ACTA CHEMICA SCANDINAVICA 23 (1969) 548–556

The Complex Formation of Bismuth(III) with Chloride in Aqueous Solution. A Solubility Study

LARS JOHANSSON

Division of Inorganic Chemistry, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden

From the variation of the solubility of BiOCl(s) with hydrogen and chloride ion concentration, the complex formation between Bi^{3+} and Cl^- has been elucidated. The complexes are mononuclear, *i.e.* of the form $BiCl_n^{(3-n)+}$, $n=1, \ldots, 6$, with the stability constants, $\beta_n = 9.2\times10^2$, 1.9×10^4, 5.0×10^6, 7.6×10^6, 4.1×10^8, and 2.3×10^8, respectively. The data refer to 25°C and a 4 M sodium perchlorate medium.

Several authors have studied the complex formation between bismuth(III) and chloride ions.[1–4] The methods used, as well as the experimental conditions such as temperature and ionic medium have differed widely, however, and the spread in the results is considerable, regarding the nature as well as the stability of the species formed. This is especially true at high $[Cl^-]$, where for instance Newman and Hume [5] explained data from spectrophotometric measurements in solutions of $[Cl^-]\leq 4$ M by assuming $BiCl_4^-$ and $BiCl_5^{2-}$ to dominate. Ahrland and Grenthe,[6] on the other hand also included $BiCl_6^{3-}$ in their explanation of potentiometric data ($[Cl^-]\leq 0.9$ M), while Haight *et al.*[2] could fit solubility data ($[Cl^-]\leq 4$ M) with $BiCl_4^-$ and $BiCl_6^{3-}$. It has usually been taken for granted that the complexes are mononuclear. That such is the case in 4 M Cl^- was shown by Haight.[2]

In the present investigation the bismuth(III) chloride system has been studied by a solubility method, employing BiOCl(s) as solid phase. Besides giving further information about the system, the investigation was also aimed at illustrating how the presence or absence of polynuclear complexes can be shown by solubility measurements. The utilization of solubility measurements has been discussed in more detail elsehwere.[7]

The solubility of BiOCl(s) has been studied earlier by, *e.g.*, Noyes *et al.*[8] and Yatsimirskiĭ.[9] Neither held the ionic strength constant, a fact which makes their results less valuable. Yatsimirskiĭ varied $[Cl^-]$ at constant $[H^+]$, as well as $[H^+]$ in chloride free solution. Ahrland and Grenthe [6] performed solubility measurements at constant ionic strength (2 M) and varied $[Cl^-]$

at constant $[H^+]$ (1 M). Under these conditions, the maximum $[Cl^-]$ attainable was low (<0.1 M).

In the present investigation, $[H^+]$ has been varied, as well as $[Cl^-]$. Consequently, the solubility can always be kept at a convenient level, and higher ligand concentrations can be reached. In addition, one is enabled to judge whether polynuclear complexes are formed or not.

EQUATIONS

The solubility S (=total bismuth concentration) of BiOCl(s) in various solutions is measured. The initial concentrations of hydrogen ion, C_H, and of chloride ion, C_L, are varied.

Under the conditions considered here BiOCl(s) may as well be written as $Bi(OH)_2Cl(s)$ or $M(OH)_2L(s)$, M and L being the species taking part in the complex formation studied (*cf.* Ref. 7). If, then, various complexes M_mL_n are formed, $m \geq 1$, $n \geq 0$, the solubility is

$$S = \sum_{m,n} m[M_mL_n] \tag{1}$$

The solubility product

$$K_s = [M][OH^-]^2[L] \tag{2}$$

may be written (since $[H^+][OH^-]=K_w$)

$$K_s^* = [M][H^+]^{-2}[L] \tag{3}$$

Introducing K_s^* and

$$\beta_{nm} = [M_mL_n]/([M]^m[L]^n)$$

into equation (1) yields

$$S = \sum_{m,n} m(K_s^*)^m \beta_{nm}[H^+]^{2m}[L]^{n-m} \tag{4}$$

From eqn. (4) the following derivatives may be obtained

$$\left(\frac{\partial \log S}{\partial \log [L]}\right)_{[H^+]} = \frac{\sum\limits_{m,n} m(n-m)[M_mL_n]}{\sum\limits_{m,n} m[M_mL_n]} = \overline{n-m} \tag{5}$$

$$\left(\frac{\partial \log S}{\partial \log [H^+]}\right)_{[L]} = 2\,\frac{\sum\limits_{m,n} m^2[M_mL_n]}{\sum\limits_{m,n} m[M_mL_n]} = 2\,\overline{m} \tag{6}$$

$$\left(\frac{\partial \log [H^+]}{\partial \log [L]}\right)_S = -\frac{1}{2}\,\frac{\sum\limits_{m,n} m(n-m)[M_mL_n]}{\sum\limits_{m,n} m^2[M_mL_n]} \tag{7}$$

The symbols $\overline{n-m}$ and $\overline{m}$ are used to indicate that these functions (defined by eqns. (5) and (6)) are averages of the prevailing values of $n-m$ and m, respectively.

In the present investigation, it turns out that only mononuclear complexes are formed, *i.e.* $m=1$ for all complexes. Then, the derivatives become simpler

$$(\partial \log S/\partial \log [\mathrm{L}])_{[\mathrm{H}^+]} = \bar{n}-1 \tag{5'}$$

$$(\partial \log S/\partial \log [\mathrm{H}^+])_{[\mathrm{L}]} = 2 \tag{6'}$$

$$(\partial \log [\mathrm{H}^+]/\partial \log [\mathrm{L}])_S = -\tfrac{1}{2}\ (\bar{n}-1) \tag{7'}$$

Here, $\bar{n}$ is the ordinary ligand number.[7] Eqn. (4) may be written, for mononuclear complexes

$$S[\mathrm{H}^+]^{-2} = \sum_n K_s{}^*\beta_n[\mathrm{L}]^{n-1} = K_s{}^*[\mathrm{L}]^{-1}\ X \tag{4'}$$

where $X=\sum\limits_n \beta_n[\mathrm{L}]^n \qquad (\beta_0=1)$

Thus, from plots of log S *vs.* log [L] and log [H$^+$], a first orientation as to which complexes are formed may be obtained by the aid of eqns. (5)—(7). $K_s{}^*[\mathrm{L}]^{-1}X$ may then be calculated (eqn. (4')). From $K_s{}^*[\mathrm{L}]^{-1}X$ as a function of [L], the constants $K_s{}^*$ and β_n may be obtained.

Hydrolysis. Eqns. (1)—(7) can easily be changed to cover also the possibility of Bi—OH and/or mixed Bi—OH—Cl complexes being formed. Any complex may then be written $\mathrm{M}_m\mathrm{L}_n(\mathrm{OH})_p$, $m\geq 1$, $n\geq 0$, $p\geq 0$. The solubility will be

$$S = \sum_{m,n,p} m[\mathrm{M}_m\mathrm{L}_n(\mathrm{OH})_p] = \sum_{m,n,p} m(K_s{}^*)^m\beta_{pnm}[\mathrm{L}]^{n-m}[\mathrm{H}^+]^{2m-p} \tag{8}$$

Eqn. (6), for instance, becomes

$$(\partial \log S/\partial \log[\mathrm{H}^+])_{[\mathrm{L}]} = \overline{2m-p} \tag{6''}$$

Computation of [H$^+$], [L] *and* $\bar{n}$. When BiOCl(s) dissolves, and complexes are formed, [L] and [H$^+$] change slightly. If only mononuclear M—L complexes are formed, the following correction equations apply

$$[\mathrm{H}^+] = C_\mathrm{H}-2S \tag{9}$$

$$[\mathrm{L}] \ = C_\mathrm{L}-(\bar{n}-1)S \tag{10}$$

Often, the differences between C_H and [H$^+$], and between C_L and [L], respectively, are negligible. When such is not the case, [H$^+$] can always be calculated by eqn. (9) while the calculation of [L] requires the knowledge of $\bar{n}$. As long as the difference between C_L and [L] is small, only approximate $\bar{n}$ values are required, which may be obtained *e.g.* from slopes of log S *vs.* log C_L at constant C_H (eqn. (5')). Since [H$^+$] is not always exactly constant along such curves, more precise $\bar{n}$ values are best obtained by eqn. (7') in the following way: log S is plotted *vs.* log [L] for each constant value of C_H. The curves are then cut at some suitable constant values of S (to fulfill the condition in eqn. (7')). [H$^+$] is calculated for each point obtained. Log [H$^+$] is then plotted *vs.* log [L], the slopes of the obtained curves being $-\frac{1}{2}(\bar{n}-1)$ according to eqn. (7'). (If necessary, $\bar{n}$ and [L] can be refined by repeating the procedure, using the obtained $\bar{n}$ in eqn. (10) to yield a better [L], which is used to improve the plots, *etc.*)

EXPERIMENTAL

Chemicals. All chemicals used were of analytical grade. A stock solution of $Bi(ClO_4)_3$, was obtained from Bi_2O_3 which was dissolved in an excess of $HClO_4$. The solution was standardized by precipitating and weighing samples as BiOI(s). Sodium chloride solutions were obtained by weighing calculated amounts of NaCl, dried at 130°C for 10 h. The sodium perchlorate solution was made from $NaClO_4 \cdot H_2O$ (Fluka). The pH of this solution was adjusted to ≈ 9 by the addition of NaOH. After about a week's standing the solution was filtered from precipitated hydroxides, neutralized by addition of $HClO_4$, and standardized by evaporating and weighing samples as $NaClO_4$. In the finally prepared 5 M stock solution, no chloride could be detected. The pH was found by a glass electrode to be about 4.

BiOCl(s) for solubility studies. 25 ml 0.5 M $Bi(ClO_4)_3$ (in excess $HClO_4$) and 25 ml 0.6 M NaCl were added slowly to ≈ 1 l of hot water, under powerful stirring. The mixture was kept hot for 6 h, whereupon the salt was transferred to the saturator (see below), washed with large amounts of a solution of $C_H = 1$ and $C_L \approx 0.1$, and allowed to stand for a week before any measurements were made.

Considerable experience [6,8,9] has shown that BiOCl(s) is the only solid phase present at the concentrations of H^+ and Cl^- prevailing in the solutions used here.

Apparatus, equilibration. About 3 g of BiOCl(s) was placed in a solubility column similar to the one described earlier.[10] The column was immersed in a thermostat at 25°C. Solutions to be saturated were pushed through the bed of solid by the aid of air pressure. With the flow rate employed, ≈ 1 cm/min ≈ 1 ml/min, the solution appeared to be at least 98 % equilibrated after one passage. Normally 5 or more passages were employed, and the equilibration was checked frequently. With one solution, equilibrium was also approached from supersaturation: The solution was first equilibrated at 30°C, where the solubility was shown to be higher, and subsequently passed through the solid a couple of times at 25°C. The solubility thus obtained did not differ significantly from that obtained from unsaturation, a fact which proves that equilibrium really was attained.

Analysis. Equilibrated solutions were analyzed for Bi spectrophotometrically at 455 nm, after addition of sodium iodide to $[I^-] = 1$ M, sodium hypophosphite (to 0.2 M), and perchloric acid (to 0.5 M). It has been shown earlier [11] that the absorbance at 455 nm is independent of $[I^-]$. Now it was checked that Beer's law was followed (within 0.3 %) for absorbances between 0.2 and 2.1. It was also found that addition of Cl^- up to 1.4 M, or additional 1 M H^+, did not affect the absorbances significantly.

Reproducibility. Normally, at least two samples of a solution were equilibrated. With few exceptions, the solubilities of these samples agreed within 1 %.

The solubilities of two different samples of BiOCl(s), the one normally used (preparation, see above) and one prepared by simple mixing of the components at room temperature were also compared. For the same solution, the solubilities agreed within the limits of error.

Concentration ranges. Check of $[H^+]$. The solutions had the composition: C_H M $HClO_4$, C_L M NaCl, $(4 - C_H - C_L)$ M $NaClO_4$. The following values of C_H were chosen: 1.0, 0.3, 0.1, 0.03, 0.01, and 0.003 M. For each C_H, values of C_L were chosen so as to give solubilities between $\approx 10^{-5}$ M and $\approx 10^{-3}$ M. The range of C_L from 0 to 1.4 M was covered. Above this upper limit, a substantial part of C_H is consumed during the dissolution of BiOCl(s), thus making $[H^+]$ rather uncertain. In the solutions of lowest C_H (highest C_L) employed, $[H^+]$ after equilibration was checked with a glass electrode. The values found agreed very well with those obtained by eqn. (9). (The values used in Table 2 are obtained by eqn. (9).)

RESULTS

The obtained solubilities are given in Table 1. For each C_H, log S was plotted *vs.* log C_L. A first inspection showed that the vertical differences between the curves were such that $(\partial \log S / \partial \log [H^+])_{[L]} = 2$, approximately, over the whole range studied. According to eqn. (6′), then, the complexes

Table 1. Experimentally determined solubility of BiOCl(s).

C_H M	$C_L \times 10^3$ M	$S \times 10^4$ M	$C_H \times 10^3$ M	C_L M	$S \times 10^4$ M
1.000	0	2.839	31.72	0.200	0.423
	1.000	1.040		0.250	0.913
	2.000	0.792		0.300	1.839
	5.000	0.715		0.400	5.41
	10.00	0.936		0.500	11.98
	20.00	1.860	10.12	0.300	0.198
	50.0	8.94	10.12	0.400	0.596
0.3160	20.00	0.174	10.12	0.500	1.441
	50.0	0.811	10.11	0.600	2.774
	100.0	4.70	10.11	0.800	7.52
	150.0	15.25	3.273	0.600	0.321
0.1001	80.0	0.230	3.266	0.800	0.998
	100.0	0.440	3.260	1.000	2.109
	150.0	1.598	3.247	1.400	5.47
	200	4.06			
	300	16.60			

are mononuclear. Eqn. (10) was therefore used to correct for the changes in [L]. Then, log S was plotted *vs.* log [L] (Fig. 1).

It was now possible to calculate $(\partial \log S/\partial \log [H^+])_{[L]}$ more accurately, from the differences between curves. For low C_H, a value of 2.00 ± 0.03 was obtained, while, between the two highest C_H the distance was slightly greater, giving $(\partial \log S/\partial \log [H^+])_{[L]} = 2.1$, on the average. This slight deviation is

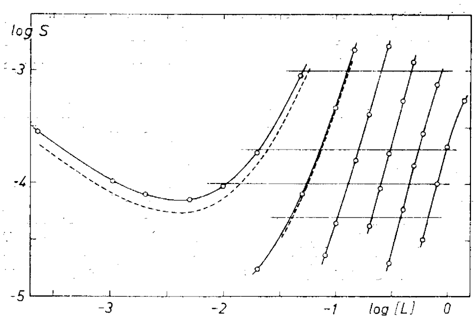

Fig. 1. Circles: Experimentally obtained solubility of BiOCl(s) as a function of [L], for various C_H, with best curves drawn. From left to right, $C_H = 1.0$, 0.3, 0.1, 0.03, 0.01, and 0.003. Dashed curves indicate corrected solubility (eqn. (11)).

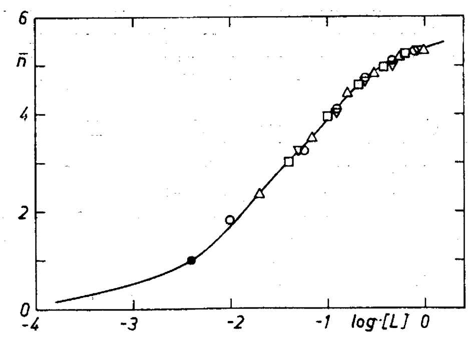

Fig. 2. Points: $\bar{n}$, obtained according to eqn. (7′) for solubilities 5×10^{-5} M (□), 1.0×10^{-4} M (○), 2×10^{-4} M (△), and 1.0×10^{-3} M (▽). The filled circle is obtained from the minimum of the curve of $C_H = 1$, in Fig. 1. *Curve:* Calculated from the final set of constants.

not thought to be due to polynuclear complex formation, since it seems to be dependent on C_H rather than, *e.g.*, on the total bismuth concentration. Hydrolysis, which might interfere at these low [Cl^-], may also be ruled out: according to eqn. (6″), hydrolysis would result in a *smaller* distance between the curves. The most natural explanation is, that the deviation is a medium effect, due to, *e.g.*, a slight change in K_s when H^+ is substituted for Na^+. A good fit with the experimental data was obtained when a linear variation with [H^+] was assumed, *i.e.* when the solubility was corrected according to the formula

$$S_{corr} = S/(1 + \alpha[H^+]) \tag{11}$$

using $\alpha = 0.3$. The correction was negligible except for the 2–3 highest C_H. The implication of this correction is that the finally computed constants are valid in 4 M $NaClO_4$, rather than in a mixed $(Na,H)ClO_4$.

The curves, log S_{corr} *vs.* log [L], (Fig. 1) were cut at log $S_{corr} = -4.3$, -4, -3.7, and -3. For each point thus obtained, [H^+] was calculated according to eqn. (9). Log [H^+] was then plotted *vs.* log [L], with S_{corr} as parameter. From the slopes of these curves, $\bar{n}$ was obtained by eqn. (7′) as described on p. 550. Fig. 2 shows $\bar{n}$ as a function of log [L]. The different values of S give concurrent values of $\bar{n}$, a fact which is another indication that the complexes

Table 2. Corresponding values of S_{corr}, [H^+] and $S_{corr}[H^+]^{-2}$, as functions of [L]. In the region where S is not given, S_{corr} has been obtained directly from Fig. 1. The values in the last column are calculated from the final set of constants.

$S \times 10^4$ M	$S_{corr} \times 10^4$ M	$[H^+] \times 10^3$ M	$[L] \times 10^3$ M	$S_{corr}[H^+]^{-2} \times 10^4$ obs	$S_{corr}[H^+]^{-2} \times 10^4$ calc
2.839	2.187	999.4	0.228	2.187	2.199
1.040	0.800	1000	1.048	0.800	0.788
0.792	0.609	1000	2.021	0.609	0.611
0.715	0.550	1000	5.00	0.550	0.557
0.936	0.720	1000	9.95	0.720	0.714
	1.995	1000	24.80	1.995	1.990
	0.501	316.0	41.45	5.02	5.04
	1.000	315.9	57.1	10.02	10.10
	1.995	315.7	75.4	20.02	19.93
	0.501	100.0	105.0	50.1	49.8
	1.000	99.9	131.6	100.2	99.6
	1.995	99.7	162.5	200.7	200.0
	0.501	31.62	211.1	501	503
	1.000	31.52	255.3	1 007	1 019
	1.995	31.32	306.3	2 034	2 048
	0.501	10.02	384	4 990	5 000
	1.000	9.92	457	10 160	10 090
	1.995	9.71	547	21 160	21 130
	0.501	3.17	670	49 800	49 300
	1.000	3.07	800	106 300	104 500
	1.995	2.86	980	244 000	250 000
5.47	5.47	2.15	1397	1 180 000	1 180 000

are mononuclear. Fig. 2 also shows clearly that $\bar{n}$ reaches values higher than 5, for high [L]. This tends to prove, that a complex with more than five ligands is formed.

K_s^* $[L]^{-1}$ X was calculated from corresponding values of S_{corr} and $[H^+]$, according to eqn. (4′) (Table 2). The values from the intersection at $\log S_{corr} = -3$ were not used here, since their $K_s^*[L]^{-1}X$ values coincide, mainly, with those at $\log S_{corr} = -4$. On the other hand, solubilities at $[L] < 10^{-2}$ M and $[L] > 1$ M were included, the experimental points being used directly.

The values of K_s^* and the various β_n were determined by graphical extrapolations.[12] The values were then refined with a least squares program on a computer, which also gave the standard deviations of the constants.

There was no indication of the formation of any complex with more than six ligands. It was therefore concluded that $N = 6$. Furthermore, the formation of a relatively strong fifth complex had to be assumed. The second and fourth complexes, on the other hand, are relatively weak.

The following values of the constants were obtained (units M^{-n}) $\beta_1 = (9.2 \pm 0.4) \times 10^2$, $\beta_2 = (1.9 \pm 0.5) \times 10^4$, $\beta_3 = (5.0 \pm 0.4) \times 10^6$, $\beta_4 = (7.6 \pm 3.3) \times$ $\times 10^6$, $\beta_5 = (4.1 \pm 0.2) \times 10^8$, $\beta_6 = (2.3 \pm 0.2) \times 10^8$ and $K_s^* = (4.1 \pm 0.1) \times 10^{-8}$.

DISCUSSION

The study presented here supports the view expressed in an earlier article,[7] that solubility measurements constitute an accurate method which can often be arranged in such a way that the number of metal ions as well as ligand ions in the complexes can be elucidated.

For the explanation of the present data, as well as those obtained by, *e.g.*, Mironov *et al.*[13] and Haight *et al.*,[2] the assumption is required that a sixth complex, $BiCl_6^{3-}$, is formed. The data of Newman and Hume [5] do not exclude the formation of $BiCl_6^{3-}$, although those authors chose $BiCl_5^{2-}$ as the final complex (*cf.* discussion by Haight [2]). $N = 5$ has also been favoured by Dyrssen.[3] However, the solvent extraction data presented in Fig. 3 of his paper [3] can quite clearly be better explained with $N = 6$, according to the present author. The measurements by Ahrland and Grenthe [6] are inconclusive, regarding the final complex, since only moderately high $[Cl^-]$ were employed, and the reproducibility was rather poor.

Regarding the existence of $BiCl_5^{2-}$, besides the final $BiCl_6^{3-}$, Haight's data [2] seem to be best explained if $BiCl_5^{2-}$ is excluded. On the other hand, the same complex is necessary to explain the data of this study as well as the data of, *e.g.*, Mironov *et al.*[13]

A Ramau study by Oertel and Plane [14] supports the view that both $BiCl_5^{2-}$ and $BiCl_6^{3-}$ exist in solution.

The observed narrow range of existence of the second complex seems to be in agreement with most other studies.[4-6,13] It may be noted that Newman and Hume [5] reported some serious trouble with establishing the stability constant and molar absorbance for $BiCl_2^+$.

Table 3. Comparison between the results of some representative studies on the $Bi^{3+}-Cl^-$ system.

$n \longrightarrow$		1	2	3	4	5	6
Ref.	I	$\log \beta_n$					
Newman [5]	1 M	2.4	3.5				
Loman [4]	1.9 M	2.3	3.9	5.3			
Ahrland [6]	2 M	2.4	3.7	5.4	6.1	6.7	6.6
Mironov [13]	3 M	2.2	3.5	5.8	6.8	7.3	7.4
This work	4 M	3.0	4.3	6.7	6.9	8.6	8.4
Newman [5]	5 M			5.8	6.2	6.7	—

As Table 3 shows, the stability constants obtained by various authors differ appreciably. Most of the differences may be explained as resulting from differences in medium. Thus, the table shows that most of the constants increase when going from 2 M to 3 M to 4 M ionic strength, a trend which also has been found by Desideri and Pantani,[15] at least for the higher complexes. The set of constants given by Newman and Hume [5] at 5 M ionic strength deviates from this pattern, however.

Summarizing, a substantial amount of data supports the view that $BiCl_6^{3-}$ is the final complex, while some disagreement remains about the existence of $BiCl_5^{2-}$.

Preliminary calculations show that the solubility method used here would unfortunately be less successful on the bismuth(III) *bromide* system: only low [L] could be reached, where the complex formation is far from completion. However, the region of high [L] is, also on this system, the one where interesting and controversial results have been claimed. In particular, Preer and Haight [16] reported the formation of $BiBr_8^{5-}$ at high [Br^-].

The author is indebted to Dr. C. G. Ekström for providing the computer program.

REFERENCES

1. Martell, A. E. and Sillén, L. G. *Stability Constants,* The Chemical Society, London 1964.
2. Haight, Jr., G. P., Springer, C. H. and Heilmann, O. J. *Inorg. Chem.* **3** (1964) 195.
3. Dyrssen, D. *Svensk Kem. Tidskr.* **77** (1965) 387.
4. Loman, H. and van Dalen, E. *J. Inorg. Nucl. Chem.* **28** (1966) 2037.
5. Newman, L. and Hume, D. N. *J. Am. Chem. Soc.* **79** (1957) 4576.
6. Ahrland, S. and Grenthe, I. *Acta Chem. Scand.* **11** (1957) 1111; *Correction, ibid.* **15** (1961) 932.
7. Johansson, L. *Coord. Chem. Rev.* **3** (1968) 293.
8. Noyes, A. A., Hall, F. W. and Beattie, J. A. *J. Am. Chem. Soc.* **39** (1917) 2526.
9. Yatsimirskiĭ, K. B. *Sb. Stateĭ Obshcheĭ Khim. Akad. Nauk SSSR* **1** (1953) 97.
10. Haight, Jr., G. P. and Johansson, L. *Acta Chem. Scand.* **22** (1968) 961.

11. Haight, Jr., G. P. and Johansson, L. *Inorg. Chem.* **7** (1968) 1255.
12. Rossotti, F. J. C. and Rossotti, H. *The Determination of Stability Constants*, McGraw, New York 1961.
13. Mironov, V. E., Kul'ba, F. Ya., Fedorov, V. A. and Nikitenko, T. F. *Zh. Neorg. Khim.* **8** (1963) 1852.
14. Oertel, R. P. and Plane, R. A. *Inorg. Chem.* **6** (1967) 1960.
15. Desideri, P. and Pantani, F. *Ric. Sci.* **29** (1959) 1436; (See Ref. 1).
16. Preer, J. R. and Haight, Jr., G. P. *Inorg. Chem.* **5** (1966) 656.

Received July 2, 1968.