Bromoaquo-complexes of Titanium(III)

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A series of bromoaquotitanium(III) complexes have been prepared of the general types $M_2TiBr_5(H_2O)_n$ [M = Cs, Rb, pyH; n = 1, 3, or 5] and $M_2(H_3O)TiBr_6(H_2O)_5$ [M = pyH, quinH]. The complexes have been characterised by magnetic and spectroscopic studies and studied by a vacuum t.g.a. technique.

ALTHOUGH the chloroaquo-complexes of titanium(III) [1-5] and the bromoaquo-complexes of vanadium(III) [6] have been known for some time, the only known bromoaquo-complex of titanium(III) is $TiBr_3(H_2O)_6$. Titanium(III) bromide hexahydrate has been shown [7,8] by diffuse reflectance and i.r. measurements to have the structure $[Ti(H_2O)_4Br_2]Br,2H_2O$. We report here the preparation of the complexes M_2TiBr_5 $(H_2O)_n$ [M = Cs, Rb, pyridinium (pyH); n = 1, 3, or 5] and M_2 $(H_3O)TiBr_6(H_2O)_5$ [M = pyH, quinolinium (quinH)]. While complexes of the type $M_2VBr_5(H_2O)_n$ [6] and $M_2TiCl_5(H_2O)$ [1-5] are known, there are no analogues to the complexes containing the $(H_3O)^+$ cation.

RESULTS AND DISCUSSION

When solutions of titanium(III) bromide and M^IBr (M^I = Cs, Rb, pyH, quinH) in hydrobromic acid are saturated with hydrogen bromide, and then cooled, the products $Cs_2TiBr_5(H_2O)_3$, $Rb_2TiBr_5(H_2O)_5$, $(pyH)_2(H_3O)TiBr_6(H_2O)_5$, and $(quinH)_2(H_3O)TiBr_6(H_2O)_5$ are formed, respectively. The exclusion of oxygen during these reactions is imperative, otherwise oxidation to titanium(IV) occurs. The relative concentration of the reactants is also important. Attempts to prepare complexes containing M : Ti ratios of 1 : 1 or 3 : 1 resulted only in the precipitation of heterogeneous mixtures. No pure complex could be isolated from the reaction with tetraethylammonium bromide.

The diffuse reflectance and i.r. spectra of the complexes are listed in the Table. As was found for the series of compounds of the general formula $[TiCl_n(CH_3OH)_{6-n}]^{3-n}$,[9] the bromoaquo-complexes prepared in this work obey Jørgensen's law of average environment,[10] and we therefore presume that they contain species of the types $[TiBr_n(H_2O)_{6-n}]^{3-n}$ as indicated in the Table. The i.r. data were in accord with these formulations {the complexes postulated to contain $[TiBr_2(H_2O)_4]^+$ showing only one ν(Ti–Br) [8]}.

Both $(pyH)_2(H_3O)TiBr_6(H_2O)_5$ and $(quinH)_2(H_3O)TiBr_6(H_2O)_5$ are stable under dry nitrogen. However, if they are kept in sealed tubes in the presence of air, within a few days they turn to red-brown or red respectively upon the surface. A controlled oxidation of the quinolinium salt led to the identification of the oxidation product as $(quinH)_2TiOBr_4(H_2O)_5$. A similar type of oxidation is postulated for the pyridinium complex. The complex $(pyH)_2TiBr_5(H_2O)$ was prepared

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from $(pyH)_2(H_3O)TiBr_6(H_2O)_5$ both by continuous evacuation and by dehydration over P_2O_5 *in vacuo*. These two methods of preparation resulted in compounds with different properties (*i.e.* stability in moist air, reflectance spectra, or magnetic moment). It is concluded that the complex prepared by dehydration is partially oxidised, containing the species $(pyH)_2TiBr_5(OH)$.

Reflectance (kK *) and i.r. spectra (cm^{-1})

	Charge transfer	$^2E_g \longleftarrow$ ν_2	$^2T_{2g}$ ν_1	ν(V–Br)	Environment of Ti^{3+}
$(pyH)_2(H_3O)TiBr_6(H_2O)_5$	43·3, 38·0, *ca.* 34·0sh, 27·0	17·8	14·3	278s	$[TiBr_2(H_2O)_4]^+$
$(pyH)_2TiBr_5(H_2O)_3$	44·2, 37·8sh, 33·3, *ca.* 27·0sh	16·3	12·4	308sh, 290s	$[TiBr_3(H_2O)_3]$
$(pyH)_2TiBr_5(H_2O)$ [a]	44·0, 37·3, 24·8	12·1		316s,br; 298s,br	$[TiBr_5(H_2O)]^{2-}$
$(pyH)_2TiBr_5(H_2O)$ [b]	44·6, 37·7, 27·6, *ca.* 22·0sh	12·1			
$(quinH)_2(H_3O)TiBr_6(H_2O)_5$	44·6, 32·7, 39·5, 25·0sh	18·0sh	13·8		$[TiBr_2(H_2O)_4]^+$
$Rb_2TiBr_5(H_2O)_5$	44·4, *ca.* 37·0sh, 33·8	19·0	13·7	277s	$[TiBr_2(H_2O)_4]^+$
$Rb_2TiBr_5(H_2O)$	44·1, 35·2sh, *ca.* 32·0, 24·6, 21·4	13·3	10·8	270sh, 256s	$[TiBr_5(H_2O)]^{2-}$
$Cs_2TiBr_5(H_2O)_3$	45·0, 36·4, 32·9	18·6	13·4	276s	?
$Cs_2TiBr_5(H_2O)$	44·4, 38·0sh, 35·5, 27·4, 21·3, 18·2	12·6	10·6	264s, 238sh	$[TiBr_5(H_2O)]^{2-}$
$TiBr_3(H_2O)_6$	44·4, *ca.* 36·0br, *ca.* 33·0br	18·5	13·9	294s	$[TiBr_2(H_2O)_4]^+$
$(pyH)_3TiBr_6$ [c]		11·4	9·65		$[TiBr_6]^{3-}$
$(quinH)_2TiOBr_4(H_2O)_5$	44·9, 33·0, *ca.* 25·5sh, 22·0				

[a] Prepared by evacuation of $(pyH)_2(H_3O)TiBr_6(H_2O)_5$. [b] Prepared by dehydration of $(pyH)_2(H_3O)TiBr_6(H_2O)_5$ over P_2O_5. [c] H. L. Schlafer, W. Lenz, and J. Staab, *Z. Physik. Chem., Neue Folge*, 1968, **62**, 290.

* 1kK = 10 ^{3}cm^{-1}

The thermogravimetric analyses of the complexes yielded some interesting results, which are listed in Supplementary Publication No. 20926 (2 pp.).* The complexes containing $(H_3O)^+$ both decompose by similar pathways, the first stable phase corresponding to $M_2TiBr_5(H_2O)$. The quinolinium salt was more thermally stable than its pyridinium counterpart, which was consistent with its stability over P_2O_5 *in vacuo*. It is interesting to note that there is no phase corresponding to the unstable $(pyH)_2TiBr_5(H_2O)_3$ observed, and that the decomposition of $(pyH)_2TiBr_5(H_2O)_3$ proceeds initially by a slightly different route. The decomposition routes for the rubidium and caesium salts are also very similar to each other, both proceeding *via* M_2TiOBr_3. The vacuum thermogram of $TiBr_3(H_2O)_6$ showed the compound decomposed without going through any stable phases apart from TiOBr:

$$TiBr_3(H_2O)_6 \xrightarrow{120-340\ ^\circ C} TiOBr \xrightarrow{340-640\ ^\circ C} TiO$$

A similar decomposition has also been found for $VBr_3(H_2O)_6$.[6]

None of the complexes underwent thermal dehydration to yield M_2TiBr_5: in all cases the following hydrolysis occurred:

$$M_2TiBr_5(H_2O) \longrightarrow M_2TiBr_4(OH)$$

Attempts to prepare M_2TiBr_5 by chemical means (heating the complexes under reflux with acetyl bromide, acetic anhydride, and thionyl chloride) also proved unsuccessful, heterogeneous mixtures being commonly formed. However the reaction of $Cs_2TiBr_5(H_2O)_3$ with acetyl bromide did yield the complex $Cs_2TiBr_5(H_2O)$. Nor was the anhydrous complex formed by storing the hydrated complexes *in vacuo* over P_2O_5 or silica gel. In this the titanium system differs from the vanadium system, as the bromoaquo-complexes of vanadium(III) may be dehydrated to form M_2VBr_5.[6]

EXPERIMENTAL

Materials.—The following materials were used without further purification: hydrogen bromide and hydrobromic acid (B.D.H.), titanium powder (Hopkin and Williams), caesium bromide (B.D.H.), rubidium bromide (Cerac), pyridine and quinoline (B.D.H.).

An aqueous stock solution of titanium(III) bromide was prepared by heating titanium powder (30 g) and hydrobromic acid (50%, 600 ml) under reflux, in a nitrogen atmosphere for 3 h. The mixture was allowed to cool, and was filtered under nitrogen. The violet solution had a titanium concentration of 1 g/20 ml.

Physical Methods and Analysis.—Electronic spectra were recorded on a Unicam SP 700C spectrophotometer. I.r. spectra (4000—200 cm^{-1}) were recorded on a Perkin-Elmer 577 instrument and far-i.r. spectra (400—40 cm^{-1}) on a Beckman–R.I.I.C. FS 720 interferometer. Magnetic moments were measured by the Gouy method at room temperature.

The vacuum thermograms were recorded upon a Stanton Massflow Thermobalance MF-FS. The balance was operated at 10^{-4} torr, the temperature rise being programmed at 6 °C min^{-1}, typical sample size being 0·15 g. The d.t.g. curves were obtained upon a time differential of 1·25 min. The temperature range for thermal reactions was measured between successive minima (or points of inflection) upon the d.t.g. curves. Thermograms of standard compounds under these conditions have been reported previously.[11]

C, H, and N Analyses were performed by the Alfred Bernhardt Microanalytical Laboratories. Titanium and bromine were determined gravimetrically as TiO_2 and AgBr respectively. The presence of water in the complexes was confirmed by i.r. spectroscopy. The acid equivalent of the complexes was determined by a conductometric titration against *ca.* 0·1 M aqueous sodium hydroxide solution.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

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Preparation of Complexes.—All reactions were carried out under nitrogen to prevent aerial oxidation. Samples undergoing dehydration were occasionally removed from the desiccator and powdered to ensure homogeneity of the final product.

$(pyH)_2(H_3O)TiBr_6(H_2O)_5$.—A solution of pyridine (12 ml) in hydrobromic acid (50%, 30 ml) was added to the aqueous titanium(III) bromide stock solution (50 ml), and the mixture was saturated with hydrogen bromide at room temperature (the mixture being cooled when necessary). The yellow-brown solution was stored at 0 °C for several days. The mixture was then filtered, and the crystals were washed twice with hydrobromic acid (50%, 20 ml) at −20 °C, and then three times with diethyl ether (15 ml). The purple crystals were dried in an evacuated desiccator over silica gel for 75 min, and then stored under nitrogen (Found: C, 14·9; H, 3·2; Br, 60·0; N, 3·5; Ti, 5·95%; μ_{eff} = 1·64 B.M.; acid equivalent = 5·97. $C_{10}H_{25}Br_6N_2O_6Ti$ requires C, 15·07; H, 3·16; Br, 60·18; N, 3·51; Ti, 6·01%; acid equivalent = 6·00).

$(pyH)_2TiBr_5(H_2O)_3$.—$(pyH)_2(H_3O)TiBr_6(H_2O)_5$ (*ca.* 6 g) was placed in a vacuum desiccator for 30 h over silica gel. A green powder formed (Found: C, 18·0; H, 2·8; Br, 60·1; N, 4·3; Ti, 7·45%; μ_{eff} = 1·64 B.M. $C_{10}H_{18}Br_5N_2O_3Ti$ requires C, 18·15; H, 2·74; Br, 60·38; N, 4·23; Ti, 7·24%).

$(pyH)_2TiBr_5(H_2O)$.—(*a*) *By evacuation.* $(pyH)_2(H_3O)TiBr_6(H_2O)_5$ (*ca.* 4 g) was continually evacuated for two weeks, to give an orange powder (Found: C, 19·35; H, 2·4; Br, 63·55; N, 4·6; Ti, 7·9%; μ_{eff} = 0·81 B.M. $C_{10}H_{14}Br_5N_2OTi$ requires C, 19·19; H, 2·26; Br, 63·86; N, 4·48; Ti, 7·66%).

(*b*) *By Dehydration.* $(pyH)_2(H_3O)TiBr_6(H_2O)_5$ (*ca.* 6 g) was placed in a vacuum desiccator for two weeks over phosphorus pentoxide. An orange-red powder formed (Found: C, 19·0; H, 2·35; Br, 63·65; N, 4·5; Ti, 7·75%; μ_{eff} = 0·68 B.M.).

$(quinH)_2(H_3O)TiBr_6(H_2O)_5$.—A solution of quinoline (11 ml) in a mixture of hydrobromic acid (60%, 30 ml) and water (10 ml) was added to the aqueous titanium(III) bromide stock solution (40 ml), and the mixture was saturated with hydrogen bromide at room temperature (the mixture being cooled when necessary). The yellow-brown solution was stored at 0 °C overnight, and the yellow-brown crystals were filtered off and washed as for the pyridinium analogue. The crystals were dried in an evacuated desiccator over silica gel for several days (Found: C, 23·95; H, 3·15; Br, 53·75; N, 3·1; Ti, 5·6%; μ_{eff} = 1·65 B.M.; acid equivalent = 5·97. $C_{18}H_{29}Br_6N_2O_6Ti$ requires C, 24·11; H, 3·26; Br, 53·46; N, 3·12; Ti, 5·34%; acid equivalent = 6·00).

$(quinH)_2TiOBr_4(H_2O)_5$.—A sample of $(quinH)_2(H_3O)TiBr_6(H_2O)_5$ was placed in a desiccator over silica gel, with restricted access of air, for several months. A red diamagnetic powder formed (Found: C, 29·65; H, 3·45; Br, 43·35; N, 3·95; Ti, 6·45%. $C_{18}H_{26}Br_4N_2O_6Ti$ requires C, 29·45; H, 3·57; Br, 43·55; N, 3·81; Ti, 6·53%).

$Rb_2TiBr_5(H_2O)_5$.—A solution of rubidium bromide (10 g) in water (25 ml) was added to the aqueous titanium(III) bromide stock solution (30 ml), and the mixture was saturated with hydrogen bromide at room temperature. The blue solution was stored at 0 °C overnight. The mixture was then filtered, and the purple solid washed three times with diethyl ether (25 ml) and dried in an evacuated desiccator over silica gel for 24 h (Found: Br, 56·25; Ti, 6·6%; μ_{eff} = 1·77 B.M. $H_{10}Br_5O_5Rb_2Ti$ requires Br, 56·39; Ti, 6·76%).

$Rb_2TiBr_5(H_2O)$.—$Rb_2TiBr_5(H_2O)_5$ (*ca.* 3 g) was heated *in vacuo* for 10 h at 80 °C, to give an orange powder (Found: Br, 61·6; Ti, 7·8%; μ_{eff} = 1·51 B.M. $H_2Br_5ORb_2Ti$ requires Br, 62·78; Ti, 7·53%).

$Cs_2TiBr_5(H_2O)_3$.—A solution of caesium bromide (8·5 g) in hydrobromic acid (50%, 40 ml) was added to the aqueous titanium(III) bromide solution (20 ml), and the mixture was saturated with hydrogen bromide at room temperature. The blue solution was stored at 0 °C overnight. The mixture was then filtered, and the red-purple solid was washed three times with diethyl ether (25 ml) and dried in an evacuated desiccator over silica gel (Found: Br, 51·4; Ti, 6·4%; μ_{eff} = 1·73 B.M. $H_6Cs_2Br_5O_3Ti$ requires Br, 52·07; Ti, 6·24%).

$Cs_2TiBr_5(H_2O)$. (*a*) *By reaction with acetyl bromide.* $Cs_2TiBr_5(H_2O)_3$ (*ca.* 5 g) was added to acetyl bromide (50 ml) and heated under reflux, in a nitrogen atmosphere, for 4 h. The mixture was then stored at 0 °C overnight, the red solid was filtered off *in vacuo*, then washed several times with diethyl ether. The red powder was dried in a desiccator over P_2O_5 (Found: Br, 54·45; Cs, 36·25; Ti, 6·5%; μ_{eff} = 1·66 B.M. $H_2Br_5Cs_2OTi$ requires Br, 54·64; Cs, 36·34; Ti, 6·56%).

(*b*) *By thermal dehydration.* $Cs_2TiBr_5(H_2O)_3$ (*ca.* 5 g) was heated *in vacuo* for 10 h at 100 °C, to give a red powder (Found: Br, 54·45; Cs, 36·4; Ti, 6·5%; μ_{eff} = 1·73 B.M.).

$TiBr_3(H_2O)_6$.—The aqueous titanium(III) bromide stock solution (50 ml) was saturated with hydrogen bromide at room temperature. The solution was stored at 0 °C overnight, the mixture was filtered, and the solid obtained was washed with diethyl ether and dried in an evacuated desiccator over silica gel (Found: μ_{eff} = 1·74 B.M.; acid equivalent = 2·96).

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