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The Complex Formation of Antimony(III) in Perchloric Acid and Nitric Acid Solutions. A Solubility Study

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The hydrolysis of antimony(III) in perchloric and nitric acid solutions has been investigated by solubility measurements at an ionic strength $I = 5.00$ M and a temperature of 25.0 °C.

In perchloric acid solutions the complexes $Sb(OH)_2^+$ and $Sb_2(OH)_2^{4+}$ exist in equilibrium with orthorhombic and cubic Sb_2O_3. The oxides are metastable for acidities over 0.26 M and 0.68 M, respectively, where $Sb_4O_5(OH)ClO_4 \cdot \frac{1}{2}H_2O$ is the stable phase. The monomer $Sb(OH)_2^+$, but not the dimer $Sb_2(OH)_2^{4+}$, is also found in equilibrium with this phase.

The only solid phase in equilibrium with nitric acid solutions of an acidity below 5.00 M is the oxide nitrate $Sb_4O_4(OH)_2(NO_3)_2$. Besides the complex $Sb(OH)_2^+$ also found in the perchloric acid solutions, the monomer $Sb(OH)^{2+}$ appears to be present.

On account of the strongly acidic properties of antimony(III), its chemistry in aqueous solution is very much dominated by hydrolytic reactions which have to be taken into account in all studies of its complex formation. Unfortunately, the course of the hydrolysis has not yet been clarified, not even in those instances where the anions present in the medium show little affinity for antimony(III) and therefore do not bring about any extensive formation of mixed complexes. Weakly complexing media should be provided by, *e.g.*, the perchlorate and nitrate ions, while the halide ions certainly form quite strong complexes. This investigation concerns the hydrolytic reactions taking place in solutions of the weakly complexing anions mentioned above.

The hydrolysis of antimony(III) has been previously studied,[1-5] mostly by the use of solubility measurements. Schuhmann[1] concluded from a study of the solubility of orthorhombic Sb_2O_3 in perchloric acid of molality between 0.231 and 1.133 that the species present in solution is SbO^+ and he calculated the constant for the corresponding equilibrium $\frac{1}{2}Sb_2O_3(s) + H^+ \rightleftharpoons SbO^+ + \frac{1}{2}H_2O$ (Table 7). Gayer and Garrett[2] found that the same equilibrium is established in hydrochloric acid of molality up to 0.1. Furthermore the value of the equilibrium constant is comparable for the two media (Table 7). Fridman *et al.*[4] verified Schuhmann's result from solubility measurements in perchloric acid. They also investigated the solubility of SbOCl in solutions of $HClO_4$ and NaCl at 25 °C and constant ionic strength $I = 6$ M (regulated by means of $NaClO_4$) and found the complexes $SbCl_5^{2-}$, $SbCl_4^-$ and $SbOHCl_3^-$. Jander and Hartmann[5] found from diffusion measurements that only monomeric SbO^+ and possibly small amounts of Sb^{3+} are present in perchloric acid solutions up to $C_H = 6$ M when the concentration of Sb(III) is ≤ 1 mM.

The present investigation started as a study of the solubility of the orthorhombic and cubic modifications of Sb_2O_3 in perchloric and nitric acid solutions of constant ionic strength, $I = 5.00$ M, maintained by sodium perchlorate and sodium nitrate, respectively. At the temperature of the measurements (25.0 °C) the orthorhombic modification, Sb_2O_3(or), is metastable but the transition into the stable cubic modification, Sb_2O_3(c), does not take place in aqueous solution. In practice, the transition is conveniently effected in the solid state at 550 °C; *cf.* below. Above 570 °C, Sb_2O_3(or) is the stable modification.

Though no conversion takes place between the oxide modifications, phase transitions are nevertheless observed. In perchloric acid, Sb_2O_3(or) is in fact stable only up to $C_H \approx 0.3$ M and Sb_2O_3(c) up to $C_H \approx 0.7$ M at the present total perchlorate concentration of 5.00 M. Both survive long enough, however, for metastable equilibria to be established even at acid concentrations up to $C_H = 4.0$ and 4.5 M, respectively. The stable phase formed at the transition is an oxide perchlorate $Sb_4O_5(OH)ClO_4 \cdot \frac{1}{2}H_2O$. A structure determination of this compound has been performed by Bovin[6] and has confirmed the above composition. At the highest acid concentrations used, $C_H = 4.50$ and 5.00 M, another perchlorate can be obtained as an intermediary metastable phase. Its empirical formula is $3Sb_2O_3.2Cl_2O_7.6H_2O$,[5] thus, as expected, corresponding to a less strongly hydrolyzed state of antimony(III) than in the former compound. This is immediately evident from the mol ratios perchlorate/antimony, Q_P, which are $Q_P = 1/4$ and 2/3 for the two phases, respectively, while a completely unhydrolyzed perchlorate would have $Q_P = 3$. The more hydrolyzed phase will, in the following, be denoted by Sbop(70) and the less hydrolyzed one by Sbop(55), the notation deriving from the antimony content (≈ 70 % and ≈ 55 %, respectively). The phase Sbop(70) can also exist in metastable equilibrium at lower values of C_H, where the oxides are the stable phases.

In order to investigate whether further transitions occur at higher acidities, resulting in compounds of even lower degrees of hydrolysis of antimony(III), the measurements have been extended to include concentrated perchloric acid, $C_H = 11.75$ M. In this higher acidity range a constant medium could not be maintained, so that identification of the species present in the solutions has not been possible. Further phase transitions have been observed, however. Besides Sbop(55), which only seems to exist as a metastable intermediate around $C_H = 5.00$ M, at least two more oxide perchlorates have been firmly identified. Thus, between $C_H = 6.7$ M and concentrated acid, $Sb(OH)_2ClO_4.H_2O$ [denoted Sbop(44)], with $Q_P = 1$, is the stable phase. In concentrated acid, an undoubtedly even less hydrolysed phase is stable. On account of the latter's extreme sensitivity to moisture, it has so far not been possible to determine its composition. The structures of these relatively little hydrolysed compounds might have features of relevance to the interpretation of the equilibria existing in solution. Efforts will therefore be made to determine the structures, although this will, particularly in the case of the least hydrolyzed compound, present great experimental difficulties.

In nitric acid at a nitrate concentration of 5.00 M, Sb_2O_3(or) and Sb_2O_3(c) are even less stable than in the perchloric acid solutions discussed above and they are transformed into an oxide nitrate of the composition $Sb_4O_4(OH)_2(NO_3)_2$, denoted in the following by Sbon. The transformation is, moreover, so fast that the oxides do not survive as metastable phases for any appreciable length of time. The mol ratio nitrate/antimony of Sbon is $Q_P = 1/2$, which means a degree of hydrolysis intermediate between Sbop(70) and Sbop(55). No other oxide nitrate has been observed up to $C_H = 5.00$ M, the highest concentration employed in the nitric acid measurements. The phase Sbon can also exist in metastable equilibrium with solutions of quite low acidity, at least down to $C_H = 0.005$ M. The crystal structure of $Sb_4O_4(OH)_2(NO_3)_2$ has been determined by Bovin[7] and has confirmed the composition.

NOTATIONS AND CALCULATIONS

Notations. The following symbols are used
S = total concentration of Sb(III)
C_H = total concentrations of hydrogen ions
S_i = concentration of the complex $Sb_l(OH)_p^{(3l-p)+}$
K_i = the calculated coefficient in the polynomial $\sum_i K_i C_H^{e_i}$
e_i = the calculated exponent in the polynomial $\sum_i K_i C_H^{e_i}$
K_i' = stability constant for complex formation
ΔG° = standard free energy change
$\mu(B)$ = chemical potential of the substance B
$a(B)$ = activity, relative activity of substance B
i to q are all integers

Calculation of complex formation. The solid phases considered in the solution equilibria here are Sb_2O_3(or), Sb_2O_3(c), $Sb_4O_5(OH)ClO_4 \cdot \frac{1}{2}H_2O$ and $Sb_4O_4(OH)_2(NO_3)_2$. In order to achieve the simplest formulation possible, the general formula $Sb_4O_{(6-j)}(OH)_j(Z)_j$, with $j = 0$, 1, 2 and $Z = ClO_4^-$

or NO_3^-, is employed in the following for these phases. The equilibria can thus be written as

$$k\mathrm{Sb_4O}_{(6-j)}(\mathrm{OH})_j(\mathrm{Z})_j(\mathrm{s})+m\mathrm{H}^+ \rightleftharpoons n\mathrm{Sb}_l(\mathrm{OH})_p{}^{(3l-p+)}+\ q\mathrm{H_2O}+kj\mathrm{Z}^-$$

with $m=n(3l-p)-kj$ (1)

and $4k=nl$ (2)

Elimination of k by combination of (1) and (2) gives

$$m/n=3l-p-lj/4 \quad (3)$$

Since the activities of H_2O and Z^- may be considered as constant in the media employed and since $[\mathrm{H}^+]\approx C_\mathrm{H}$, an equilibrium constant K_i' can be defined as follows:

$$K_i'=\frac{[\mathrm{Sb}_l(\mathrm{OH})_p{}^{(3l-p)+}]^n}{[\mathrm{H}^+]^m}\approx\frac{(S_i)^n}{C_\mathrm{H}{}^m} \quad (4)$$

and hence

$$S_i=(K_i')^{1/n}C_\mathrm{H}{}^{m/n} \quad (5)$$

The total concentration of Sb(III) in solution may be written as

$$S=\sum_i l_iS_i \quad (6)$$

(5) and (6) gives

$$S=\sum_i l_i(K_i')^{1/n}\ C_\mathrm{H}{}^{m/n} \quad (7)$$

and

$$S=\sum_i K_iC_\mathrm{H}{}^{e_i} \quad (8)$$

if

$$K_i=l_i(K_i')^{1/n} \quad (9)$$

and

$$m/n=e_i \quad (10)$$

From an experimental determination of S as a function of C_H it is clearly possible to derive the exponents e_i and the coefficients K_i. Each e_i-value allows several combinations of l and p in the complex $\mathrm{Sb}_l(\mathrm{OH})_p{}^{(3l-p)+}$. However, when the solubility S is measured for different solid phases, as is the case in this investigation, the number of combinations become more restricted. The calculation of e_i and K_i has been made both graphically and by a computer. When the e_i values are known it is possible to compute connected values of l and p from (10) and (3), since the value of j for the solid phase is known.

The graphical treatment was carried out in the following way: From the graph $S=\mathrm{f}(C_\mathrm{H})$ (*cf.* Figs. 3, 8) it is obvious that the polynomial (8) must contain a constant term K_1, *i.e.* $e_1=0$. The numerical value of K_1 was determined by a graphical extrapolation to $C_\mathrm{H}=0$. This value is not identical with the solubility of the particular solid phase in 5.00 M sodium perchlorate and sodium nitrate solution, the latter being found by direct measurements to be about twice as high (*cf.* Table 3). For $C_\mathrm{H}<0.005$ M other reactions resulting in a higher solubility evidently occur. In the following K_1 and e_1 are therefore treated as mathematical constants. Eqn. (8) can be written as

$$S-K_1=\sum_{i-1}K_{i-1}C_\mathrm{H}{}^{e_{i-1}} \quad (11)$$

which for low values of C_H can be approximated to

$$S-K_1\approx K_2C_\mathrm{H}{}^{e_2} \quad (11')$$

Hence

$$\ln\,(S-K_1)=e_2\ln C_\mathrm{H}+\ln K_2 \quad (11'')$$

A plot of $\ln\,(S-K_1)$ *versus* $\ln C_\mathrm{H}$ should yield e_2 as the slope and $\ln K_2$ as the intercept of a straight line. When the values of e_2 and K_2 are known eqn. (8) can be written as

$$S-K_1-K_2C_\mathrm{H}{}^{e_2}=\sum_{i-2}K_{i-2}C_\mathrm{H}{}^{e_{i-2}} \quad (12)$$

or, if terms of $i>3$ are neglected as

$$S-K_1-K_2C_\mathrm{H}{}^{e_2}\approx K_3C_\mathrm{H}{}^{e_3}. \quad (12')$$

It is then possible to determine the constant e_3 in the same way as e_2. Within the range of C_H investigated, the polynomial (8) could in fact be fitted with at most three terms.

In the computer treatment, a curve of the form $S=\sum_i K_iC_\mathrm{H}{}^{e_i}$ was fitted to the experimental data $((C_\mathrm{H})_r,S_r)$ by the least-squares program CURVEFIT.[8] The error square sum

$$\mathrm{CHISQ}=\sum_i\frac{1}{\sigma S_r}\,(S_{\mathrm{calc},r}-S_r)^2 \quad (13)$$

was minimized by the subroutine STEPIT,[9] where

$$S_{\mathrm{calc},r}=\sum_i K_i(C_\mathrm{H})_r{}^{e_i} \quad (14)$$

The least-squares treatment was first made with $e_1=0$ and with e_{i-1} and K_i as variables. Because the value of e_i must be rational, the nearest rational value was then chosen and kept constant in a subsequent refinement cycle which yield the final values of the constants K_i.

EXPERIMENTAL

Chemicals. Orthorhombic antimony(III)oxide [Sb_2O_3*(or)*] was prepared from Sb_2O_3 (Riedel-DeHaen *p.a.*) as follows. The oxide was dissolved in concentrated hydrochloric acid. After filtration, a sixfold volume of water was added to the solution. After three days in the mother liquor, the crystalline precipitate formed was separated and dissolved in a minimum amount of concentrated hydrochloric acid. This solution was then poured into a boiling solution of sodium carbonate. The Sb_2O_3(or) obtained was washed free of chloride ions with hot water and then dried at 110 °C. The antimony(III) content was checked (see below; found: 83.3 %, calc. for Sb_2O_3: 83.5 %) and a Guinier-Hägg powder photograph was taken to verify the orthorhombic phase.

Cubic antimony(III)oxide [Sb_2O_3*(c)*] was prepared from Sb_2O_3(or) as follows. A thick-walled glass tube was filled with Sb_2O_3(or), evacuated and heated to 550 °C. After 24 h the transformation to Sb_2O_3(c) was complete.[10] The antimony(III) content was checked (found: 83.3 %, calc. 83.5 %) and a Guinier-Hägg powder photograph verified the cubic phase.

During the investigation it was found accidentally that Sb_2O_3(c) could in fact be prepared at room temperature by washing of the metastable phase Sbop(55) with methanol. On prolonged treatment, all perchlorate is displaced and pure Sb_2O_3(c) is obtained.

All other chemicals used were *pro analysi* grade.

Procedure. The equilibrium of solid phase and solution was effected in 50 ml polyethylene flasks agitated in a thermostat at 25.0 °C. The agitation time varied between a few hours and more than two hundred days. (*cf.* below). Afterwards, the phases were separated within a few seconds by filtration through a membrane filter. Only the solid phases Sb_2O_3 (or and c) and Sbop(70) were washed with 5 ml methanol (*cf.* above) and dried. The other solid phases were only dried. The solution was immediately analysed for antimony(III).

Analysis. The solid phases, as well as the perchloric acid solutions with $C_H \geq 0.250$ M, were analysed for antimony(III) titrimetrically. The procedure employed was that described by Belcher,[11] Schulek and Rózsa,[12] and Schulek.[13] This method was not applicable to the nitric acid solutions. In this case, as well as for the perchloric acid solutions with $C_H \leq 0.250$ M, where the concentration of antimony(III) was very low, the analyses were performed spectrophotometrically with a Zeiss Spectrophotometer PMQII at 330 nm, by the method described by Elkind, Gayer and Baltz.[14] It was checked that Beer's law was obeyed (to within ± 3.0 %) for absorbances between 0.2 – 1.5. Both analytical methods were suitable for the measurement of the solubility in 250 mM perchloric acid and gave the same result within the limits of error. At least two samples were equilibrated with each solution. The solubilities could all be reproduced to within ± 3 %. The lower limit of $C_H = 0.0052$ M, was chosen for the reason that at lower acidities the solubility becomes too low even for the sensitive spectrophotometric method of analysis. Almost all solid phases were checked after equilibration by Guinier-Hägg X-ray photographs.

The 5.00 M stock solutions of sodium perchlorate and sodium nitrate were analyzed both by cation exchange and be weighing a dried sample, with concordant result. The C_H values of all perchloric and nitric acid solutions were checked alkalimetrically.

MEASUREMENTS AND RESULTS

Phase transformation in perchloric acid. In order to determine the time necessary to establish the various metastable and stable equilibria existing in perchloric acid solutions, Sb_2O_3(or) was shaken at $C_H = 3.00$ M and 5.00 M, and Sb_2O_3(c) at $C_H = 5.00$ M for a length of time varying from 5 min to more than 200 days (*cf.* Fig. 1). In 5.00 M acid, Sb_2O_3(or) never reached equilibrium before a transformation set in. For several hours the solid phase is a mixture

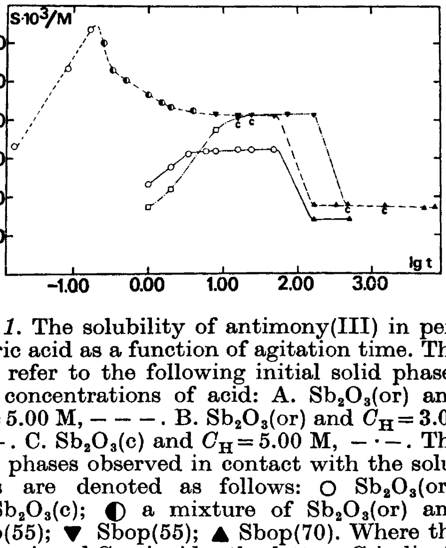

Fig. 1. The solubility of antimony(III) in perchloric acid as a function of agitation time. The lines refer to the following initial solid phases and concentrations of acid: A. Sb_2O_3(or) and $C_H = 5.00$ M, — — —. B. Sb_2O_3(or) and $C_H = 3.00$ M, —. C. Sb_2O_3(c) and $C_H = 5.00$ M, — · —. The solid phases observed in contact with the solutions are denoted as follows: ○ Sb_2O_3(or); □ Sb_2O_3(c); ◐ a mixture of Sb_2O_3(or) and Sbop(55); ▼ Sbop(55); ▲ Sbop(70). Where the curves A and C coincide, the letters C indicate that the points ▼ and ▲ originate from Sb_2O_3(c).

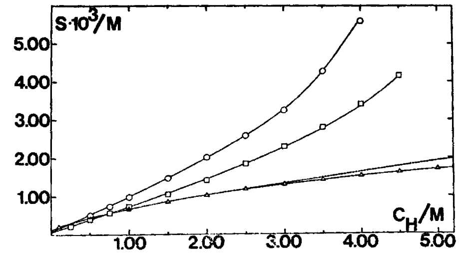

Fig. 2. The solubility of antimony(III) in perchloric acid solutions, at $I = 5.00$ M, up to $C_H = 5.00$ M. The symbols refer to the solid phases: ○ Sb_2O_3(or), □ Sb_2O_3(c) and △ Sbop(70). The dotted line refers to the computed polynomial, S_{calc}, for Sbop(70).

of Sb_2O_3(or) and Sbop(55), as evidenced both by determination of the antimony content and by Guinier-Hägg powder photographs. The phase Sbop(55) is then in metastable equilibrium for about 2 days. Transformation to the stable phase Sbop(70) then begins, being complete after a week or more. Transformation of Sb_2O_3 (c) to Sbop(55) takes place long before the equilibrium with Sb_2O_3(c) has been attained. In this case, the metastable equilibrium involving Sbop(55) is therefore attained from below saturation (*cf.* Fig. 1). After another few days, the final transformation into the stable phase Sbop(70) begins. Some fifteen days later the transformation is complete and the solution has attained equilibrium. In 3.00 M acid, Sb_2O_3(or) remains unchanged for at least thirty hours, which is time enough for a metastable equilibrium to be established. The transformation to Sbop(70) then begins and after fourteen days the equilibrium between the stable phase Sbop(70) and the solution has been attained. There is no evidence for a phase transformation from Sb_2O_3(or) *via* Sb_2O_3(c) to Sbop(70).

Solubility of Sb_2O_3(or) and Sb_2O_3(c) in perchloric acid. The solubilities of Sb_2O_3(or) and Sb_2O_3(c) in perchloric acid of varying concentration are given in Figs. 2 and 3. Between $C_H =$ 1.00 and 4.50 M, where both oxides are metastable, the agitation time was 24 – 30 h. Between $C_H = 0.250$ and 1.00 M the time could be extended up to eighty days without any transformation. Below $C_H = 0.68$ and 0.26 M, respectively, Sb_2O_3(c) and Sb_2O_3(or) are stable relative to Sbop(70). For $C_H > 4.00$ M the solubility of

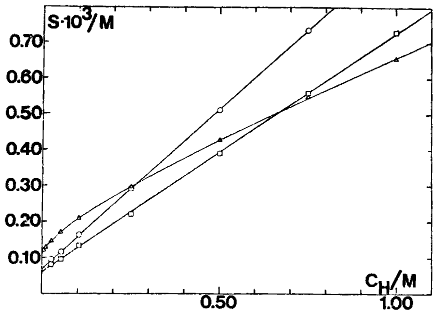

Fig. 3. The solubility of antimony(III) in perchloric acid solutions, at $I = 5.00$ M, up to $C_H = 1.00$ M. The symbols refer to the solid phases: ○ Sb_2O_3(or), □ Sb_2O_3(c) and △ Sbop(70).

Sb_2O_3(or) cannot be determined, because the transformation to Sbop(70), mostly *via* Sbop(55), is too rapid. The same is true for Sb_2O_3(c) when $C_H > 4.50$ M.

From eqn. (14), values of $e_2 = 1.0$ and $e_3 = 3.9$ were computed for Sb_2O_3(c), and 1.0 and 4.1 for Sb_2O_3(or), by means of the CURVEFIT-program. The least-squares treatment was repeated using the nearest integers $e_2 = 1$ and $e_3 = 4$. The calculated constants K_i and integer exponents e_i are given in Table 1. For both oxides the graphical treatment gives $e_2 = 1.0$ as the slope of the function $f(\ln C_H) = \ln (S - K_1)$ for $C_H < 3.0$ M (*cf.* Fig. 4). In Fig. 5, the function $f(\ln C_H) = \ln (S - K_1 - K_2 C_H^{e_2})$ is plotted for $1.5 < C_H < 5.00$ M and the slopes of the curves give $e_3 = 4.0$ for both oxides. The relative differences between calculated and experimental data are given in Table 2.

As $j = 0$ for Sb_2O_3(s), eqns. (3) and (10) give $e_i = m/n = 3l - p$, *i.e.* in this case the values of e_i yield directly the charges of the complexes formed, *viz.* +1 and +4. Explicitly

$$1 = 3l - p \qquad (3^{\mathrm{I}})$$

$$4 = 3l - p \qquad (3^{\mathrm{II}})$$

The only mononuclear complex with charge 1+ is $Sb(OH)_2^+$, but all polynuclear complexes $Sb(OH)_2(Sb(OH)_3)_{l-1}^+$ also fulfil the condition. No mononuclear complex with the charge 4+ is feasible, but all polynuclear species of the composition $Sb_2(OH)_2(Sb(OH)_3)_{l-2}^{4+}$ do fit. In the simplest case the equilibrium would involve the dinuclear complex $Sb_2(OH)_2^{4+}$:

$$Sb_4O_6(\text{or or c}) + 8H^+ \rightleftharpoons 2Sb_2(OH)_2^{4+} + 2H_2O$$

Table 1. The factors K_i and exponents e_i in the polynomial S_{calc}, calculated by a least squares computer program. The standard deviation in S was found to be approximately $S/100$. The numbers in parentheses are the standard deviations calculated by the least-squares program and refer to the last significant digit in each value. The polynomial is: $S_{\text{calc}} = K_1 + K_2C_H^{e_2} + K_3C_H^{e_3}$.

Solid phase Factors and exponents	Sb_2O_3(or)	Sb_2O_3(c)	$Sb_4O_5(OH)ClO_4 \cdot \frac{1}{2}H_2O$	$Sb_4O_4(OH)_2(NO_3)_2$
K_1	$0.705(3) \times 10^{-4}$	$0.621(2) \times 10^{-4}$	$0.1105(5) \times 10^{-3}$	$0.747(8) \times 10^{-4}$
K_2	$0.880(3) \times 10^{-3}$	$0.660(2) \times 10^{-3}$	$0.541(1) \times 10^{-3}$	$0.432(3) \times 10^{-3}$
e_2	1	1	3/4	1/2
K_3	$0.742(8) \times 10^{-5}$	$0.278(4) \times 10^{-5}$	–	$0.601(9) \times 10^{-4}$
e_3	4	4	–	3/2

In Table 4, a survey of the complexes compatible with the values of m/n is given.

The solubility of $Sb_4O_5(OH)ClO_4 \cdot \frac{1}{2}H_2O$- [Sbop (70)] in perchloric acid. In Fig. 2 and 3 the solubility of Sbop(70) as a function of C_H is plotted. A complete transformation of Sb_2O_3(or) into Sbop(70) can be achieved in the range $1.00 < C_H < 5.00$ M, though for the lowest value of C_H a very long agitation time is needed, at least 200 days. The transformation was checked by Guinier-Hägg powder photographs and titrimetric analysis of the solid phase. For $C_H = 0.75$ M, transformation was not complete in all samples even after 290 days, which is understandable as the difference in stability between the two phases is quite small at this value of C_H (*cf.* Fig. 3). All samples starting with Sb_2O_3(or) as solid phase reach equilibrium from supersaturation (*cf.* Fig. 1). In order that the equilibrium should be reached also from below saturation, samples of Sbop(70) were shaken with acid of C_H between 0.250 and 5.00 M for 82 days. Within experimental error, the same values of S were found by both methods. For $C_H < 0.68$ M, Sbop(70) is metastable relative to Sb_2O_3(c) and for $C_H < 0.26$ M also relative to Sb_2O_3(or), but no transformation to any of the oxides was ever found in these C_H regions. At values of $C_H < 0.250$ M the samples were agitated for 22 and 46 h with results that agreed well. When all data up to $C_H = 5$ M were inserted in eqn. (14), the best fit was obtained for $e_2 = e_3 = 0.71$. If only the values for $C_H \leq 3.50$ M

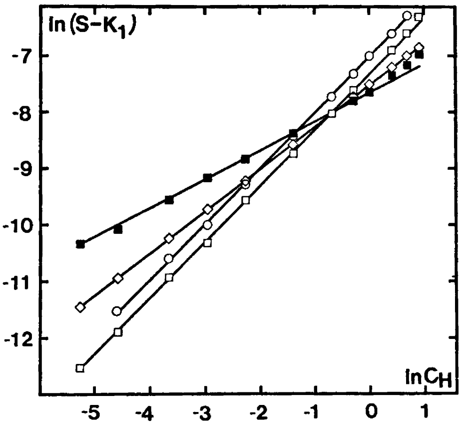

Fig. 4. ln $(S - K_1) = f(\ln C_H)$ for $C_H \leq 3.00$ M The slope of the plot is the e_2-value. The symbols refer to the solid phases: ○ Sb_2O_3(or), □ Sb_2O_3(c), ◇ Sbop(70) and ■ Sbon.

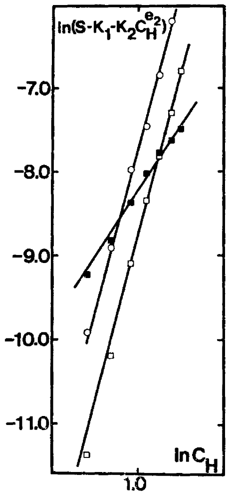

Fig. 5. ln $(S - K_1 - K_2C_H^{e_2}) = f(\ln C_H)$ for $C_H \geq 2.00$ M. The slope of the lines give the e_2-values. The symbols refer to the solid phases: ○ Sb_2O_3(or), □ Sb_2O_3(c) and ■ Sbon.

Table 2. The relative difference between experimental and calculated solubilities. S is the mean of several experimental values. S_{calc} is calculated with the polynomial $S_{\text{calc}} = K_1 + K_2 C_H^{e_2} + K_3 C_H^{e_2}$.

C_H	$100(S_{\text{calc}} - S)/S_{\text{calc}}$ Sb_2O_3(c)	Sb_2O_3(or)	$Sb_4O_5(OH)ClO_4 \cdot \frac{1}{2}H_2O$	$Sb_4O_4(OH)_2(NO_3)_2$
5.00			10.77	3.82
4.50	0.12		9.22	−0.64
4.00	0.32	−0.87	7.70	−1.81
3.50	−0.12	0.42	5.39	−3.31
3.00	−1.05	2.08	3.62	−3.04
2.50	−1.84	−0.65	0.77	−1.13
2.00	0.50	0.55	0.07	1.88
1.50	1.29	0.55	−1.68	−0.05
1.00	−1.14	−1.49	−0.71	3.03
0.750	−0.03	−0.13	−0.18	2.10
0.500	0.88	0.03	1.14	0.69
0.250	2.53	0.33	1.92	−1.85
0.1032	−0.62	−0.95	0.10	−1.53
0.0516	1.05	0.35	−0.83	−3.00
0.0258	−0.42	−1.62	−0.58	−1.20
0.0103	−0.31	−0.51	−0.14	2.55
0.0052	−0.58	1.28	−0.11	0.88

were used, $e_2 = e_3 = 0.75$ was obtained. A new treatment with all experimental data and with $e_2 = 3/4$ fixed, gave a negative K_3 value. The differences between calculated and experimental solubilities for $C_H > 3.50$ M could consequently not be explained in terms of complex formation reactions characterised by other values of m/n than 3/4. The most plausible explanation is the strong medium change from 5.00 M sodium perchlorate to 5.00 M perchloric acid. The constants K_i calculated using $e_2 = 3/4$ are given in Table 1 and the resulting polynomial presented graphically in Fig. 3 as a dotted line. The relative differences between calculated and experimental data are given in Table 2. The exponent e_2 can also be determined graphically from the slope of the function $f(\ln C_H) = \ln(S - K_1)$. If only values of S for $C_H < 3.50$ M are used, a slope of 0.75 is in fact found (*cf.* Fig. 4).

Table 3. The solubility (S) of antimony(III) in 5.00 M sodium perchlorate and 5.00 M sodium nitrate in equilibrium with the various solid phases. Temperature 25.0 °C.

Medium	Solid phase	$S \times 10^3$(M)
$NaClO_4$	Sb_2O_3(or)	0.137
$NaClO_4$	Sb_2O_3(c)	0.122
$NaClO_4$	Sbop(70)	0.192
$NaNO_3$	Sbon	0.166

The solid phase Sbop(70) has $j = 1$. Hence, from eqns. (3) and (10), for $e_2 = 3/4$:

$$3/4 = 3l - p - l/4 \qquad (3^{\text{III}})$$

The complex $Sb_l(OH)_p^{3l-p}$ satisfying this condition are listed in Table 4. Only one combination of l and p, *viz.* $l = 1$ and $p = 2$, satisfies the equation system (3^{I}), (3^{III}). This means that of the complexes $Sb(OH)_2(Sb(OH)_3)_{l-2}^{+}$ which are compatible with the solubility curves of the oxides, only the first one, $Sb(OH)_2^{+}$, is also compatible with the solubility curve of the oxide perchlorate. The equilibria established are therefore

$$Sb_4O_6(\text{or or c}) + 4H^+ + 2H_2O \rightleftharpoons 4Sb(OH)_2^+$$

and

$$Sb_4O_5(OH)ClO_4 \cdot \tfrac{1}{2}H_2O(s) + 3H^+ + \tfrac{3}{2}H_2O \rightleftharpoons$$
$$4Sb(OH)_2^+ + ClO_4^-$$

with the equilibrium constants given in Table 6. The equation system (3^{II}), (3^{III}) is satisfied by $l = 13$ and $p = 35$, *i.e.* in the series of complexes $Sb_2(OH)_2(Sb(OH)_3)_{l-2}^{4+}$ only $Sb_{13}(OH)_{35}^{4+}$ fits the solubility curves of both the oxides and the oxide perchlorate. It is most unlikely, however,

Table 4. Complexes compatible with the ratios m/n determined experimentally for the various solid phases.

Sb_2O_3(or, c)	$Sb_4O_5(OH)ClO_4\cdot\frac{1}{2}H_2O$	$Sb_4O_4(OH)_2(NO_3)_2$
$m/n = 1$	$m/n = 3/4$	$m/n = 1/2$
$Sb(OH)_2^+$	$Sb(OH)_2^+$	$Sb(OH)_2^+$
$Sb_2(OH)_5^+$	$Sb_5(OH)_{13}^{2+}$	$Sb_3(OH)_7^{2+}$
$Sb_3(OH)_8^+$	$Sb_9(OH)_{24}^{3+}$	$Sb_5(OH)_{12}^{3+}$
$Sb_4(OH)_{11}^+$	$Sb_{13}(OH)_{35}^{4+}$	$Sb_7(OH)_{17}^{4+}$
=	=	=
$Sb_i(OH)_{3i-1}^+$	$Sb_{4i-3}(OH)_{11i-9}^{i}$	$Sb_{2i-1}(OH)_{5i-3}^{i}$
$m/n = 4$		$m/n = 3/2$
$Sb_2(OH)_2^{4+}$		$Sb(OH)^{2+}$
$Sb_3(OH)_5^{4+}$		$Sb_3(OH)_6^{3+}$
$Sb_4(OH)_8^{4+}$		$Sb_5(OH)_{11}^{4+}$
$Sb_5(OH)_{11}^{4+}$		$Sb_7(OH)_{16}^{5+}$
=		=
$Sb_i(OH)_{3i-4}^{4+}$		$Sb_{2i-3}(OH)_{5i-9}^{i}$

that a complex of such high nuclearity would be in equilibrium with Sbop(70) since the concentration of the central ions is very low. On the other hand, the complex $Sb_2(OH)_2^{4+}$, which is the simplest one compatible with the solubility curves of Sb_2O_3(or) and Sb_2O_3(c), does not satisfy (3^{III}). As the antimony(III) concentration in equilibrium with the oxides is much higher, it is nevertheless quite possible that the dinuclear complex exists in those solutions in spite of the fact that it is not present in perceptible amount in equilibrium with Sbop(70).

The solubility of Sb(III) in perchloric acid with $C_H > 5.00$ M. The surveying investigation performed at varying ionic strength for $C_H > 5.00$ M is illustrated in Fig. 6. The solid phase Sbop(70) is stable up to $C_H \approx 6.7$ M. At $C_H = 7.00$ M a phase transformation takes place after three days. The new phase contains 44.6 % Sb. Its composition is very probably $Sb(OH)_2ClO_4\cdot H_2O$ (calc. 44.3 % Sb). It is most probably identical with the compound earlier formulated as $SbO.ClO_4.2H_2O$ by Fichter and Jenny.[15] This solid phase is stable up to $C_H \approx 11.75$ M. In concentrated perchloric acid, however, still another phase is formed. As already mentioned, this compound is extremely sensitive to moisture. Thus, if the solution is allowed to take up moisture from the air for a few days, a complete transformation to Sbop(44) takes place. At $C_H = 4.50$ and 5.00 M, Sbop(55) exists as a metastable phase. This compound contains 54.4 % Sb which corresponds very closely to the composition $3Sb_2O_3.2Cl_2O_7.6H_2O$ (calc. 54.2 %). At $C_H = 6.00$ M, however, the solid phase in metastable equilibrium with the solution has neither the Guinier-Hägg powder pattern of Sbop(55) nor that of Sbop(44). This new phase has not yet been identified. Like Sbop(55), it evidently does not exist in stable equilibrium with any solution studied here.

Calculation of $\Delta G°$ for $Sb_2O_3(or) \rightarrow Sb_2O_3(c)$. The free energy change $\Delta G°$ for the transformation $Sb_2O_3(or) \rightarrow Sb_2O_3(c)$ at 25.0 °C can be computed from the present measurements as follows. In perchloric acid solutions of $C_H < 1.00$ M the complex $Sb(OH)_2^+$ is predominant (*cf.*

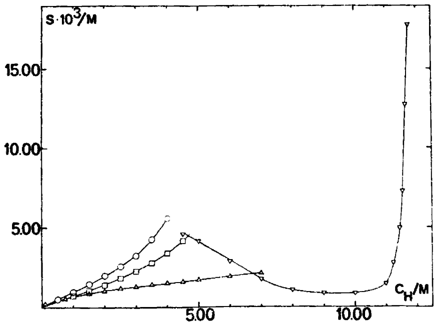

Fig. 6. The solubility of antimony(III) in perchloric acid solutions up to concentrated acid. For $C_H \leq 5.00$ M the ionic strength is constant at $I = 5.00$ M and for $C_H > 5.00$ M it varies. The different solid phases in equilibria with the solutions are indicated by the symbols: ○ Sb_2O_3(or), □ Sb_2O_3(c), △ Sbop(70) and ▽ other antimony(III)-oxide-perchlorates.

Table 5. Calculated value of ΔG° for the phase transformation Sb_2O_3 (orthorhombic)→Sb_2O_3 (cubic) at 25 °C, (*cf.* eqn. (20).

C_H (M)	ΔG° (kJ mol^{-1})
0.0258	−1.2
0.0516	−1.5
0.1032	−1.3
0.250	−1.5
0.500	−1.5
0.750	−1.4
1.00	−1.6

Fig. 3). The free energy changes on dissolution are therefore:

$$\Delta G_{or} = \mu_{or}(H_2O) + 2\mu_{or}(Sb(OH)_2{}^+) - 2\mu_{or}(H^+) - \mu_{or}(Sb_2O_3) \qquad (15)$$

$$\Delta G_c = \mu_c(H_2O) + 2\mu_c(Sb(OH)_2{}^+) - 2\mu_c(H^+) - \mu_c(Sb_2O_3) \qquad (16)$$

where for each species B:

$$\mu(B) = \mu^\circ(B) + RT \ln a(B) \qquad (17)$$

At equilibrium, *i.e.* for saturated solutions,

$$\Delta G_{or} = \Delta G_c = 0 \qquad (18)$$

and hence the free energy change of transition

$$\Delta G^\circ = \mu_c{}^\circ(Sb_2O_3) - \mu_{or}{}^\circ(Sb_2O_3)$$

is given by

$$\Delta G^\circ = -2RT \ln \frac{a_{or}(Sb)OH)_2{}^+)}{a_c(Sb(OH)_2{}^+)} + 2RT \ln \frac{a_{or}(H^+)}{a_c(H^+)} \qquad (19)$$

If it assumed that the activity coefficients for $Sb(OH)_2{}^+$ and H^+ are constants in the solutions considered, concentrations may be substituted for the activities a. Further, if the solubilities of the two phases at the same value of $[H^+] \approx C_H$ are considered

$$\Delta G^\circ = -2RT \ln \frac{(S_{or} - K_{1,or})}{(S_o - K_{1,c})} \, . \qquad (20)$$

Values of ΔG° calculated for different values of C_H are presented in Table 5. No systematic variation with the acidity can be discerned which shows that the assumptions made are permissible. The mean value is $\Delta G^\circ = -1.4 \pm 0.2$ kJ mol^{-1} at 25.0 °C. Pitman *et al.*[16] have earlier reported the value −7.5 kJ.

The nitric acid system. It is impossible to measure the solubility of Sb_2O_3(or) or Sb_2O_3(c) in nitric acid, as the transformation to the stable oxide nitrate phase $Sb_4O_4(OH)_2(NO_3)_2$ takes place in a few hours, *i.e.* before the metastable oxide equilibria are established.

The solubility of $Sb_4O_4(OH)_2(NO_3)_2$ in nitric acid is plotted as a function of C_H in Figs. 7 and 8. To make certain that Sb_2O_3(or) was fully transformed even at the lowest values of C_H used, the samples were agitated for 57 days. In these experiments, the equilibrium was approached from the side of supersaturated solution. To check that the equilibrium had really been established, some experiments were also performed with Sbon as the initial solid phase. No significant difference was found between the final values of S in the two cases. For $0.0051 < C_H < 0.1020$ M the experiments were always conducted with Sbon as solid phase.

The best fit to polynomial (14) was achieved with the values $e_2 = 0.49$ and $e_3 = 1.49$. The least-squares treatment was repeated with $e_2 = 1/2$ and $e_3 = 3/2$ as constants. The resulting constants K_i and the exponents e_i are given in Table 1. The exponents e_2 and e_3 were also determined graphically by plotting $f(\ln C_H) = \ln (S - K_1)$ for $C_H < 3.0$ M and $f(\ln C_H) = \ln (S - K_1 - K_2 C_H{}^{e_2})$ for $1.5 < C_H < 5.00$ M (*cf.* Figs. 4 and 5). The slopes of the functions give $e_2 = 0.5$ and $e_3 = 1.5$. The relative differences between calculated and experimental data are given in Table 2.

The solid phase Sbon has $j = 2$, hence, from eqns. (3) and (10)

$$1/2 = 3l - p - 2l/4 \qquad (3^{IV})$$
$$3/2 = 3l - p - 2l/4 \qquad (3^{V})$$

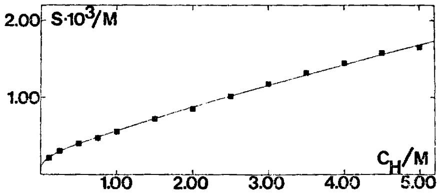

Fig. 7. The solubility of antimony(III) in nitric acid solutions at $I = 5.00$ M. The solid phase in equilibria with the solutions is Sbon.

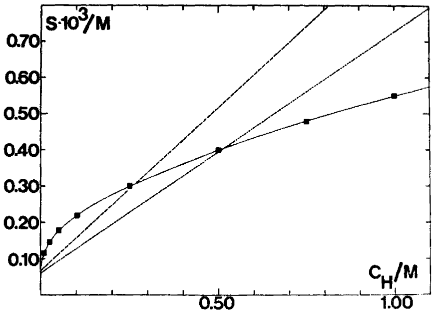

Fig. 8. The solubility of antimony(III) in nitric acid solutions, at $I = 5.00$ M, up to $C_H = 1.00$ M. (■ and —; solid phase Sbon). The solubilities of Sb_2O_3(or) (— — —) and Sb_2O_3(c) (···) in perchloric acid are plotted for comparison.

The complexes $Sb_l(OH)_p^{3l-p}$ compatible with these conditions are listed in Table 4. The only possible complex of charge +1 is $Sb(OH)_2^+$, which thus is the only one of the series $Sb(OH)_2(Sb(OH)_3)_{l-2}^+$, indicated by the oxide measurements, which is also compatible with the solubility curve of the oxide nitrate. The following equilibrium is thus established between Sbon and the solution:

$$Sb_4O_4(OH)_2(NO_3)_2(s) + 2H^+ + 2H_2O \rightleftharpoons 4Sb(OH)_2^+ + 2NO_3^-$$

with the equilibrium constant given in Table 6. Among the complexes of charge +4 which may, according to the oxide measurements possibly be present only $Sb_5(OH)_{11}^{4+}$ (with $m/n = 3/2$) and $Sb_7(OH)_{17}^{4+}$ (with $m/n = 1/2$) are compatible with the oxide nitrate curve (*cf.* Table 4). As the concentrations of antimony(III) in equilibrium with Sbon is very low, complexes of such high nuclearity are not likely to exist. This inference is further strengthened by the fact that none of the complexes mentioned are compatible with the oxide perchlorate curve. A much more plausible species which also satisfies eqn. (3V) is $Sb(OH)^{2+}$. This monomer admittedly does not exist in perceptible amounts in any of the perchlorate solutions investigated but it is known from other systems [17] that the formation of mononuclear complexes is favoured in nitrate solutions, evidently due to the stronger tendency of nitrate to enter the coordination sphere of the acceptor, thereby making the formation of hydroxo or oxo bridges more difficult. The complex [4] $Sb(OH)Cl_3^-$ provides another example of the same tendency which should be even more marked in chloride systems on account of the much stronger affinity of this ligand to antimony(III). The existence of the monomer $Sb(OH)^{2+}$ in nitric acid is therefore compatible throughout with the existence of the dimer $Sb_2(OH)_2^{4+}$ in perchloric acid. The equilibrium most likely to account for $m/n = 3/2$ would thus be

$$Sb_4O_4(OH)_2(NO_3)_2 + 6H^+ \rightleftharpoons 4Sb(OH)^{2+} + 2NO_3^- + 2H_2O$$

with the equilibrium constant given in Table 6.

DISCUSSION

This investigation has shown that in aqueous perchloric and nitric acid solutions of $C_H \leq 2.00$ M the predominating complex is $Sb(OH)_2^+$. This complex exists in equilibrium with all the solid phases employed. It has also been postulated by several previous investigators.[1-5] As

Table 6. Equilibrium constants K_i' (*cf.* eqn. (4)) for the reactions $Sb_4O_{(6-j)}(OH)_j(Z)_j(s) + mH^+ \rightleftharpoons nSb_l(OH)_p^{(3l-p)} + qH_2O + kjZ^-$ at $I = 5$ M and 25.0 °C. The errors stated correspond to 3σ.

Solid phase	Complex formed; constant K_i'								
	$Sb(OH)_2^+$			$Sb(OH)^{2+}$			$Sb_2(OH)_2^{4+}$		
	m	n	$K_2' \times 10^{14}$	m	n	$K_3' \times 10^{17}$	m	n	$K_3' \times 10^{12}$
Sb_4O_6(or)	4	4	60 ± 2			—	8	2	13.8 ± 0.9 (M^{-6})
Sb_4O_6(c)	4	4	19.0 ± 0.6			—	8	2	1.93 ± 0.02 (M^{-6})
$Sb_4O_5(OH)ClO_4 \cdot \frac{1}{2}H_2O$	3	4	8.6 ± 0.2 (M)			—			—
$Sb_4O_4(OH)_2(NO_3)_2$	2	4	3.5 ± 0.3 (M^2)	6	4	1.3 ± 0.2 (M^{-2})			—

Table 7. Determinations of the equilibrium constant of the reaction
$\frac{1}{2}Sb_2O_3(s)+H^+ +H_2O \rightleftharpoons Sb(OH)_2^+ + \frac{1}{2}H_2O$.
All determinations have been performed by solubility measurements.

Ref.	Solid phase	Medium	Equilibrium constant $\times 10^4$
1	Sb_2O_3(or)	$HClO_4$	9
2	Sb_2O_3(or)	HCl	8
4	Sb_2O_3(or)	$HClO_4$	8.5
This work	Sb_2O_3(or)	$HClO_4$	8.8 ± 0.1
This work	Sb_2O_3(c)	$HClO_4$	6.6 ± 0.1

already mentioned, some of these have also calculated the equilibrium constants for its formation from Sb_2O_3(or), the reaction generally being written in the form $1/2\ Sb_2O_3(or)+H^+ + H_2O \rightleftharpoons Sb(OH)_2^+ + 1/2\ H_2O$. Our value is in very good accord with these previous measurements, especially if the fairly large differences in medium are taken into account (*cf.* Table 7).

Generally, the complex has been written in the form SbO^+. From measurements of the present type it is of course impossible to differentiate between the two formulae. It seems nevertheless extremely improbable that both protons dissociate from one molecule of water and we therefore prefer the formulation $Sb(OH)_2^+$.

Besides the well-established $Sb(OH)_2^+$, at least two further complexes have been found in this investigation. Thus in perchloric acid solutions in equilibrium with Sb_2O_3 (orthorhombic or cubic) a complex of charge 4+ exists. Its concentration becomes perceptible (≈ 10 % of the total solubility S) at a value of $C_H \approx 2.4$ M (corresponding to $S\ \approx 2.5$ mM) for Sb_2O_3(or) and at a value of $C_H \approx 3.0$ M (corresponding to $S \approx 2.3$ mM) for Sb_2O_3(c). At the highest values of S reached, *viz.* 5.59 mM for Sb_2O_3(or) at $C_H = 4.0$ M, and 4.14 mM for Sb_2O_3(c) at $C_H = 4.5$ M, considerable amount of the antimony is present as the dimer, to the extent of 34 and 27 %, respectively. The equilibrium constant $K_d[=(K_3'/K_2')^{\frac{1}{2}}]$ for the reaction

$$2Sb(OH)_2^+ + 2H^+ \rightleftharpoons Sb_2(OH)_2^{4+} + 2H_2O$$

is found to be $4.8 \pm 0.3\ M^{-3}$ if the values of K_3' and K_2' found from the Sb_2O_3(or) curve are used, and $3.2 \pm 0.1\ M^{-3}$ if the values from the Sb_2O_3(c) curve are used. Presumably, this difference is mainly due to the fairly rapid change of the activity conditions which has been postulated as the most likely cause of the slightly low values of S found when Sbop(70) in the solid phase and $C_H \gtrsim 3$. It is quite probable that a corresponding deviation takes place also for the oxide curves. If so, it should be relatively more marked for Sb_2O_3(c) than for Sb_2O_3(or), especially as the solutions where the dimer is the predominant species are more acid in the former case. Such a deviation should result in values of K_3' for both oxides which are rather too low, especially in the case of Sb_2O_3(c).

Though great caution must always be taken when deducing the structures of hydrolytic complexes in solution from those found for solid oxide salts, valuable information may nevertheless be obtained in this way, as has been shown in several instances. Thus, the entities $Th(OH)_2Th^{6+}$ and $UO_2(OH)_2UO_2^{2+}$ which have been established in solution both by emf and X-ray investigations [18-20] are also found in solids.[21,22] Also, the complexes $Pb_4(OH)_4^{4+}$ and $Pb_6(OH)_8^{4+}$ indicated in solution by emf measurements [23] have later been found as discrete entities in crystalline oxide salts.[24-26]

The dimer $Sb_2(OH)_2^{4+}$ compatible with the present measurements, could have at least three different structures. The antimony atoms may be joined by a double hydroxo bridge: $Sb(OH)_2Sb^{4+}$, which would be similar to the arrangement in the thorium(IV) and uranyl(VI) complexes mentioned above, or the complex may contain a single hydroxo bridge: $Sb(OH)Sb(OH)^{4+}$. The final possibility would involve a single oxo bridge: $SbOSb^{4+}$.

In oxide salts, antimony(III) is three or four coordinated. The most common polyhedron is the trigonal bipyramid, where one of the equatorial corners is occupied by the lone pair of electrons. The other common coordination geometry is that of the tetrahedron, with the lone pair of electrons at one corner. If the complex with the double hydroxo bridge is a fragment of the solid oxide salt, then polyhedra with shared edges must be a feature of their structure. It also seems reasonable that the distance between the antimony atoms within the units is significantly shorter than any other Sb – Sb-distances in the oxide salt. The complexes with single hydroxo or oxo bridges are consistent with crystal structures containing polyhedra with shared equatorial corners. In such cases the antimony atoms should be joined only by single oxygen bridges in the solid state.

In this serie of investigations, the structures[6,7] of $Sb_4O_5(OH)ClO_4 \cdot \frac{1}{2}H_2O$ [=Sbop(70)] and $Sb_4O_4(OH)_2(NO_3)_2$ (=Sbon) have been determined. In both compounds coordination polyhedra share edges, the shortest antimony-to-antimony distance being that between antimony atoms joined *via* two oxygens. This is also the case in the structure of $Sb_4O_5Cl_2$.[27,28] The only known structure which contains polyhedra sharing equatorial corners is $SbPO_4$.[29] The model for $Sb_2(OH)_2^{4+}$ most consistent with the crystal structures seems to be a complex in which two antimony atoms are joined by a double hydroxo bridge. A complex of similar structure, *viz.* $[Bi(OH)_2Bi]^{4+}$, has also been found by Aurivillius[30,31] in the crystal structures of $Bi(OH)CrO_4$ and $Bi(OH)SeO_4.H_2O$.

The monomer $Sb(OH)^{2+}$, which has been postulated to exist in the nitrate medium, has a counterpart in the complex $Bi(OH)^{2+}$. The latter is present in hydrolysed perchloric acid solutions of bismuth(III), although admittedly not as a predominating species.[32] The concentration of $SbOH^{2+}$ becomes perceptible (≈ 10 % of S) at $C_H \approx 1$ M. At the highest concentration of nitric acid used (5 M) it reaches ≈ 40 %. The equilibrium constant $K(=(K_3'/K_2')^{\frac{1}{4}}$ for the reaction

$$Sb(OH)_2^+ + H^+ \rightleftharpoons SbOH^{2+} + H_2O$$

is found to be 0.139 ± 0.008 M^{-1}, corresponding to an acid dissociation constant $K_s(=1/K) = 7.2 \pm 0.4$ M for $SbOH^{2+}$. This very high value of K_s found for a partly hydrolysed species illustrates the strongly acidic properties of antimony(III).

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