Py)(OH^-)$ gives a fairly constant value at different pH's (Table IV),

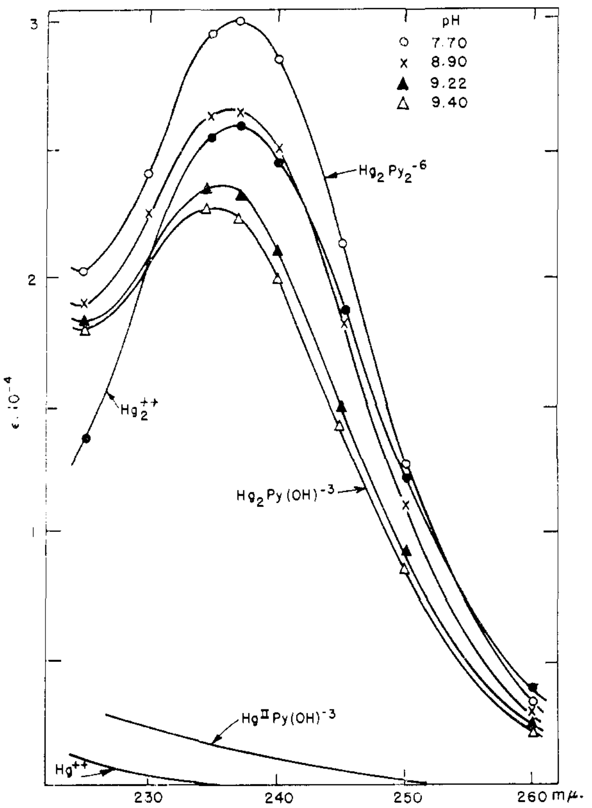


Fig. 2.—Molar absorptivity, $\epsilon = (1/lc) \log (I_0/I)$, of several mercurous solutions. Conditions: $(\Sigma Hg_2{}^I) = 7.50 \times 10^{-5}$ *F*, $(\Sigma Py) = 0.020$ *F*, $\mu = 0.75$ *F* ($NaClO_4$). Using the equilibrium constants in the text, the curve labelled $Hg_2Py_2^{-6}$ at *p*H 7.70 is calculated to contain 90% $Hg_2Py_2^{-6}$ and 10% $Hg_2(OH)Py^{-3}$; the curve labelled $Hg_2(OH)Py^{-3}$ is calculated to contain 71% $Hg_2(OH)Py^{-3}$ and 29% $Hg_2Py_2^{-6}$. In agreement with these constants, the spectrum changes but slightly in the range 6.70–8.00. The curve labelled Hg_2^{++} was a $Hg_2(ClO_4)_2$ solution in 0.1 *M* $HClO_4$ and 0.75 *M* $NaClO_4$. The $Hg^{II}(OH)Py^{-3}$ curve was obtained from a solution $(\Sigma Hg^{II}) = 3.0 \times 10^{-4}$ *F* and $(\Sigma Py) = 0.020$ *F* at *p*H 8.60; the Hg^{++} curve was a $Hg(ClO_4)_2$ solution, 0.5 *M* in $HClO_4$ and $\mu = 0.75$ *M* ($NaClO_4$).

which indicates that the main species in these media is $Hg^{II}(OH)Py^{-3}$ with a formation constant of $K_{II} = 2.8 \times 10^{17}\ M^{-2}$. It is to be noted that the data were taken at *p*H's where the main mercurous species is $Hg_2Py_2^{-6}$, so the uncertainties about K_1 considered below do not affect the evaluation of K_{II}.

TABLE IV

MERCURY(II) PYROPHOSPHATE COMPLEXES

*p*H	(ΣHg^{II}), *F*	(ΣPy), *F*	$\frac{(\Sigma Hg^{II})/(Hg^{++})}{(Py^{-4})(OH^-)}$
7.62	1.0×10^{-4}	5×10^{-3}–3×10^{-2}	3.42×10^{17}
8.00	5×10^{-5}–4×10^{-4}	2×10^{-2}	2.41×10^{17}
8.00	5×10^{-5}–4×10^{-4}	9×10^{-3}	3.37×10^{17}
8.42	2×10^{-4}–2×10^{-3}	5×10^{-3}	2.29×10^{17}
		Av.	$K_{II} = (2.8 \pm 0.6)10^{17}\ M^{-2}$

We may now inquire as to the possibility of the disproportionation reaction

$$Hg_2{}^I(OH)Py^{-3} = Hg^{II}(OH)Py^{-3} + Hg \qquad K_D \qquad (12)$$

From the equilibria

$$Hg^{++} + Hg = Hg_2^{++} \qquad K = 130$$

$$Hg^{II}(OH)Py^{-3} = Hg^{++} + OH^- + Py^{-4} \qquad K = 1/K_{II}$$

$$Hg_2^{++} + OH^- + Py^{-4} = Hg_2{}^I(OH)Py^{-3} \qquad K_1$$

we calculate for equation 12, using for K_1 the value of K_1' of Table II, $K_D = 0.33$. This value is of the order of unity, indicating significant disproportionation of $Hg_2{}^I(OH)Py^{-3}$ to $Hg^{II}(OH)Py^{-3}$. Thus, the solutions used for determining the formation constant of $Hg^I(OH)Py^{-3}$ contained significant quantities of $Hg^{II}(OH)Py^{-3}$. It should be noted that the occurrence of this disproportionation reaction would not affect the functional dependence of the potential on Hg^I, Py and OH^- concentrations in the mercurous experiments. However, equation 7 would now become

$$\frac{\frac{(\Sigma Hg_2{}^I)}{(Hg_2^{++})} - 1}{(Py^{-4})} = K_1(1 + K_D)(OH^-) + K_2(Py^{-4}) \qquad (13)$$

Thus, the constant K' is $K_1(1 + K_D)$.

From the equations

$$K_1' = 6.5 \times 10^{15} = K_1(1 + K_D)$$

$$K_{II} = 2.8 \times 10^{17}$$

$$K_D = \frac{K_{II}}{K_1 \cdot 130}$$

we obtain as corrected values

$$K_D = 0.49$$

$$K_1 = 4.4(\pm 0.6) \times 10^{15}\ M^{-2}$$

However, the possibility remains that our data are quantitatively in error and that the complex we have identified as $Hg_2{}^I(OH)Py^{-3}$ is entirely $Hg^{II}(OH)Py^{-3}$. We believe that this possibility is eliminated by direct observations of the equilibrium of equation 12 by chemical analysis and ultraviolet spectrophotometry.

A Hg(II)-pyrophosphate solution $((\Sigma Hg(II)) = 4.7 \times 10^{-4}$ *F*, $(\Sigma Py) = 0.02$ *F*) at *p*H 9.4 was equilibrated with elementary mercury. The amount of $Hg_2{}^I$ formed was analyzed by taking its characteristic ultraviolet spectrum and also by separating it in the form of Hg_2Cl_2. These analyses gave an average of 3.8×10^{-4} *F* for $(\Sigma Hg_2{}^I)$. Since the ratio $(Hg_2{}^I(OH)Py^{-3})/(Hg_2{}^I(Py)_2{}^{-6}) = 2.34$ at *p*H 9.4 and $(\Sigma Py) = 0.02$ *F*, the K_D from this experiment for equation 12 comes out 0.31 in good agreement with the calculated value from the potential measurements.

As shown in Fig. 2, there is a characteristic ultraviolet spectrum for mercury(I) which is just about the same for Hg_2^{++}, $Hg_2{}^I(Py)_2{}^{-6}$ and $Hg_2{}^I(OH)Py^{-3}$. The change in absorbance with *p*H is just as expected on the basis of the equilibrium constants derived previously, which also tends to confirm the existence of $Hg_2{}^I(OH)Py^{-3}$ (Fig. 3). It should also be mentioned that in the alkaline solutions air oxidation of $Hg_2{}^I(OH)Py^{-3}$ to $Hg^{II}(OH)Py^{-3}$ is rapid and difficult to avoid.

In summary, then, we believe the evidence strongly proves the existence of the complex $Hg_2{}^I(OH)Py^{-3}$, as well as the complexes $Hg_2{}^IPy^{-6}$ and $Hg^{II}(OH)Py^{-3}$. Roughly speaking of the mercurous complexes, $Hg_2Py_2^{-6}$ is the main species at $(\Sigma Py) = 0.02$ *F* for *p*H's between 7 and 8.5; $Hg_2{}^I$-

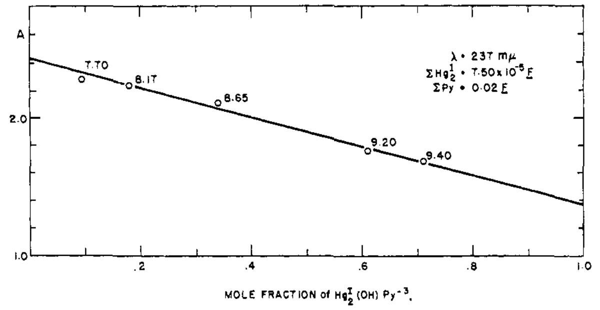


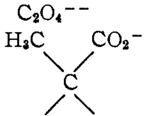
Fig. 3.—Plot of A (absorbance) = log (I_0/I) for λ = 237 mμ for mercurous pyrophosphate solutions at different pH's, *vs.* mole fraction of $Hg_2(OH)Py^{-3}$ calculated from the equilibrium constants in the text. This graph shows that the change in A with pH is consistent with K_1 and K_2 determined potentiometrically. The pH is given next to the points.

$(OH)Py^{-3}$ is predominant in the pH range 9.3 to 10. In the strongly alkaline solutions, $Hg(OH)_2$ forms at low Py concentrations. There is no evidence for soluble complexes containing HPy^{-3} species; at pH's less than 6.5, however, insoluble pyrophosphate salts precipitate. A precipitate also forms in the pH range 7–9.5 if the Hg_2^I concentration is raised above 10^{-3}. (However, in 6 F $K_4P_2O_7$ solution, the Hg_2^I concentration could be raised to about 0.07 M before precipitation occurred.)

Mercury(I) Complexes of Tripolyphosphate and Dicarboxylate Anions.—Fig. 4 shows the plots of equation 7 for the anions tripolyphosphate (Tp^{-5}), oxalate (Ox^{-2}), α-dimethylmalonate (Ma^{-2}) and succinate (Su^{-2}). The plots all indicate formation of $Hg_2^IL_2$ and $Hg_2^I(OH)L$ complexes. Especially for the dicarboxylic acids, the complexes are less stable than the pyrophosphate complexes and rather high concentrations of ligand are needed to keep the potential below that for the formation of mercuric oxide. The values of K_1 and K_2 are given in Table V.

TABLE V

COMPLEX FORMATION CONSTANTS

Ligand	$Hg_2L_2^{-2q+2}$ $K_2(M^{-2})$	$Hg_2(OH)L^{-q+1}$ $K_1(M^{-2})$
$P_2O_7^{-4}$	$(2.4 \pm 0.6)10^{12}$	$(4.4 \pm 0.6)10^{15}$
$P_3O_{10}^{-5}$	$(1.7 \pm 0.3)10^{11}$	$(1.0 \pm 0.2)10^{15}$
$C_2O_4^{--}$	$(9.5 \pm 0.2)10^{6}$	$(1.1 \pm 0.2)10^{13}$
	$(3.3 \pm 0.6)10^{7}$	$(3.8 \pm 0.5)10^{13}$
$H_2C—CO_2^-$ | $H_2C—CO_2^-$	$(1.9 \pm 0.3)10^{7}$	$(2.8 \pm 0.6)10^{13}$

In all cases clear solutions were obtained on adding mercurous solution to the ligand solution, indicating no disproportionation and in all cases calomel could be precipitated from these resulting clear solutions. The following quantitative experiment is of interest. A solution at pH 7.0, 0.30 F in sodium α-dimethylmalonate and containing 5.65 × 10^{-4} F Hg(II) was stirred in the presence of elementary mercury for 15 hr. After separation from the mercury pool, the solution was made 1 M in $HClO_4$. It showed the characteristic Hg_2^{++} absorption. The concentrations of Hg_2^{++} (by spectrophotometry and by precipitation of Hg_2Cl_2) and of Hg^{++} (dithizone extraction into $CHCl_3$) obtained were (Hg_2^I) = 4.7 × 10^{-4} and (Hg^{II}) = 0.8 × 10^{-4} F. According to Table V, the ratio of $Hg_2^I(OH)L$ to Hg_2L_2 should be about 3 in this solution. Thus the result clearly shows that the complexes obtained are Hg_2^I complexes and that both $Hg_2Ma_2^{-2}$ and $Hg_2(OH)Ma^{-1}$ exist.

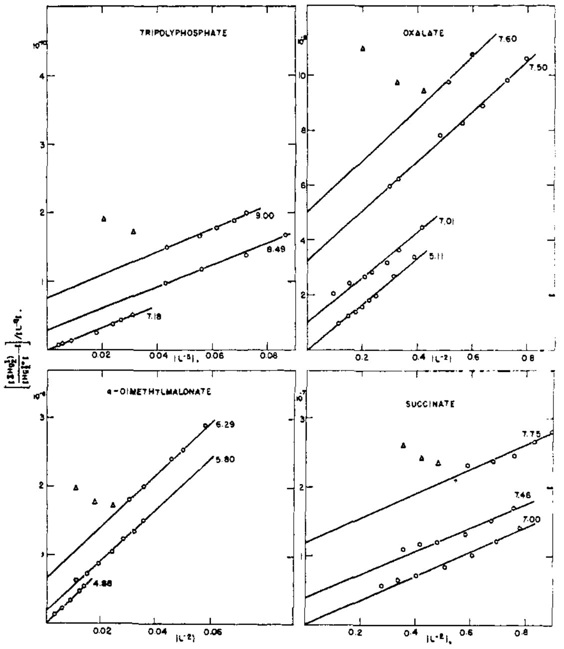


Fig. 4.—Plots of equation 7 for the determination of K_1 and K_2; $(\Sigma Hg_2^I) \approx 5 \times 10^{-6}$–$8 \times 10^{-5}$ F. Only a rather narrow range of Hg_2^{++} concentration could be used as Hg_2L precipitated at higher (Hg_2^I), and at lower (Hg_2^I) the e.m.f.'s ceased to be well reproducible; (ΣTp) ≈ 0.01–0.1 F; (ΣOx) ≈ 0.05–0.7 F; (ΣMa) ≈ 0.01–0.05 F; (ΣSu) ≈ 0.1–0.8 F; Δ refers to the potentials close to that of Hg,HgO electrode. The numbers next to the curves give the pH for the particular set of measurements.

High concentrations of the complexing anions are also necessary to prevent precipitation of insoluble salts.

It should be mentioned that non-reproducible results, potentials that varied with time and the formation of a black precipitate were observed with unsubstituted malonic acid. There is probably mercuration of the reactive α-hydrogens and disproportionation to α-mercuric malonate and mercury. Malonic ester derivatives are known to form mercury derivatives.[16]

Discussion

The values of K_1 and K_2 for all ligands studied are given in Table V. Tripolyphosphate has a negative charge of 5 and can be a tridentate ligand[17] and Hirschfelder–Taylor models indicate that bonding of the metal ion to the two terminal phosphate tetrahedra and to the center tetrahedron as well can occur without strain in either a square planar or an octahedral complex, whereas pyrophosphate has

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[16] See *e.g.*, F. C. Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., New York, N. Y., 1921, p. 152.

[17] A. E. Martell and G. Schwarzenbach, *Helv. Chim. Acta*, **39**, 653 (1956).

a charge of −4 and is bidentate. Tripolyphosphate is usually a much stronger complexer than is pyrophosphate but this order is reversed for the mercurous complexes.

The dicarboxylate complexes are substantially weaker than the pyrophosphate complexes. The six-membered ring of α-dimethylmalonate appears to give slightly stronger complexing than for the 5 and 7 membered rings of oxalate and succinate respectively.

The square root of K_2 may be taken as a rough estimate for the binding of a single L^{-q} by $\mathrm{Hg_2^{++}}$

$$\mathrm{Hg_2^{++}} + \mathrm{L}^{-q} = \mathrm{Hg_2L}^{-q+2} \quad K \simeq K_2^{1/2}$$

Then the ratio $K_1/K_2^{1/2}$ is an estimate of the equilibrium constant for the reaction $\mathrm{Hg_2L}^{-q+2} + \mathrm{OH}^- = \mathrm{Hg_2L(OH)}^{-q+1}$. It comes out fairly constant as can be seen in Table VI.

TABLE VI

VALUES OF $K_1/K_2^{1/2}$

Ligand	$K_1/K_2^{1/2} \times 10^{-9}\ M$
Pyrophosphate	2
Tripolyphosphate	3
Oxalate	4
α-Dimethylmalonate	6
Succinate	6

$$\mathrm{Hg_2^{++}} + \mathrm{OH}^- = \mathrm{Hg_2OH}^+,\ K \simeq 1 \times 10^{9,13}\ 8 \times 10^{-9,18}$$

Values given in the literature for the reaction

$$\mathrm{Hg_2^{++}} + \mathrm{OH}^- = \mathrm{Hg_2OH}^+$$

are included and are of the same order of magnitude as $K_1/K_2^{1/2}$. Thus this very crude argument indicates that the binding of OH^- by $\mathrm{Hg_2L}^{-q+2}$ is approximately constant, independent of the nature of L and of the charge $-q + 2$.

If L is a ligand which can form complexes with both Hg(I) and Hg(II), $\mathrm{Hg_2{}^{I}L}_n$ and $\mathrm{Hg^{II}L}_m$, respectively, we can write the disproportionation equation

$$\mathrm{Hg} + \mathrm{Hg^{II}L}_m = \mathrm{Hg_2{}^{I}L}_n + (m - n)\mathrm{L}$$

What are the structural and electronic characteristics of L which make the mercurous complexes either stable or unstable for disproportionation?

We first recall that $\mathrm{Hg^{++}}$ tends to bind two monodentate ligands strongly in a linear configuration and additional ligands are bound with much weaker affinity. In the crystal structure for many mercuric compounds, there are two short Hg–X distances in a linear configuration and additional long Hg–X bonds to give a distorted octahedral arrangement.[19] There are also some cases of tetrahedral $\mathrm{HgX_4}$ structures, *viz.*, crystalline $\mathrm{HgI_2}$ and $\mathrm{HgCl_4^{=}}$[20] ions in solution but $\mathrm{HgI_2}$ and $\mathrm{HgCl_2}$[19] are linear in the gas phase. The first two binding constants for $\mathrm{Hg^{++}}$ with $\mathrm{Cl^-}$, $\mathrm{Br^-}$ and $\mathrm{I^-}$ are much greater than K_3 and K_4.[21,22]

For the few crystal structures which are known for mercurous compounds, there are linear X–Hg–Hg–X structures, with additional ligands at larger distances around each Hg atom to give a distorted octahedral coördination. From an electronic and structural point of view, therefore, mercurous compounds are just like linear $\mathrm{HgX_2}$ compounds, except that one of the bonds is a Hg–Hg bond.

Table VII displays the mercury–mercury and mercury-ligand distances for some mercurous compounds. The substance mercurous diacethydrazide has the structure

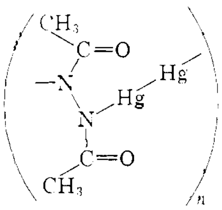


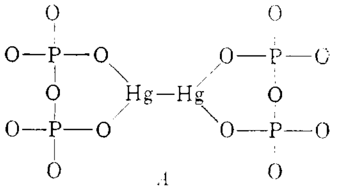
TABLE VII

INTERATOMIC DISTANCES IN SOME MERCUROUS COMPOUNDS IN Å.

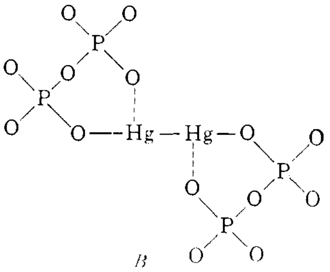
	Hg-Hg	Hg-X	Ref.
$\mathrm{Hg_2F_2}$	2.43	2.13	23
$\mathrm{Hg_2Cl_2}$	2.53	2.52	23
$\mathrm{Hg_2Br_2}$	2.58	2.57	23
$\mathrm{Hg_2I_2}$	2.69	2.68	23
$\mathrm{Hg_2N_2Ac_2}$[a]	2.90		24

[a] Mercurous diacethydrazide.

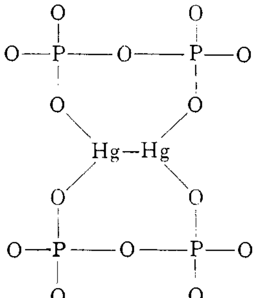
The binding constants for complex formation with $\mathrm{Hg^{++}}$ increase in the order $\mathrm{F^-}$, $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$ and $\mathrm{NH_3}$,[21,22,25] and if we take a very rough point of view that the nitrogen in the diacetylhydrazine is about as good a complexer as is $\mathrm{NH_3}$, then Table VIII shows that the stronger the Hg–X bond, the longer and weaker the Hg–Hg bond.



A



B



C

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[18] E. Newberry, *Trans. Electrochem. Soc.*, **69**, 57 (1936).

[19] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1950, pp. 631–634.

[20] L. A. Woodward and A. A. Nord, *J. Chem. Soc.*, 3721 (1956).

[21] L. G. Sillén, *Acta Chem. Scand.*, **3**, 539 (1949).

[22] Y. Marcus, *ibid.*, **11**, 599 (1957).

[23] R. Wyckoff, "Crystal Structures," Vol. I, Interscience Publishers, Inc., New York, N. Y., Chap. III, p. 43; H. Grdenić, *J. Chem. Soc.*, 1312, 1316 (1956).

[24] K. Brodersen and L. Kunkel, *Chem. Ber.*, **91**, 2698 (1958).

[25] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," Thesis, 1941, reprinted 1957, P. Haase and Son, Copenhagen, p. 173.

Ligands which form good covalent bonds to mercury such as NH_3 or CN^- cause disproportionation of the hypothetical $Hg^{I}L_2$ into $Hg^{II}L_2$ complexes and elementary mercury. Thus, our hypothesis is that a tendency to form a strong covalent Hg–X complex weakens the Hg–Hg bond and leads to disproportionation. In order to get good mercurous complexes, therefore, one should use strong "ionic" ligands, such as $P_2O_7^{-4}$, $C_2O_4^{--}$, etc., which complex by virtue of their charge and chelating characteristics. With these ligands, the contribution of covalent bond formation to the binding is small, as indicated by their relatively strong binding for the alkaline earth and group IIIb tripositive ions. These are in fact the complexing agents which do form mercurous complexes which are stable to disproportionation.[26]

The structure of the mercurous pyrophosphate and other mercurous complexes which were studied here is an interesting problem in structural chemistry. The three structures A, B and C already shown are all conceivable. The evidence that OH^- binds all Hg_2L^{-q+2} ligands equally tends to indicate that the chelate L is attached to only one mercury as in structures A and B.

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[26] Several interesting facts may be mentioned incidentally. R. Rosen and E. E. Reid report the existence of the compound $HO–CH_2–CH_2–S–Hg–Hg–S–CH_2–CH_2–OH$, a yellow solid, soluble in hot alcohol and melting at 108° (THIS JOURNAL, **44**, 635 (1922)). It is not known whether this substance is stable to disproportionation. There are the curious facts that the substances $Hg_2(CO_2CX_3)_2$(X = Cl or F) exist and are soluble in benzene (N. Davidson and L. E. Sutton, *J. Chem. Soc.*, 565 (1942)). See also J. Sand, *Ber.*, **34**, 2913 (1901); K. A. Hofmann and J. Sand, *Ber.*, **33**, 2700 (1900).

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN, AND KANSAS STATE UNIVERSITY, MANHATTAN, KANSAS]

The Iodine Complexes of Some Saturated Cyclic Ethers.[1,2] I. The Visible Region

BY SISTER MARY BRANDON, O.P.,[3] MILTON TAMRES AND SCOTT SEARLES, JR.

RECEIVED MAY 1, 1959

The thermodynamic constants in *n*-heptane for the iodine complexes of a series of cyclic ethers—namely, trimethylene oxide, tetrahydrofuran, 2-methyltetrahydrofuran, tetrahydropyran and propylene oxide—were obtained by a study of the temperature dependence of the absorption spectra in the visible region. The thermodynamic results show that the order of electron donor ability of the cyclic ethers is 4- > 5- > 6- > 3-membered ring. These results are in agreement with those reported previously from studies on hydrogen bonding and nuclear magnetic resonance and offer strong support for the proposal that the redistribution of electrons with change in ring size has a pronounced effect on the properties of cyclic compounds.

Introduction

The work of Benesi and Hildebrand[4] on the spectroscopic study of iodine in various solvents established the formation of 1:1 complexes of iodine with several electron donor species. Since that report there has been a rapid growth in the number of publications on molecular complex formation,[5] particularly with regard to use of the spectroscopic method. This growth has been prompted not only by the theoretical import of Mulliken's charge transfer theory[6] but also by the general consideration of acid–base theory which seems to offer the best interpretation for the formation of these complexes.[4,7]

Although it is known that side reactions often occur when iodine is dissolved in oxygenated solvents, it has been shown that the spectroscopic technique is applicable to the determination of the thermodynamic characteristics of 1:1 complexes formed by iodine with a large number of oxygen containing compounds,[8] notably with ethers. Among the ethers for which spectral characteristics and equilibrium constants, and in some cases enthalpy and entropy data, have been reported for the formation of 1:1 complexes with iodine are *n*-butyl ether,[9] 1,4-dioxane,[10] ethyl ether,[11] methyl butyl ether[12] and isopropyl ether.[10c] These data indicate that the interaction is rather moderate, the enthalpy of interaction being of the order of magnitude of that shown in formation of stronger hydrogen bonds. Consequently, it is reasonable to assume that the interaction will produce no major alteration in the character of the lone pair electrons on the oxygen and that this interaction

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, New Jersey, Sept., 1956.

[2] Taken in part from the Ph.D. thesis of Sister Mary Brandon Hudson, University of Michigan, June, 1957.

[3] Department of Chemistry, Rosary College, River Forest, Illinois.

[4] (a) H. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2832 (1948); (b) **71**, 2703 (1949).

[5] A review of this subject is given by L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

[6] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

[7] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[8] P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1199 (1957), summarizes literature data.

[9] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **75**, 3561 (1953).

[10] (a) J. A. A. Ketelaar, C. van de Stolpe and H. R. Gersmann, *Rec. trav. chim.*, **70**, 499 (1951); (b) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *ibid.*, **71**, 1104 (1952); (c) C. van de Stolpe, Ph.D. thesis, Amsterdam, 1953.

[11] (a) J. Ham, *J. Chem. Phys.*, **20**, 1170 (1952); (b) P. A. D. de Maine, *ibid.*, **26**, 1192 (1957).

[12] G. Kortum and M. Kortum-Sieler, *Z. Naturforsch.*, **5a**, 544 (1950).