Conclusion

A series of complexes of titanium(IV), vanadium(IV), and tin(IV) with bidentate sulfur-donor ligands has been isolated and characterized. It is shown that, with the possible exception of the complexes of the ligand *cis*-dimethylthiomaleonitrile, the complexes are monomers with metal–sulfur bonding and the *gauche* conformation for the complexed ligand. While no quantitative information is available, the complexes are apparently of comparable stability to those formed with oxygen-, nitrogen-, and arsenic-donor ligands. This suggests that titanium(IV) is close to the borderline of class A–class B behavior.

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Solubility Studies of Tetramethylammonium Salts of Complex Halides. V. Tris(tetramethylammonium) Enneabromodibismuthate(III)

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The solubility of $[(CH_3)_4N]_3Bi_2Br_9$ has been studied over the range 0.000 $M < [Br^-] < 4.0$ M in 4 M ($H_2SO_4 + HBr$) at 25°. The data are interpreted as evidence for equilibria between the solid phase and solutions containing Bi^{3+}, $BiBr^+$, $BiBr_2^+$, $BiBr_4^-$, $BiBr_6^{3-}$, and $BiBr_8^{5-}$. $\beta_1 = 1500$, $\beta_2 = 9.50 \times 10^4$, $\beta_4 = 6.2 \times 10^8$, $\beta_6 = 9.2 \times 10^{10}$, $\beta_8 = 9.6 \times 10^9$. The spectra of $BiBr_6^{3-}$ and $BiBr_8^{5-}$ show a nearly identical band, λ_{max} 376 mμ, $\epsilon_6 \approx 16{,}000$, $\epsilon_8 \approx 16{,}900$. No evidence of ion-pair formation between negative $BiBr_n^{3-n}$ complexes and $(CH_3)_4N^+$ or H^+ was obtained. The evidence for $BiBr_8^{5-}$ is tenuous, and the existence of this species must be considered still in doubt.

Previous study[3] of the solubility of $[(CH_3)_4N]_3Bi_2Cl_9$ as a function of $[Cl^-]$ indicated that only $BiCl_4^-$ and $BiCl_6^{3-}$ are present at high $[Cl^-]$. On finding that only $[(CH_3)_4N]_3Bi_2Br_9$ precipitates when $(CH_3)_4NBr$ is added to solutions of BiOBr in HBr, a study of $BiBr_n^{3-n}$ complex equilibria was undertaken for purposes of comparison with $BiCl_n^{3-n}$.

Experimental Section

Preparation of $[(CH_3)_4N]_3Bi_2Br_9$.—Seven grams of $Bi(NO_3)_3 \cdot 5H_2O$ was treated with 5 ml of 8.8 M HBr. The mixture was hydrolyzed with 1 l. of H_2O. BiOBr was filtered, washed, and redissolved in 8.8 M HBr. $(CH_3)_4NBr$ (3.2 g) dissolved in 25 ml of 4 M HBr was slowly added to give hexagonal crystals of $[(CH_3)_4N]_3Bi_2Br_9$ in 70% yield. The salt, which is stable in air, was dried *in vacuo* at room temperature.

Analysis of the salt for C, H, and N was made by the Clark Microanalytical Laboratory. Analysis for Bi and Br was made by hydrolyzing the salt according to the equation

$$2H_2O + [(CH_3)_4N]_3Bi_2Br_9 \longrightarrow \underline{2BiOBr} + 4H^+ + 3(CH_3)_4N^+ + 7Br^-$$

BiOBr was filtered, dried, and weighed. H^+ was titrated with standard NaOH, and Br^- titrated with Ag^+.

Anal. Calcd for $[(CH_3)_4N]_3Bi_2Br_9$: C, 10.5; H, 2.67; N, 3.09; Bi, 30.7; Br, 53.0; H^+, 2.94 mequiv/g. Found: C, 10.9; H, 2.55; N, 2.94; Bi, 30.9; Br, 53.2; H^+, 2.92 mequiv/g.

Solubility studies on the salt were done as before[3] using a Brønsted saturator in a thermostat regulated at 25.0 ± 0.1°. Stock 4 M H_2SO_4 and 4 M HBr were prepared by dilution of concentrated acids and standardized against anhydrous sodium carbonate. Mixtures of the stock solutions covering the entire range $0 \le [Br^-] \le 4.0$ M were prepared as solvents and used immediately. No oxidation of Br^- by 4 M H_2SO_4 was ever observed. Saturated solutions were diluted to give $\sim 10^{-4}$ M Bi(III) in 6 M HCl. Analysis of the dilute solutions was made by measuring absorbance at 328 mμ as recommended by Merritt, Hershenson, and Rogers.[4] Dilutions were so great as to eliminate any interference from Br^- in the original solvent.

The spectra of $BiBr_n^{3-n}$ complexes in HBr were also studied. All spectrophotometric measurements were made with a Beckman D.U. spectrophotometer using 1.000-cm Corex cells.

Working Equations and Definitions of Terms

For purposes of data analysis, the chemical equilibria are assumed

$$[(CH_3)_4N]_3Bi_2Br_9 \rightleftharpoons 3(CH_3)_4N^+ + 2BiBr_4^- + Br^- \tag{1}$$

$$BiBr_4^- + (n - 4)Br^- \rightleftharpoons BiBr_n^{3-n} \tag{2}$$

If no polynuclear complexes are formed and the law of mass action holds, the following equations may be derived

$$10.4S^{5/2}[Br^-]^{1/2} = \frac{K_s^{\ 1/2}}{\beta_4} \sum_0^N \beta_n [Br^-]^{n-4} \tag{3}$$

$$[Br^-] = \frac{[Br^-]_0}{1 + 5\frac{dS}{d[Br^-]}} \tag{4}$$

$$\frac{d \log S}{d \log [Br^-]} = \frac{2\bar{n} - 9}{5} \tag{5}$$

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[3] G. P. Haight, Jr., C. H. Springer, and O. J. Heilmann, *Inorg. Chem.*, **3**, 195 (1964).

[4] C. Merritt, H. M. Hershenson, and L. B. Rogers, *Anal. Chem.*, **25**, 572 (1953).

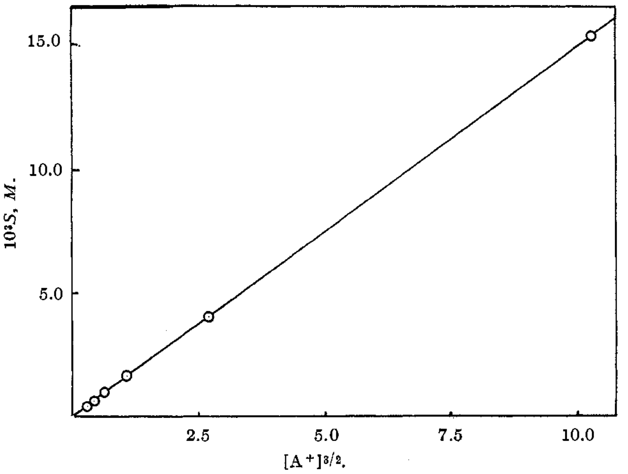

Figure 1.—Test for absence of polynuclear complexes and ion pairs with $(CH_3)_4N^+$. Dependence of S on $[(CH_3)_4N^+]$ at constant $[Br^-] = 4.0$ M.

where S = solubility of the salt (M); $[Br^-]$ = concentration of free bromide ion (M); $[Br^-]_0$ = concentration of bromide ion initially in the solvent; $K_s = [(CH_3)_4N^+]^3[BiBr_4^-]^2[Br^-]$; $K_n = [BiBr_n^{3-n}]/[BiBr_{n-1}^{4-n}][Br^-]$; $\beta_n = \prod_1^n K_n = [BiBr_n^{3-n}]/[Bi^{3+}][Br^-]^n$; $\bar{n}$ = average number of bromide ions attached to Bi^{3+} in any given solvent.

Results

Test for Polynuclear Complexes.—If no polynuclear complexes are formed, at any given $[Br^-]$, the relationship

$$S \propto [(CH_3)_4N^+]^{3/2} \qquad (6)$$

should hold where S = solubility of the salt in moles/liter. Figure 1 shows that such a relationship is found very precisely over a nearly 100-fold variation in $[(CH_3)_4N^+]$ and in S. Such a relationship is also possible only if $(CH_3)_4N^+$ does not undergo significant ion-pair formation with either Br^- or $BiBr_n^{3-n}$. In 1 M HBr + 3 M H_2SO_4, substitution of up to 1 M $(CH_3)_4N^+$ for H^+ has a very small effect on the $BiBr_n^{3-n}$ spectrum. The effect near the wavelength of maximum absorbance increases absorbance slightly (<1%) and shifts the maximum to a higher wavelength (<1 mμ). The observed changes are not in excess of experimental error and could be caused by a very small *increase* in activity (or concentration) of Br^-. The combined evidence indicates that $(CH_3)_4N^+$ exhibits very nearly "ideal" behavior in 4 M (HBr + H_2SO_4).

Solubility Studies.—Figure 2 shows the solubility of the salt as a function of $[Br^-]$ in 4 M (H_2SO_4 + HBr). The portion of the curve to the left of the minimum is shown on an expanded scale in the upper left corner. The corrected curve is obtained as follows. At high $[Br^-]$ it is sufficient to apply corrections using the slope of the S *vs.* $[Br^-]_0$ curve since convergence is complete after two iterations. At low $[Br^-]_0$ the slope of the initial curve is too shallow for the points at lowest $[Br^-]_0$, and one must add the criterion that the slope should monotonically become more negative with decreasing $[Br^-]$ approaching −0.2 as a limit at $[Br^-]_0 = 0$. By trial and error a curve is obtained which fits eq 2. From this curve constants β_1, β_2, and β_4 are deduced. Finally $[Br^-]$ values and β values are adjusted until calculation of $[Bi^{3+}]$, $[BiBr^{2+}]$, and $[BiBr_4^-]$ values for each point using eq 1 give values for which the equation

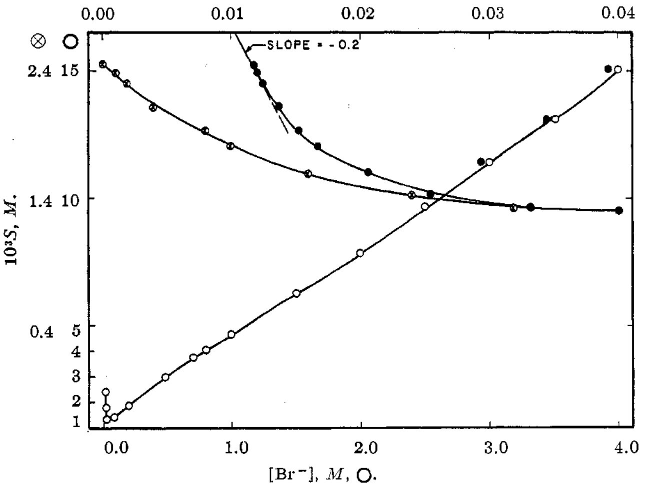

Figure 2.—Dependence of S on $[Br^-]$. Open circles show relationship over entire range of solubility data taken. Closed and split circles show the effect of the correction for $[Br^-]$ from the salt at low $[Br^-]_0$. Split circles indicate plot of S *vs.* $[Br^-]_0$; closed circles, S *vs.* $[Br^-]$, as calculated from eq 2.

$$[Br^-] = 4[Bi^{3+}] + 3[BiBr^{2+}] + [Br^-]_0 + S$$

gives the value of $[Br^-]$ on the curve. The final corrections were very sensitive to estimates for $[Br^-]$ and to β_4. Thus, although $[Br^-]$ corrections are very large, the values for the various ratios β_1/β_4, β_2/β_4, etc. are thought to be accurate so far as order of magnitude is concerned. The values of β_6/β_4, β_8/β_4, and K_s obtained from the points to the right of the minimum in the solubility curve are accurate within 5%. β_4 itself was estimated strictly by difference for the two points of lowest $[Br^-]$. The slope of the plotted line used to determine β_4 is very shallow indicating that $[Bi^{3+}(aq)]$ is a minor species. Thus, estimates of β_4 must be only of order of magnitude accuracy.

β values were obtained by the method of Leden[5] as follows. Let

$$F_n = \frac{K_s^{1/2}\beta_n[Br]^{n-4}}{\beta_4}; \quad y = \sum_0^n F_n$$

by successive approximations each F_n was obtained as $y - (F_1 + \ldots + F_{n-1} + F_{n+1} + \ldots + F_N)$. When all F_n *vs.* $[Br^-]^{n-4}$ gave good straight-line plots with the common intercept $F_4 = K_s^{1/2}$, slopes and intercepts were used to calculate β values. Equilibrium constants calculated from these plots are: $K_s = 7.7 \times 10^{-15}$ M^6; $K_1 = 1500$ M^{-1}; $K_2 = 58$ M^{-1}; $K_3K_4 = \beta_4/\beta_2 = 7100$ M^{-2}; $K_7K_8 = \beta_8/\beta_6 = 0.104$ M^{-2}.

Table I shows corrected values for $[Br^-]$ and the

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[5] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

Table I

Solubility of $[(CH_3)_4N]_3Bi_2Br_9$

$[Br^-]_0$, M	$[Br^-]$,[a] M	$[Br^-]$,[b] M	10^3S_{obsd}, M	10^3S_{calcd}, M c	d
4.00	3.92		15.1	15.3	12.6
3.50	3.44		13.1	13.3	11.6
3.00	2.95		11.4	11.3	10.6
2.50	2.46		9.70	9.60	9.5
2.00	1.96		7.84	7.88	8.35
1.50	1.47		6.24	6.29	7.00
1.000	0.983		4.64	4.73	5.50
0.800	0.786		4.08	4.09	4.83
0.700	0.688		3.76	3.76	4.47
0.480	0.472		2.96	2.98	3.58
0.200	0.196		1.88	1.88	2.18
0.0800	0.0786		1.37	1.34	1.49
0.0480	0.0480		1.29	1.30	1.36
0.0400	0.0400		1.30	1.32	1.35
0.0320	0.0332	0.0336	1.32	1.32	1.33
0.0240	0.0265	0.0268	1.43	1.39	1.39
0.0160	0.0206	0.0205	1.59	1.52	1.52
0.0100	0.0166	0.0165	1.80	1.79	1.79
0.0080	0.0152	0.0156	1.92	1.95	1.95
0.0040	0.0136	0.0131	2.11	2.11	2.11
0.0020	0.0124	0.0124	2.30	2.23	2.23
0.0010	0.01195	0.0121	2.38	2.37	2.37
0.000	0.0116	0.0118	2.44	2.43	2.43

[a] $[Br^-]$ calculated graphically. [b] $[Br^-] = 4[Bi^{3+}] + 3[BiBr^{2+}] + Br^{2+} + S + [Br^-]_0$. Terms on the right calculated using constants below and $[Br^-]$. [c] Calculated using the following constants: $\beta_8/\beta_4 = 15.4$; $\beta_6/\beta_4 = 148$; $\beta_2/\beta_4 = 2.00 \times 10^{-4}$; $K_s = 1.0 \times 10^{-14}$; $\beta_1/\beta_4 = 3.60 \times 10^{-7}$; $1/\beta_4 = 2.0 \times 10^{-8}$. [d] Best fit assuming $BiBr_6^{3-}$ is complex of highest n, $\beta_6/\beta_4 = 240$, showing serious deviations at highest and intermediate $[Br^-]$.

agreement between measured solubilities and those calculated using the constants above. The large deviations at high $[Br^-]$ if $BiBr_8^{5-}$ formation is ignored are also indicated.

Table II lists calculated values of the maximum relative concentration of each species and the bromide ion concentration at which each maximum is attained.

Table II

Maximum Relative Concentrations of $BiBr_n^{3-n}$

Species	Max %	$[Br^-]_{max}$, M
Bi^{2+}	100	$<10^{-1}$
$BiBr^{2+}$	84	3.25×10^{-3}
$BiBr_2^+$	31	1.06×10^{-2}
$BiBr_3$[a]	<10	1.25×10^{-2}
$BiBr_4^-$	77	3.25×10^{-2}
$BiBr_5^{2-}$[a]	<10	8.2×10^{-2}
$BiBr_6^{3-}$	95	5.02×10^{-1}
$BiBr_8^{5-}$	?	>10

[a] No evidence for $BiBr_3$ or $BiBr_5^{2-}$.

Figure 3 shows spectra of Bi(III) obtained when $\bar{n}$ = 4, 6, and 7.2, respectively. The change in spectrum between $BiBr_6^{3-}$ and $BiBr_8^{5-}$ is very small compared with other changes previously observed. The molar absorbance at 376 mμ appears to be leveling off as $\bar{n}$ approaches 6 but then continues to increase slowly over the range $1.0 \leq [Br^-] \leq 4.0$ M. The spectral change is consistent with the value $\beta_8/\beta_6 = 0.104$, but the change is too small to be used to deduce the value of β_8/β_6.

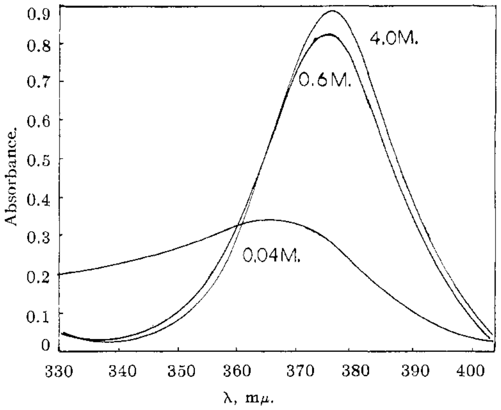

Figure 3.—Absorption spectrum of 5.3×10^{-5} M Bi(III) at various $[Br^-]$; $[H^+] = 4.0$ M.

Discussion

The results of this study indicate that Br^- forms more stable complexes than Cl^- with Bi^{3+} if $n > 4.0$. Ahrland and Grenthe[6] have shown that there is little difference between K_1 and K_2 for the chloride and bromide complexes. Thus, a change from chloride to bromide leads to a narrowing of regions of existence for intermediate complexes. Bjerrum and Wright[7] have observed with the ligand triphenylphosphine that only complexes of $n = 1$ and $n = 6$ are formed with bismuth, consistent with the above trend if triphenylphosphine is considered a sort of superhalogen. Of interest as well, is the ability of Bi^{3+} to attain ligand number 6 (and perhaps higher) with halide ions while Tl^{3+} is limited to ligand number 4, except at very high concentrations of halide ion (chloride[8]). This suggests that the lone pair of electrons of Bi^{3+} may be involved in back bonding with π orbitals on the halide ions. The π-acceptor ability of halogens increases with increasing atomic number.

The existence of $BiBr_8^{5-}$ must be considered a tentative finding. The spectral change from $\bar{n} = 6$ to $\bar{n} = 7.3$ is so small that it may be a medium effect. Some means will have to be found to test the constancy of the activity coefficient of Br^- in this system before the existence of $BiBr_6^{3-}$–$BiBr_8^{5-}$ equilibrium can be considered established.

Acknowledgment.—This work was supported by a grant from the National Science Foundation. The spectrophotometer is on loan to Swarthmore College from the Office of Ordnance Research, U. S. Army.

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(6) S. Ahrland and S. Grenthe, *Acta Chem. Scand.*, **11**, 1111 (1957).

(7) G. Wright and J. Bjerrum, *ibid.*, **16**, 1262 (1962).

(8) T. Spiro, *Inorg. Chem.*, **4**, 731 (1965).