

## The Stability Constants of Mixed Chloro-Bromo-Aurate(III) Complexes

LENA ALMGREN

*Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg, P.O. Box, S-402 20 Göteborg 5, Sweden*

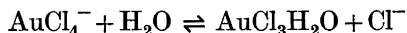
The replacement of chloride by bromide in the tetrachloroaurate (III) ion has been studied at 25°C in 3 M perchloric acid medium by spectrophotometric measurements at 311, 325, 340, 360, and 382 nm. The total concentrations of gold, chloride, and bromide ranged from 0.1000 to 1.800 mM, 7.200 to 100.0 mM, and 0 to 7.200 mM, respectively. The experimental data can be explained assuming the equilibria  $\text{AuCl}_4^- + p\text{Br}^- \rightleftharpoons \text{AuCl}_{4-p}\text{Br}_p^- + p\text{Cl}^-$ ,  $p=1, 2, 3, 4$ , with

$$\begin{array}{ll} \log \beta_1 = 2.46 \pm 0.06 & \log \beta_2 = 4.59 \pm 0.06 \\ \log \beta_3 = 6.40 \pm 0.06 & \log \beta_4 = 7.77 \pm 0.04 \end{array}$$

the errors being given as  $3\sigma$  where  $\sigma$  is the standard deviation. The preliminary constants were obtained graphically and refined by a generalized least squares method using a CD 3 600 computer and the spectrophotometric version, "Spefo", of the "Letagrop Vrid" program.

In aqueous solutions containing gold(III), chloride, and bromide ions, complexes of the general formula  $[\text{AuCl}_c\text{Br}_b(\text{OH})_a(\text{H}_2\text{O})_{4-a-b-c}]^{3-a-b-c}$  may be formed. In the main only the more simple systems with  $b$  or  $c=0$  have hitherto been studied.

Whereas the hydrolysis of the tetrachloroaurate(III) ion has been the subject of several investigations,<sup>1-10</sup> the hydrolysis of the tetrabromoaurate(III) ion has been the subject of only one.<sup>9</sup> For the aquation reaction

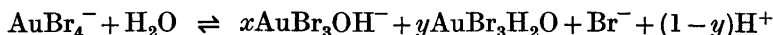


the values reported for the equilibrium constant range from  $10^{-2.6}$  M to  $10^{-5.4}$  M, and for the dissociation reaction



from  $10^{-5.63}$  M to  $10^{-6.84}$  M. At sufficiently low pH and high concentration of chloride ions, all hydrolyzed forms of the tetrachloroaurate(III) ion can thus be neglected.

For the bromoaurate(III) system, the constant reported is that for the reaction



which was determined to be  $3 \times 10^{-9} \text{ M}^2$ ,  $y$  being assumed to be 0. A comparison of this value with the corresponding value,  $10^{-6.32} \text{ M}^2$  (Ref. 8), for the chloroaurate(III) system suggests that the extent of hydrolysis is greater in the latter system. Thus, under conditions when the hydrolyzed species of the chloroaurate(III) system can be neglected, the same must be valid for the bromoaurate(III) system.

No investigations of the equilibria



have been reported until fairly recently.<sup>11-13</sup> Pouradier and Coquard<sup>12</sup> have studied the reactions at 25°C in chloride medium of varying concentrations by potentiometric titration, using a silver-silver bromide electrode. The equilibrium constants were obtained by computer calculations. Peshchevitskii and Belevantsev<sup>13</sup> made spectrophotometric measurements at 17–21°C in 0.1 M NaClO<sub>4</sub> and used Bjerrum's method of corresponding solutions to calculate the constants.

In this work the equilibria have been studied spectrophotometrically at 25°C in 3 M HClO<sub>4</sub> and the experimental data have been evaluated with a computer.

## EXPERIMENTAL

*Equipment.* Spectra were obtained with the help of a Bausch and Lomb recording spectrophotometer, Spectronic 505. Measurements at constant wavelengths were performed on a Beckman Quartz Spectrophotometer, Model DU, with the cell compartment thermostated to  $25.0 \pm 0.1^\circ\text{C}$ . Spectrosil Quartz cells of lengths 10, 5, 2, 1, 0.5, 0.2, and 0.1 cm were calibrated before use.

*Reagents.* Tetrachloroauric acid was prepared by dissolving metallic gold of min. 99.95 % (average 99.98 %) purity, supplied by Johnson, Matthey and Co., London, in *aqua regia* and evaporating several times with hydrochloric acid.<sup>14</sup>

The stock solution was analyzed electrogravimetrically for gold. The chloride content was determined by potentiometric titration with silver nitrate, after reduction of the gold with hydrazine sulphate. The ratio of the concentrations of chloride and gold was found to be 4 with a maximum error of 0.2 %.

Stock solutions of sodium chloride were prepared from NaCl (Merck's Suprapur) by accurate weighing and dilution.

The perchloric acid stock solution was prepared from HClO<sub>4</sub> (Merck's *p.a.*) and standardized against recrystallized borax, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O.

Sodium bromide was prepared by neutralizing Na<sub>2</sub>CO<sub>3</sub> (Merck's *p.a.*) with HBr (Merck's *p.a.*) following the directions given in Ref. 15 for the preparation of sodium perchlorate. The stock solution was analyzed by evaporating and drying at 125°C. The analytical hydrogen ion concentration of the stock solution was checked by the method described in Ref. 16, and was found to be negligible.

The water used was doubly distilled.

The stock solutions were used to prepare ten different series of solutions with constant total concentrations of gold and chloride within each series and with varying bromide concentrations. In all, 227 solutions were used, the total concentrations of gold, chloride, and bromide ranging from 0.1000 to 1.800 mM, 7.200 to 100.0 mM, and 0 to 7.200 mM, respectively. All solutions were made 3.000 M in H<sup>+</sup> + Na<sup>+</sup> by adding HClO<sub>4</sub>. The halide concentration was held high enough to suppress the hydrolysis of the gold halide complex ions. The solutions were stored in the dark in a thermostat at  $25.0 \pm 0.1^\circ\text{C}$ .

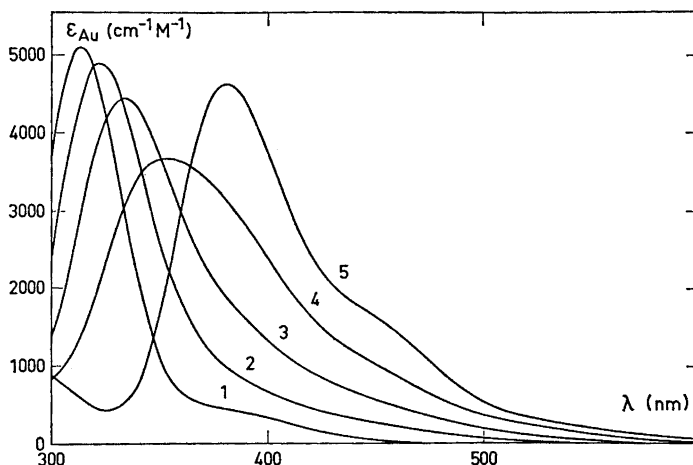


Fig. 1. Absorption spectra of solutions with constant  $C_{\text{Au}}$  and variable  $C_{\text{Br}}/C_{\text{Cl}}$  in 3 M  $\text{HClO}_4$ . In all solutions the gold concentration was equal to 0.1800 mM. In solutions 1–4 the chloride concentration was 10.72 mM and in solution 5 0.7200 mM. The bromide concentrations in the different solutions were No. 1, 0; No. 2, 0.2519; No. 3, 0.5896; No. 4, 1.286; No. 5, 10.72 mM.

Preliminary absorbance measurements showed (cf. Fig. 1) that the absorbance maximum<sup>17,18</sup> of  $\text{AuCl}_4^-$  at 314 nm shifts with increasing bromide concentration towards the  $\text{AuBr}_4^-$  maximum<sup>17,19</sup> at 382 nm.

Consequently, the accurate absorbance measurements were performed at 311, 325, 340, 360, and 382 nm. The measurements were started 1 h after the mixing of the solutions and completed within 12 h. During this time the absorbance was constant within the limits of experimental error.

#### CALCULATIONS

The preliminary values of the constants were obtained by the method of corresponding solutions in a way similar to that described by Elding and Leden.<sup>20</sup>

Assuming the complexes  $\text{AuBr}_p\text{Cl}_{4-p}^-$  ( $p=0, 1, 2, 3, 4$ ) to be present in the solutions, the total concentration of gold,  $C_{\text{Au}}$ , can be written:

$$C_{\text{Au}} = [\text{AuCl}_4^-] \sum_{p=0}^4 \beta_p r^p \quad (1)$$

where  $r = [\text{Br}^-]/[\text{Cl}^-]$

The average number,  $\bar{n}$ , of bromide ligands bound per gold atom is:

$$\bar{n} = \frac{C_{\text{Br}} - [\text{Br}^-]}{C_{\text{Au}}} \quad (2)$$

and

$$4 - \bar{n} = \frac{C_{\text{Cl}} - [\text{Cl}^-]}{C_{\text{Au}}} \quad (3)$$

where  $C_{\text{Br}}$  and  $C_{\text{Cl}}$  are the total concentrations of  $\text{Br}^-$  and  $\text{Cl}^-$ , respectively. From (2) and (3) it can be seen that:

$$\frac{C_{\text{Br}} - \bar{n}C_{\text{Au}}}{C_{\text{Cl}} - (4 - \bar{n})C_{\text{Au}}} = \frac{[\text{Br}^-]}{[\text{Cl}^-]} = r \quad (4)$$

By introducing the definition  $R = C_{\text{Br}}/C_{\text{Cl}}$  and eliminating  $C_{\text{Br}}$  from (4), the expression:

$$R = r + \frac{C_{\text{Au}}}{C_{\text{Cl}}} (\bar{n} - (4 - \bar{n})r) \quad (5)$$

is obtained.

Representative data from the spectrophotometric measurements are given for one series of solutions in Table 1 and for all series at 340 nm in Fig. 2. From

Table 1.  $\epsilon_{\text{Au}}$  data at different wavelengths for solutions with  $C_{\text{Au}}/C_{\text{Cl}} = 0.0700$  (the values within brackets are calculated).

$R \times 10^3$	$\epsilon_{\text{Au}} \text{ (cm}^{-1} \text{ M}^{-1}\text{)}$				
	311 nm	325 nm	340 nm	360 nm	382 nm
0	5424 (5379)	4568 (4529)	2230 (2191)	670 (670)	463 (457)
2.500	5364 (5359)	4611 (4579)	2269 (2259)	702 (705)	474 (470)
5.000	5310 (5338)	4631 (4627)	2327 (2328)	737 (742)	488 (483)
7.500	5317 (5315)	4708 (4673)	2398 (2395)	775 (779)	500 (497)
10.00	5295 (5289)	4741 (4716)	2494 (2463)	812 (817)	513 (512)
15.00	5232 (5234)	4817 (4795)	2590 (2595)	887 (894)	544 (542)
20.00	5170 (5173)	4870 (4866)	2747 (2725)	963 (973)	576 (575)
30.00	5024 (5034)	4975 (4981)	2965 (2976)	1132 (1135)	644 (644)
40.00	4903 (4878)	5092 (5064)	3226 (3213)	1294 (1302)	721 (720)
50.00	4720 (4706)	5155 (5117)	3440 (3433)	1465 (1472)	808 (803)
60.00	4559 (4524)	5155 (5141)	3654 (3637)	1625 (1644)	884 (890)
70.00	4359 (4332)	5169 (5138)	3823 (3822)	1794 (1816)	980 (984)
80.00	4155 (4132)	5140 (5109)	3999 (3987)	1966 (1989)	1078 (1082)
90.00	3919 (3929)	5065 (5056)	4120 (4131)	2137 (2158)	1182 (1185)
100.0	3761 (3721)	5034 (4979)	4266 (4254)	2348 (2325)	1299 (1294)
110.0	3519 (3514)	4908 (4882)	4381 (4353)	2495 (2487)	1407 (1406)
125.0	3214 (3202)	4730 (4697)	4487 (4460)	2736 (2720)	1574 (1584)
140.0	2921 (2895)	4499 (4473)	4543 (4513)	2962 (2937)	1782 (1771)
160.0	2489 (2505)	4109 (4123)	4516 (4499)	3198 (3194)	2032 (2032)
180.0	2164 (2145)	3743 (3731)	4400 (4392)	3421 (3406)	2316 (2304)
200.0	1810 (1826)	3320 (3317)	4162 (4200)	3556 (3567)	2590 (2582)
220.0	1552 (1552)	2941 (2903)	3981 (3938)	3698 (3673)	2881 (2859)
240.0	1328 (1332)	2527 (2514)	3622 (3632)	3710 (3726)	3135 (3124)
260.0	1165 (1161)	2198 (2169)	3341 (3311)	3763 (3735)	3389 (3367)
280.0	1034 (1035)	1865 (1878)	3002 (3002)	3702 (3713)	3575 (3581)
300.0	951 (944)	1658 (1643)	2739 (2724)	3680 (3673)	3776 (3762)

the data corresponding values of  $R$  and  $C_{\text{Au}}/C_{\text{Cl}}$  (yielding the same absorptivity,  $\epsilon_{\text{Au}}$ , per M Au) were obtained (cf. Ref 20). According to eqn. (5), a plot of  $R$  versus  $C_{\text{Au}}/C_{\text{Cl}}$  should give a straight line, from the intercept and slope of which  $r$  and  $\bar{n}$ , respectively, can be calculated (cf. Fig. 3). The results for

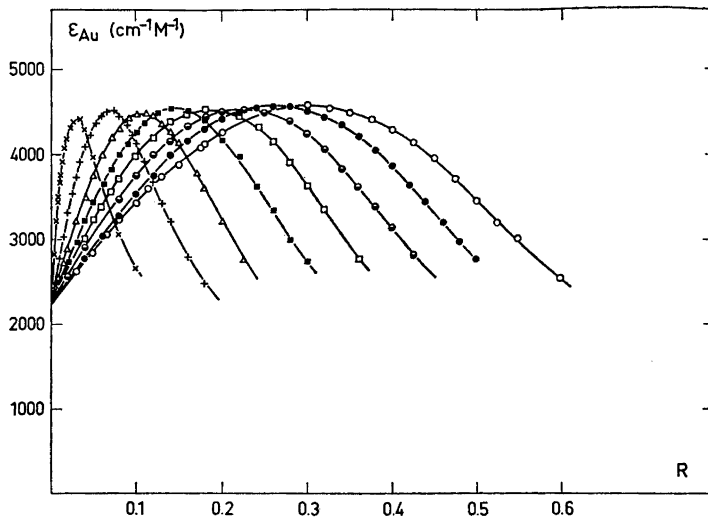


Fig. 2. Measurements at 340 nm.  $\epsilon_{Au}$  versus  $R$  at different  $C_{Au}/C_{Cl}$ .  $C_{Au}/C_{Cl}$ :  $\times$  0.01;  $+$  0.03;  $\triangle$  0.05;  $\blacksquare$  0.07;  $\square$  0.09;  $\ominus$  0.11;  $\bullet$  0.13;  $\circ$  0.15.

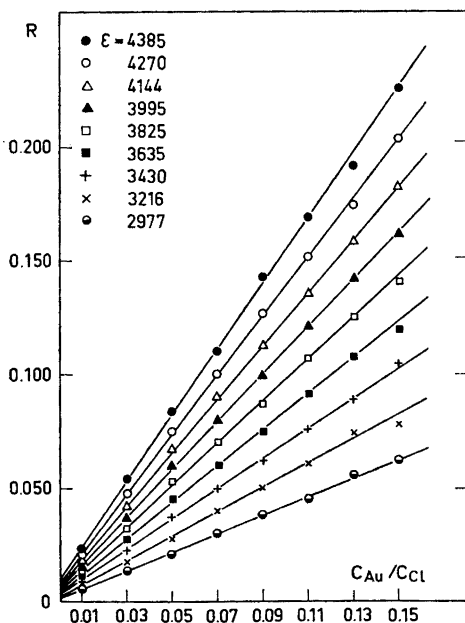


Fig. 3.  $R$  versus  $C_{Au}/C_{Cl}$  at different  $\epsilon_{Au}$  at 340 nm ( $\epsilon_{Au}$  in  $\text{cm}^{-1}\text{M}^{-1}$ ).

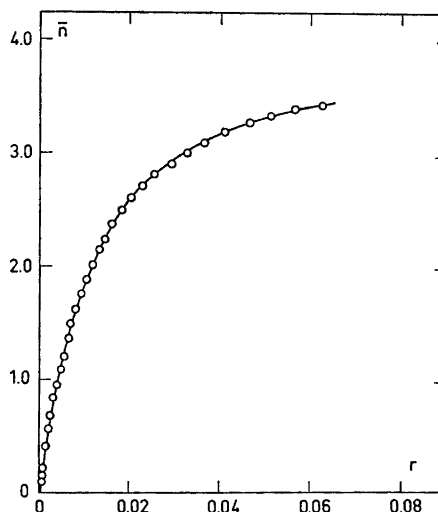


Fig. 4.  $\bar{n}$  versus  $r$ .

all the wavelengths were treated in this way. Mean values of  $\bar{n}$  and  $r$  were calculated, and have been plotted against each other in Fig. 4. To the  $\bar{n}$ ,  $r$  data the extrapolation method of Rossotti and Rossotti<sup>21</sup> was then applied (cf. Fig. 5). The following approximate values of the constants were obtained:

$$\beta_1 \sim 2.8 \times 10^2, \beta_2 \sim 3 \times 10^4, \text{ and } \beta_3 \sim 3 \times 10^6.$$

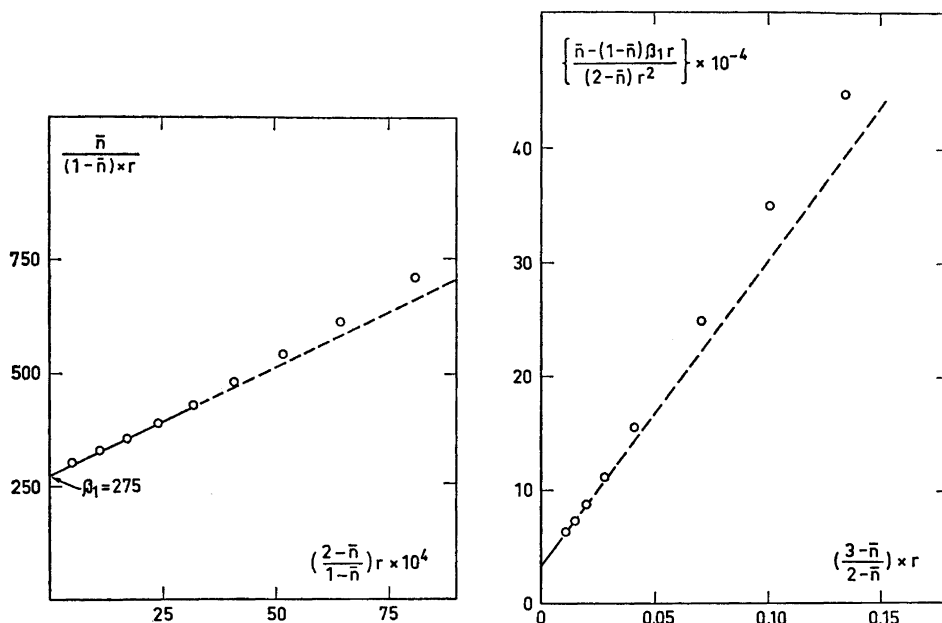


Fig. 5.  $\bar{n}$ ,  $r$  data treated by the extrapolation method of Rossotti and Rossotti. Approximate values of  $\beta_1$  and  $\beta_2$  were obtained from the intercepts in a and b, respectively.  $\beta_3$  has been estimated from the slope in b.

These values indicate that even at low  $\bar{n}$  values all the complexes coexist, making the estimates of  $\beta_2$  and  $\beta_3$  very crude. By taking the values of the ratios  $\beta_3/\beta_2$  and  $\beta_2/\beta_1$  into consideration  $\beta_4$  was assigned the value  $10^8$ , based on the assumption that  $\beta_{n+1}/\beta_n$  is approximately constant. A refinement was then performed on a CD 3 600 computer at the Uppsala University Computing Centre using the spectrophotometric version, Spefo, of Sillén's Letagrop Vrid program.<sup>22,23</sup>

## RESULTS AND DISCUSSION

The refinement of the constants gave the following "best" values:

$$\log \beta_1 = 2.46 \pm 0.06$$

$$\log \beta_2 = 4.59 \pm 0.06$$

$$\log \beta_3 = 6.40 \pm 0.06$$

$$\log \beta_4 = 7.77 \pm 0.04$$

The assigned errors are calculated as  $3\sigma$ , where  $\sigma$  is the standard deviation in  $\log \beta_p$ . The error squares sum  $U$ , defined as

$$U = \sum (\epsilon_{\text{Au,calc.}} - \epsilon_{\text{Au,exp.}})^2$$

was  $1.2 \times 10^6 \text{ cm}^{-2} \text{ M}^{-2}$  for 1100  $\epsilon_{\text{Au}}$  values. Since  $\epsilon_{\text{Au}}$  ranged from 1000 to 5400  $\text{cm}^{-1} \text{ M}^{-1}$ , the precision is satisfactory.

In order to test the assumption that only complexes of formulae  $\text{AuBr}_p\text{Cl}_{4-p}^-$  ( $p=0, 1, 2, 3, 4$ ) are present in the solutions, other complexes were included in the calculations, the most probable additional complex being  $\text{AuCl}_3\text{H}_2\text{O}$ . On addition of this complex, however, quite inconceivable values of  $\epsilon_p$  and  $\beta_p$  were obtained. It was therefore concluded that the original assumption was correct.

A survey of reported values for the stability constants of the chlorobromoaurate(III) system is given in Table 2. The values determined by Peshche-

Table 2. Survey of reported values for the stability constants.

Author	Ref.	Method	Temp.°C	Medium	log $\beta_1$	log $\beta_2$	log $\beta_3$	log $\beta_4$
Peshchevitskii, Kazakov and Erenburg	11	Emf	25	0.2 M KCl	—	—	—	6.60
Pouradier and Coquard	12	Emf	25	0.1–0.8 M $\text{Cl}^-$	2.57	4.38	6.18	7.30
Peshchevitskii and Belevantsev	13	Spectr.	17–21	0.1 M $\text{NaClO}_4$	2.53	4.57	6.27	7.78
This work		Spectr.	25	3 M $\text{HClO}_4$	2.46	4.59	6.40	7.77

vitskii and Belevantsev show the best agreement with those obtained in this work, and with the exception of  $\beta_3$  they lie within or nearly within the present error limits. Since the ionic media and temperatures were not the same in the two investigations, exactly the same values for  $\beta_p$  cannot be expected.

In addition to  $\beta_p$ , the program Spefo calculates values of the molar absorptivity,  $\epsilon_p$ . The "best" values obtained are given in Table 3.

Table 3. Molar absorptivities,  $\epsilon_p$ , at different wavelengths. The errors are given as  $3\sigma$ .

$\epsilon_p$	311	325	340	360	382 nm
$p=0$	$5379 \pm 8$	$4529 \pm 10$	$2191 \pm 8$	$670 \pm 5$	$457 \pm 4$
$p=1$	$4846 \pm 38$	$6024 \pm 48$	$4184 \pm 35$	$1710 \pm 25$	$828 \pm 21$
$p=2$	$2418 \pm 72$	$5327 \pm 89$	$5907 \pm 69$	$3353 \pm 49$	$1668 \pm 39$
$p=3$	$862 \pm 74$	$2213 \pm 92$	$4967 \pm 70$	$4614 \pm 51$	$2877 \pm 41$
$p=4$	$673 \pm 51$	$551 \pm 64$	$963 \pm 50$	$3128 \pm 36$	$4776 \pm 29$

In Pouradier and Coquard's paper<sup>12</sup> a diagram of  $\epsilon_p$  versus  $\lambda$  in the region 300 to 400 nm is shown. The discrepancies in the  $\epsilon_p$  values obtained in the two investigations can be directly correlated with the discrepancies in the  $\beta_p$  values.

The late Professor Lars Gunnar Sillén modified his program Spefo especially to fit this problem. The author is most grateful to him for this and for the considerable time he spent in helping her to carry out the calculations. She would also like to thank Professor Georg Lundgren for having suggested this problem, for many helpful discussions and for invaluable help during the preparation of this paper. She is indebted to Dr. Susan Jagner for revising the English text of this paper. Financial support from the *Swedish Natural Science Research Council* (Contract No. 2318) is gratefully acknowledged.

## REFERENCES

1. Bjerrum, N. *Bull. Soc. Chim. Belges* **57** (1948) 432.
2. Rich, R. L. and Taube, H. *J. Phys. Chem.* **58** (1954) 1.
3. Bardet, L. and Bontoux, J. *Trav. Soc. Pharm. Montpellier* **21** (1961) 111.
4. Fry, F. H. *Thesis*, Department of Chemistry, Princeton University 1964.
5. Fry, F. H., Hamilton, G. A. and Turkevich, J. *Inorg. Chem.* **5** (1966) 1943.
6. Robb, W. *Inorg. Chem.* **6** (1967) 382.
7. Bryngelsson, B. and Lundgren, G. *Acta Chem. Scand.* To be published.
8. Bergström, L. and Lundgren, G. *Acta Chem. Scand.* To be published.
9. Chateau, H., Gadet, M.-C. and Pouradier, J. *J. Chim. Phys.* **63** (1966) 269.
10. Peshchevitskii, B. I. and Belevantsev, V. I. *Izv. Sibirsk. Otd. Akad. Nauk SSSR* **1969** 82.
11. Peshchevitskii, B. I., Kazakov, V. P. and Erenburg, A. M. *Russ. J. Inorg. Chem.* **8** (1963) 437.
12. Pouradier, J. and Coquard, M. *J. Chim. Phys.* **63** (1966) 1072.
13. Peshchevitskii, B. I. and Belevantsev, V. I. *Russ. J. Inorg. Chem.* **12** (1967) 161.
14. Biltz, W. and Wein, W. *Z. anorg. allgem. Chem.* **148** (1925) 192.
15. *Some Laboratory Methods*, Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm, manuscript 1959.
16. Gobom, S. *Acta Chem. Scand.* **17** (1963) 2181.
17. Gangopadhyay, A. K. and Chakravorty, A. *J. Chem. Phys.* **35** (1961) 2206.
18. Lingane, J. J. *Electroanal. Chem.* **4** (1962) 332.
19. Lingane, J. J. *Electroanal. Chem.* **6** (1963) 1.
20. Elding, L. I. and Leden, I. *Acta Chem. Scand.* **20** (1966) 706.
21. Rossotti, F. J. C. and Rossotti, H. *The Determination of Stability Constants*, McGraw, New York 1961, p. 110.
22. Sillén, L. G. and Warnqvist, B. *Arkiv Kemi* **31** (1969) 377.
23. Sillén, L. G. *Mimeoogr.*, Royal Institute of Technology, Stockholm Jan. 1969.

Received February 19, 1971.