FLUOROSILICATE EQUILIBRIA IN ACID SOLUTION

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Abstract—The reaction between silicic acid and the fluoride ion in aqueous solution has been investigated at 25°C in a 3 m (Li)ClO₄ medium, by potentiometric methods employing a fluoride ion-selective electrode to observe the free hydrogen fluoride concentration. The acidity varied between 0.3 and 3 m, while the concentration of silicic acid was maintained below 2.5×10^{-3} m which is thought to be the saturation level of amorphous silica.

The experimental data have been explained in terms of Si(OH)₃F, SiF₄, SiF₆²⁻, HSiF₆⁻ and a minor species to which the composition Si(OH)₂F⁺ has been tentatively assigned.

The reactions that occur between the fluoride ion and silicic acid in aqueous solution are poorly understood. The only species whose identity is well established from Raman and NMR spectroscopy¹ as well as potentiometric evidence² is SiF_6^{2-} . On the other hand, there are no definitive conclusions on equilibria involving the intermediate species of the type $Si(OH)_t F_n^{4-t-n}$ which may be formed. These are of considerable interest if a detailed and complete discription is to be made in naturally occurring systems, such as geothermal brines, where both the F^- ion and $Si(OH)_4$ are usually present.

Busey et al.² investigated the fluorosilicate equilibria in the acidity range $10^{-2}-10^{-6}$ m. Under these conditions, in addition to SiF_6^{2-} , a minor species, whose composition could not be uniquely defined, seems to be present in a small amount. The inter-

- A total fluoride ion concentration.
- B total Si(IV) concentration.
- $\beta_{p,n}$ equilibrium constant for the formation of $Si(OH)_i F_n^{4-n-i}$, eq. (1).
- h concentration of H⁺.
- H analytical concentration excess of H^+ , = $[ClO_4^-]-[Li^+]-[Na^+]$.
- K_n conditional constant for all species with $n F^-$, eq. (7).
- Z average number of fluoride ions bound per silicon(IV), = $(A a [F^-] 2[HF_2^-])/B$.

Concentrations and equilibrium constants are expressed in molal units.

mediate complexes are more conveniently examined by extending the acidity range to values higher than 10^{-2} m. In fact, the general reaction scheme

$$Si(OH)_4 + nHF$$

 $\Leftrightarrow \operatorname{Si}(\operatorname{OH})_{t} F_{n}^{4-t-n} + p \operatorname{H}^{+} + s \operatorname{H}_{2} \operatorname{O} \quad (1)$

clearly indicates that an acidity increase quenches the formation of SiF_6^{2-} and favours complexes bearing less than six fluoride ions which are produced with p = 0.

The aim of this investigation was that of studying the fluorosilicate equilibria at 25° C in the acidity range 0.3-3 m.

METHOD

The method consisted of the determination of the hydrogen fluoride concentration, a, using a fluoride ion-selective electrode (EF), in a series of solutions containing silicon(IV) and hydrofluoric acid in various amounts. To minimize the variation in the activity coefficients, the solutions were maintained at 3 m ClO₄, by adding LiClO₄. This salt, instead of NaClO₄, was chosen because of the premature precipitation of Na₂SiF₆ if a large excess of Na⁺ is present. 3 m LiClO₄ was used as the reference state and consequently the activity coefficient of a reacting species is defined as tending to unity as the composition of the test solution approaches this pure salt solution.

The test solutions (TS) had the general composition $B \,\mathrm{m}\,\mathrm{Si}(\mathrm{IV})$, $A \,\mathrm{m}\,\mathrm{F}^-$, $H \,\mathrm{m}\,\mathrm{H}^+$, $2B \,\mathrm{m}\,\mathrm{Na}^+$, $(3-H-2B) \,\mathrm{m}\,\mathrm{Li}^+$, $3 \,\mathrm{m}\,\mathrm{ClO}_4^- = \mathrm{TS}$,[†] The silicon

^{*}Author to whom correspondence should be addressed. † Symbols :

a concentration of HF.

concentration was varied from 0.65×10^{-3} to 2.5×10^{-3} m, which we believe is below the saturation level of amorphous silica. The *H* values were in the range 0.3–3 m. Under these conditions the F⁻ and HF₂⁻ ions attain negligible concentrations³ compared to those of other fluoride-bearing species, so that *Z* could be calculated without knowledge of their exact concentrations.

The *a* values in TS were determined with cell(I)

$$-EF/TS, Q \cdot QH_2(s)/Au^+$$
 (I)

where EF and $Q \cdot QH_2$ stand for the fluoride ionselective electrode and quinhydrone, respectively. The EMF of cell(I) can be expressed at 25°C by

$$E = E'_0 + 0.05916 \log (a\gamma_{\rm HF}) + E_{\rm g}$$
(2)

in which E'_0 is a constant, $\gamma_{\rm HF}$ is the activity coefficient of HF and E_q is a correction term for the basicity of *p*-benzoquinone.⁴ In each experiment, carried out as by potentiometric titration, *H* was kept constant while *Z* was varied. Since B < 0.01*H*, the composition of TS did not change sensibly to cause variations in $\gamma_{\rm HF}$ and E_q . Consequently, *a* could be calculated from eq. (3)

$$E = E_0 + 0.05916 \log a \tag{3}$$

where $E_0 = E_0(H)$ includes $\gamma_{\rm HF}$ and $E_{\rm q}$.

Each titration was divided into two parts. In the first, E_0 was determined in the absence of Si^(IV). Under the chosen experimental conditions [F⁻] and [HF₂⁻] are negligible so that reliable E_0 values could be calculated by putting a = A in eq. (3). E_0 values which are constant to within 0.1 mV were obtained in the A range from 10^{-4} to 4×10^{-3} m.

In the second part silicic acid was added and the complex formation was followed by increasing the A/B ratio. In a few instances the A/B ratio was decreased by adding Si(OH)₄ to the HF solutions. The coincidental nature of the data obtained in the forward and backward titrations served as the criterion for true equilibrium. With E_0 being known, a could be deduced from eq. (3) and the average number of fluoride ions bound per Si^(IV), Z, could be obtained, neglecting [F⁻] and [HF₂⁻], as Z = (A-a)/B. The $Z(\log a, B)_H$ data form the basis of the following treatment.

EXPERIMENTAL

Materials and analysis

A freshly prepared silicic acid solution was employed for each experiment and no attempt was made to store stock solutions. The silicon source was "sodium metasilicate" Na₂SiO₃ \cdot 9H₂O. The salt, dissolved in the minimum amount of water, was added in portions under vigorous stirring to an acidic medium with an H^+ excess. Prior to the addition of silicate the weight of the acid medium was about 90% of the final one. The resulting clear solution was immediately employed for the EMF measurements. Solutions after leaving for a few hours gave coinciding data within 0.2 mV. On the other hand, systematic deviations were observed with samples stored for two days.

 $Na_2SiO_3 \cdot 9H_2O$, Baker p.a., was used without purification. It was kept in a desiccator filled with the $Na_2SiO_3 \cdot 9H_2O$ so that the vapour pressure remained constant and the silicate composition did not vary appreciably. The percentage of Na^+ was determined acidimetrically with standardized HCl. The amount of Si^(IV) was established gravimetrically using silica insolubilization by repeated acid treatment. The analyses agreed to within 0.2%.

Lithium fluoride, lithium perchlorate and perchloric acid were prepared and analysed as described in previous publications.^{5,6} The quinhydrone, Merck p.a., was recrystallized from water and dried over conc. H_2SO_4 . No Fe^(III) or Cl⁻ ions could be detected in the final product.

Details of the EMF measurements

The potentiometric titration was performed by immersing cell (I) in a silicone oil thermostat maintained at $25.00 \pm 0.02^{\circ}$ C. The fluoride electrode and apparatus were the same as described in a previous paper.⁷ The EMF values were measured within ± 0.1 mV with a Keithly 195 system DMM multimeter. To measure the potential of the membrane electrode a preamplifier Analog Device 309 K was used. The constancy of the potential was reached 10 min after the addition of reagents and remained unchanged for several hours within 0.1 mV.

DATA AND CALCULATIONS

The $Z(\log a, B)_H$ data are collected in Table 1 and are graphically represented in Fig. 1. As this shows, the Z values for increasing a tend to six and the points, for a different B but the same H value, form a single curve. This means that we are dealing with mononuclear silicon complexes Si(OH)_t F_n^{A-t-b} with $n \le 6$. In order to assess the t, n and $\beta_{p,n}$ values of the predominating complexes, the data were processed as follows. Firstly, the number of F⁻ bound per Si^(IV) and the conditional constants K_n were determined by considering separately data for a given H. Then, by examining the dependence of K_n on H the values of t and preliminary $\beta_{p,n}$ values were calculated. Finally, the equilibrium constants were $H = 0.3 \text{ m}, Z(-\log a, B \times 10^3)$

- (a) 0.170 (3.100, 2.431); 0.192 (3.043, 2.421); 0.219 (2.988, 2.410); 0.261 (2.909, 2.391);
 0.323 (2.838, 2.369); 0.411 (2.767, 2.341); 0.561 (2.691, 2.301); 0.745 (2.637, 2.260); 0.972 (2.591, 2.216); 1.25 (2.554, 2.168); 1.60 (2.514, 2.110); 2.03 (2.476, 2.046); 2.44 (2.444, 1.987); 2.93 (2.410, 1.922); 3.57 (2.368, 1.840); 4.03 (2.334, 1.782); 4.43 (2.302, 1.731);
 4.84 (2.267, 1.677); 5.14 (2.229, 1.631); 5.37 (2.197, 1.593); 5.55 (2.162, 1.555); 5.75 (2.108, 1.500); 5.86 (2.054, 1.446); 5.93 (2.008, 1.397); 5.98 (1.952, 1.334); 5.85 (2.040, 1.653).
- (b) 0.232 (2.980, 1.296); 0.294 (2.879, 1.284); 0.359 (2.814, 1.275); 0.410 (2.770, 1.267); 0.511 (2.721, 1.257); 0.604 (2.681, 1.247); 0.844 (2.618, 1.227); 1.25 (2.554, 1.199); 1.79 (2.498, 1.168); 2.68 (2.431, 1.120); 3.48 (2.377, 1.080); 4.28 (2.322, 1.039); 4.92 (2.265, 1.001); 5.41 (2.201, 0.963); 5.66 (2.143, 0.932); 5.80 (2.106, 0.911); 5.91 (2.027, 0.865); 5.42 (2.182, 1.382); 4.46 (2.290, 1.905); 2.91 (2.399, 2.992).

$$H = 1.0 \text{ m}, Z(-\log a, B \times 10^3)$$

- (a) 0.448 (2.716, 1.897); 0.595 (2.608, 1.882); 0.801 (2.552, 1.867); 1.09 (2.493, 1.849); 1.43 (2.444, 1.830); 1.78 (2.396, 1.810); 2.39 (2.344, 1.780); 3.01 (2.295, 1.749); 3.65 (2.244, 1.718); 4.36 (2.190, 1.682); 4.71 (2.136, 1.656); 5.13 (2.080, 1.626); 5.45 (2.018, 1.594); 5.63 (1.959, 1.565); 5.64 (1.915, 1.544); 5.80 (1.855, 1.508); 5.92 (1.798, 1.471); 6.01 (1.751, 1.437).
- (b) 0.295 (2.880, 1.346); 0.404 (2.732, 1.337); 0.539 (2.669, 1.330); 0.797 (2.559, 1.317); 1.04 (2.507, 1.308); 1.47 (2.441, 1.294); 1.87 (2.384, 1.280); 2.48 (2.341, 1.264); 3.36 (2.267, 1.239); 4.15 (2.203, 1.215); 4.73 (2.131, 1.191); 5.21 (2.062, 1.167); 5.52 (2.023, 1.153).

$$H = 3.0 \text{ m}, Z(-\log a, B \times 10^3)$$

0.248 (3.065, 1.866); 0.313 (2.956, 1.859); 0.372 (2.863, 1.852); 0.452 (2.769, 1.843); 0.538 (2.694, 1.834); 0.683 (2.603, 1.820); 0.876 (2.520, 1.804); 1.21 (2.432, 1.780); 1.55 (2.375, 1.760); 2.07 (2.306, 1.730); 2.52 (2.258, 1.705); 3.02 (2.209, 1.678); 3.64 (2.145, 1.642); 4.27 (2.071, 1.601); 4.64 (2.015, 1.570); 5.05 (1.942, 1.529); 5.37 (1.868, 1.484); 5.55 (1.810, 1.447).



Fig. 1. Z, the average number of fluoride ions bound per silicon(IV), as a function of $\log a$, at three acidities. The experimental uncertainty is shown when it is significantly larger than the symbol used. The curves were calculated using the equilibrium constants of Table 3.

refined using numerical methods based on the principle of least-squares.

Treatment of data at constant H

In this section we consider data for every H value separately. If only mononuclear complexes are formed we may express Z as in eq. (4)

$$Z = \sum n\beta_{p,n}\Gamma_{p,n}h^{-p}a^n/(1+\Sigma\beta_{p,n}\Gamma_{p,n}h^{-p}a^n) \quad (4)$$

where *n* and *p*, = n+t-4, are integers, $\beta_{p,n}$ is the equilibrium constant for the formation of Si(OH)_t F_n^{4-n-t} , eq. (1) and $\Gamma_{p,n}$ stands for

$$\Gamma_{p,n} = \gamma_{\rm HF}^n \gamma_{\rm Si(OH)_4} \gamma_{\rm H}^{-p} \gamma_{t,n}^{-1}$$
(5)

where γ is the activity coefficient. At a given *H* level, since $B < 0.01 \ H$, $\Gamma_{p,n}$ by good approximation is constant and furthermore, *h* must be very close to *H*. As a consequence, eq. (4) can be written as follows:

$$Z = \sum n K_n a^n / (1 + \sum K_n a^n) \tag{6}$$

where

$$K_n = K_n(H) = \Sigma \beta_{p,n} \Gamma_{p,n} H^{-p}.$$
 (7)

To determine n and K_n the experimental data were compared with model functions representing various hypotheses. Acceptable agreement was observed by assuming three complexes with n = 1, 4 and 6. The essential steps of the curve-fitting procedure are briefly described. Firstly, the *P* function, eq. (8), was constructed

$$\log P = \int_0^a Z \operatorname{d} \log a = \int_0^{a_0} Z \operatorname{d} \log a + \int_{a_0}^a Z \operatorname{d} \log a = \log (1 + \Sigma K_n a^n) \quad (8)$$

where a_0 represents the lowest measured *a* value. $\int_{a_0}^{a} Z d \log a$ was evaluated by the trapezoid rule, while the residual integral was found by extrapolation of the plot antilog ($\int_{a_0}^{a} Z d \log a$) against *a* which was linear for the lowest three or four points.

Secondly, the $\log \{(P-1)/a\}(\log a)$ data were

confronted with the normalized form $Y(\log u)_L$, eqs. (9)-(11), corresponding to the presence of complexes with n = 1, 4 and 6

$$Y = \log \{ (P-1)/a \} - \log K_1 = \log(1 + Lu^3 + u^5)$$
(9)

$$\log u = \log a + (1/5) \log (K_6/K_1)$$
(10)

$$L = K_4 K_1^{-2/5} K_6^{-3/5}.$$
(11)

The conditional constants given in Table 2 were computed, using eqs. (9)-(11), from the differences $Y-\log(P-1)+\log a$, $\log u-\log a$ and L which were read off at the position of best agreement.

More direct evidence for the presence of species with n = 4, instead of 3 or 5, was afforded by comparison of the data in the form of $\log \{[P(Z-1)+1]/a^6\}$ versus $\log a$, with the family of theoretical functions $F_N(\log w)$, eqs. (12) and (13), and calculated with N = 3, 4 and 5

$$F_N = \log\left(1 + ((N-1)/5)w^{(N-6)}\right) \tag{12}$$

$$K_N K_6^{-1} a^{(N-6)} = w^{(N-6)}.$$
 (13)

The comparison of data at H = 3 m is shown in Fig. 2. Clearly, a good fit is observed only with N = 4, while systematic trends are produced by neighbours. The position of best agreement gave the K_4 and K_6 constants in Table 2.

Evaluation of the most probable t

To determine t we examined the dependence of K_n on H, according to eq. (7). The correct interpretation of the data requires the knowledge of how $\Gamma_{p,n}$ varies when Li⁺ is replaced by H⁺. Medium effects were estimated by the specific interaction theory.⁸ For unchanged ionic strength and ClO₄⁻ molality, the activity coefficient of positively charged ions can be taken as constant. Activity coefficients for anions and for neutral molecules vary in the extent to which interactions with Li⁺ and H⁺ differ. Owing to the similarities of H⁺ and Li⁺, we postulated constant activity coefficients for anions and neutral species. Thus, $\Gamma_{p,n}$ equals unity in the medium scale.

As Table 2 indicates, K_4 within the limits of esti-

<i>H</i> , m	$\log K_1$	$\log K_4$		$\log K_6$		
		eqs (9–11)	eqs (12, 13)	eqs (9–11)	eqs (12, 13)	
0.3	2.45 ± 0.02	9.46 ± 0.1	9.48 ± 0.1	14.65 ± 0.03	14.60 ± 0.05	
1.0	2.52 ± 0.03	9.39 <u>+</u> 0.1	9.30 ± 0.1	13.97±0.03	14.00 ± 0.05	
3.0	2.59 ± 0.02	9.40±0.1	9.37±0.1	13.44 ± 0.03	13.45 ± 0.05	

Table 2. Survey of the conditional K_n constants



Fig. 2. Measurements at 3 m H⁺. Comparison of $\log \{[P(Z-1)+1]/a^6\}$ versus $\log a$ with the family of model curves, eqs (12) and (13), calculated for 6-N = 1, 2 and 3.

mated error, does not depend on H, which means that SiF₄ is present. The average K_4 was taken as the preliminary $\beta_{0,4}$ value (Table 3).

On the other hand, K_1 varies slightly with H, hence species with $p \neq 0$ are also formed. The plot of K_1 versus H (Fig. 3) can be well approximated by a straight line, indicating the presence of Si(OH)₃F and Si(OH)₂F⁺. The $\beta_{0,1}$ and $\beta_{-1,1}$ values, evaluated from the intercept and slope of the best line drawn through the points, are given in Table 3.

The variation of K_6 with H was explained by the presence of HSiF_6^- and SiF_6^{2-} . The validity of this hypothesis is demonstrated by the linear dependence of K_6H with H^{-1} , shown in Fig. 4. The $\beta_{1,6}$ and $\beta_{2,6}$ constants are listed in Table 3.

Refinement of the equilibrium constants

The equilibrium constants were refined by numerical procedures founded on the principles of least-squares, proposed by Sillén.⁹ The computation consisted of minimizing the sum.

$$U = \Sigma (1 - Z_c/Z)^2,$$
 (14)

in which Z_c indicates a value calculated with a given set of $\beta_{p,n}$. The results are given in Table 3. The



Fig. 3. K_1 as a function of *H*. The straight line represents 270+43H.

constants are seen to differ insignificantly from those found graphically.

As a quantitative measure of the agreement between experimental data and the proposed model we considered the distribution of the deviations $(1-Z_c/Z)$. From a total of 95 data points, 59 showed an average positive deviation of 1.8%, whilst 36 showed a negative deviation of 2.1%. No systematic trend was observed in the *H* and *Z* functions.

CONCLUSION

The main result of the present investigation can be summarized by stating that in solutions where $0.3 \le H \le 3$ m the predominating fluorosilicate complexes are Si(OH)₃F, SiF₄, HSiF₆⁻ and SiF₆²⁻. The minor species, Si(OH)₂F⁺ is tentatively suggested on the basis of small changes of K_1 with H. We feel that the assignment of such a complex calls for more detailed information about the medium effects caused by the substitution of LiClO₄ with HClO₄ on the variation of activity coefficients of neutral species (Si(OH)₃F and HF).

Figure 5 illustrates the distribution of fluorosilicates as a function of the hydrofluoric acid concentration at different acidity levels. Clearly, if $Si(OH)_2F^+$ exists, it amounts to only 2% of the total $Si^{(IV)}$ at 1 m H⁺. It is evident that the acidity promotes displacement of the curves representing SiF_6^{2-} and $HSiF_6^-$ so that room is left for intermediate species.

Table 3. Survey of equilibrium constants

	$\log \beta_{0,1}$	$\log \beta_{-1,1}$	$\log \beta_{0,4}$	$\log \beta_{1,6}$	$\log \beta_{2,6}$
Graphical	2.43 ± 0.03	1.63±0.15	9.43±0.1	13.88 ± 0.05	13.23 ± 0.1
Least-squares (3σ)	2.40 + 0.01	1.66±0.10	9.35±0.03	13.88 ± 0.03	13.23 ± 0.06



Fig. 4. K_6H as a function of H^{-1} . The line was calculated with $K_6H = 0.76 \times 10^{14} + 0.17 \times 10^{14} H^{-1}$.

COMPARISON WITH OTHER DATA

From the data of Busey *et al.*² at 25°C in 1 m NaCl, we calculate, using an equilibrium constant of $10^{2.89}$ for H⁺ + F⁻ \rightleftharpoons HF, $\log \beta_{2,6} = 12.4$ which, on account of medium differences, compares well with our 13.23. At the highest acidity studied by these authors, i.e. 10^{-2} m, SiF₄ is present in small amounts and explains its escape of detection. Also Si(OH)₃F accounts for less than 12% of the total Si^(IV). Owing to the difficulties of uniquely defining the composition of minor complexes, Busey *et al.* assigned the formula Si(OH)₂F₂ to this component.

Borodin and Kim Zao employed the ¹⁹F NMR method to investigate Li₂SiF₆—HClO₄¹⁰ as well as HF—SiO₂—HClO₄¹¹ solutions. The species SiF₄ and SiF₅⁻ were postulated. From the constants proposed by these authors we derived log $\beta_{2,6} = 11.6$ and log $\beta_{0,4} = 7.60$. The discrepancies of the constants in Table 3 are explainable in terms of the different ionic media and also from the neglect of HSiF₆⁻ and Si(OH)₃F species which are important components in the strongly acidic media employed by Borodin and Kim Zao.

Plakhotnik and Kotlyar¹² have determined the solubility of K_2SiF_6 as a function of the HCl concentration in a 0.4 M (Li)Cl medium. The data were explained with SiF_5^- . However, according to our findings, relatively high concentrations of $Si(OH)_4$, [Si(OH)₃F] and SiF₄ would also be produced. The limited number of data points, six, makes the recalculation arduous.

There have been several reports on the solubility equilibria of amorphous silica in concentrated H_2SiF_6 . Kleboth¹³ measured the solubility of "precipitated" silicic acid as a function of H_2SiF_6 and $HClO_4$ concentration at 25°C in 4 M LiClO₄. From data at the highest concentrations of these com-



Fig. 5. Distribution of fluorosilicates as a function of the free hydrofluoric acid concentration. Results are shown for the following three acidities: (a) 1 m H⁺ (b) 0.1 m H⁺ and (c) 0.01 m H⁺. (1) Si(OH)₄; (2) Si(OH)₃F; (3) Si(OH)₂F⁺; (4) SiF₄; (5) SiF₆²⁻; (6) HSiF₆⁻.

ponents, where the main species are SiF_4 and $HSiF_6^-$, evaluate for $SiO_2(s) + 2H^+ + 2HSiF_6^- \rightleftharpoons$ we $3SiF_4 + 2H_2O$ a constant of $10^{-2.5 \pm 0.3}$ which agrees fairly well with $10^{-2.4}$, obtainable from the data of Table 3, and the solubility of SiO₂, $\sim 10^{-2.7}$ m. On the contrary, the solubility determinations by Thomsen¹⁴ and Ryss and Plakhotnik¹⁵ indicate values which are three times greater than those predictable from our results. Plausible explanations are either the presence of additional complexes in concentrated H₂SiF₆ solutions, or highly active silica involved in the heterogeneous equilibria. The authors furnish no information on the composition or properties of the solid phase, thus making the comparison difficult.

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REFERENCES

1. P. A. W. Dean and D. F. Evans, J. Chem. Soc., A 1967, 698.

- 2. R. H. Busey, E. Schwartz and R. E. Mesmer, *Inorg. Chem.* 1980, **19**, 758.
- 3. L. Ciavatta, Arkiv Kemi 1963, 21, 129.
- 4. G. Biedermann, Acta Chem. Scand. 1956, 10, 1340.
- L. Ciavatta, R. De Capua and R. Palombari, J. Inorg. Nucl. Chem. 1981, 43, 1305.
- L. Ciavatta, M. Iuliano and R. Porto, Polyhedron 1987, 6, 1283.
- 7. L. Ciavatta and A. Pirozzi, Polyhedron 1983, 2, 769.
- 8. L. Ciavatta, Annal. Chim. (Rome) 1980, 70, 551.
- 9. L. G. Sillén, Acta Chem. Scand. 1962, 16, 159.

- P. M. Borodin and N. Kim Zao, Russ. J. Inorg. Chem. 1971, 16, 1720.
- 11. P. M. Borodin and N. Kim Zao, Russ. J. Inorg. Chem. 1972, 17, 959.
- 12. V. N. Plakhotnik and T. N. Kotlyar, Russ. J. Phys. Chem. 1976, 50, 723.
- 13. K. Kleboth, Monatsh Chem. 1968, 99, 1177.
- 14. S. M. Thomsen, J. Am. Chem. Soc. 1952, 74, 1690.
- 15. I. G. Ryss and V. N. Plakhotnik, Russ. J. Inorg. Chem. 1970, 15, 1742.