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Double Oxides Containing Niobium, Tantalum, or Protactinium.
IV. Further Systems Involving Alkali Metals

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The binary systems A_2O–B_2O_5 (where A = Rb or Cs and B = Nb or Ta) and A_2O–Pa_2O_5 (where A = Li, Na or K) have been partially examined. Unit-cell data are reported for most of the compounds prepared. In the Na_2O–Pa_2O_5 system, $NaPaO_3$ having a rhombohedrally distorted perovskite structure, and $NaPa_3O_8$ with a hexagonal unit cell have been observed. A value of 0·86 Å has been calculated for the ionic radius of protactinium from the cell parameters of $KPaO_3$ and $RbPaO_3$. The formation of APaO$_3$ compounds is discussed.

Introduction

Double oxides containing niobium or tantalum and alkali metals lithium to potassium, and some of those with caesium were reported on in the first paper of the present series (Whiston & Smith, 1965). This study is extended in the present paper to include the remaining rubidium and caesium compounds with niobium and tantalum, and also those of protactinium with the lighter alkali metals. These latter compounds have also been extensively studied by Keller in recent years.

Experimental

Preparative and X-ray techniques were outlined in part I (Whiston & Smith, 1965) and part III (Iyer & Smith, 1967). Fuller details of the experimental conditions are given by Iyer (1965).

The system Rb_2O–Nb_2O_5

Reisman & Holtzberg (1960) identified eight intermediate phases in the system Rb_2O–Nb_2O_5. The compositions and melting points are given in Table 1. None of the complex X-ray powder diffraction patterns were indexed by these authors. We have not been able to prepare single crystals of rubidium-rich phases (including $RbNbO_3$) for X-ray examination because of their highly hygroscopic nature. We obtained crystals of '$Rb_4Nb_6O_{17}$' and the lattice was found to be orthorhombic with

$$a=6{\cdot}42,\ b=7{\cdot}68,\ c=38{\cdot}55\ \text{Å}\ .$$

The density measured (4·45 g.cm.$^{-3}$) does not agree with the calculated value (4·09 g.cm.$^{-3}$) with $Z=4$ for the above composition. However the calculated density (4·56 g.cm.$^{-3}$) for $Rb_8Nb_{14}O_{39}$ with $Z=2$ agrees quite well with the measured density.

Table 1. *Compositions and melting points*

Compound	Melting point	
$Rb_4Nb_{30}O_{77}$	1351 °C	(incongruent)
$Rb_2Nb_8O_{21}$	1315	(congruent)
$Rb_8Nb_{22}O_{59}$	1319	(congruent)
$Rb_2Nb_4O_{11}$	1185	(incongruent)
$Rb_4Nb_6O_{17}$	1148	(incongruent)
$RbNbO_3$	964	(incongruent)
$Rb_8Nb_6O_{19}$	830	(congruent)
$Rb_8Nb_2O_9$	1300	(congruent)

Crystals of $Rb_2Nb_4O_{11}$ suitable for X-ray examination were prepared by firing a mixture of carbonate and oxide, containing slight excess of the carbonate, over extended periods. The lattice was found to be monoclinic with

$$a=12{\cdot}95,\ b=7{\cdot}48,\ c=14{\cdot}92\ \text{Å},\ \beta=106{\cdot}4^\circ\ .$$

The space group was Cm, $C2$, or $C2/m$. The density measured (4·86 g.cm^{-3}) shows rather poor agreement

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with the 5·16 g.cm^{-3} calculated for $Z=6$, but reformulation as $Rb_{12}Nb_{22}O_{61}$ gives 4·85 g.cm^{-3}. This formula would require at least one oxygen atom to be disordered in a *C*-centred space group but it seems the best available.

Powder patterns obtained from products with starting compositions of 1:3 and 4:11 ($Rb_2CO_3:Nb_2O_5$) were identical. Pale yellow irregularly shaped crystals were obtained from a slow-cooled melt of '$Rb_8Nb_{22}O_{59}$' and showed hexagonal symmetry with

$$a=7{\cdot}45,\ c=7{\cdot}66\ \text{Å}\,,$$

the space group being $P6_322$. The density measured (4·44 g.cm^{-3}) agrees with the calculated value for $RbNb_3O_8$ of 4·44 g.cm^{-3} with $Z=2$. Therefore we consider the correct composition to be $RbNb_3O_8$ rather than $Rb_8Nb_{22}O_{59}$.

Pale yellow needle-shaped crystals of $Rb_2Nb_8O_{21}$ were obtained from the appropriate starting mixture. This compound has tetragonal symmetry with

$$a=26{\cdot}55,\ c=3{\cdot}85\ \text{Å}\,.$$

The experimentally determined density of 4·59 g.cm^{-3} agrees well with 4·59 g.cm^{-3} calculated for six formula units per unit cell. This compound is possibly structurally related to $K_2Nb_8O_{21}$ (Whiston & Smith, 1965).

Reisman & Holtzberg suggested $Rb_4Nb_{30}O_{77}$ as the end member of the compounds existing in the system Rb_2O–Nb_2O_5. For compositions ranging from 1:6 to 2:15 of $Rb_2O:Nb_2O_5$ we obtained powder patterns resembling that of the high temperature form of Nb_2O_5. A needle-shaped crystal was obtained from a mixture of starting composition 1:6. This crystal possessed monoclinic symmetry with

$$a=20{\cdot}17,\ b=3{\cdot}83,\ c=20{\cdot}75\ \text{Å},\ \beta=123{\cdot}5^\circ\,,$$

the space group being *P*2, *Pm* or *P*2/*m*. The measured density (4·60 g.cm^{-3}) agrees well with the value of 4·59 g.cm^{-3} reported by Reisman & Holtzberg though the calculated value for $Rb_4Nb_{30}O_{77}$ is 5·46 g.cm^{-3}. The true composition is thought to be $Rb_2Nb_{26}O_{66}$ which gives a calculated density of 4·57 g.cm^{-3}. We consider this only as a tentative formula as the resemblance of the unit cell to that of the high temperature form of Nb_2O_5 (Gatehouse & Wadsley, 1964) suggests solid solution formation. However, we have not been able to establish this owing to the complexity and weak nature of the powder patterns obtained in the range investigated. Structures related to the high temperature form of Nb_2O_5 have also been observed in Na_2O–Nb_2O_5 systems (Whiston & Smith, 1965).

The system Cs_2O–Nb_2O_5

Of the five compounds reported by Reisman & Mineo (1961) the lattice parameters of $Cs_4Nb_{30}O_{77}$ and $Cs_5Nb_{13}O_{35}$ were reported by Whiston & Smith (1965).

We obtained colourless irregular crystals of $CsNbO_3$ from a slow-cooled melt at 870 °C. The crystals showed orthorhombic symmetry with

$$a=7{\cdot}24,\ b=15{\cdot}13,\ c=9{\cdot}77\ \text{Å}\,.$$

Plate-like crystals of the compound $CsNb_4O_{11}$ obtained from a melt at 1170 °C showed orthorhombic symmetry with

$$a=13{\cdot}03,\ b=7{\cdot}60,\ c=14{\cdot}36\ \text{Å}\,.$$

The measured density (5·68 g.cm^{-3}) agrees with the calculated value of 5·70 g.cm^{-3} for $Z=6$. This compound may be isostructural with $Rb_2Nb_4O_{11}$, though the latter has monoclinic symmetry.

The system Rb_2O–Ta_2O_5

A partial study of the system was made by Whiston (1963) and unit-cell data were obtained for $RbTaO_3$ and $Rb_3Ta_7O_{19}$. We investigated the tantalum-rich end of the system and found one compound, $RbTa_3O_8$, characterized by its powder pattern. Identical powder patterns were given by crystals grown from slowly cooled melts of initial composition $Rb_2CO_3+2Ta_2O_5$. The needle-shaped crystals thus obtained showed orthorhombic symmetry with

$$a=13{\cdot}07,\ b=7{\cdot}26,\ c=3{\cdot}85\ \text{Å}\,,$$

and space group *C*222, *Cmm*2, *Cm*2*m*, or *Cmmm*. The density of 6·76 g.cm^{-3} agreed well enough with the calculated value of 6·87 g.cm^{-3} for $Z=2$.

The system Cs_2O–Ta_2O_5

We examined this system only partially and prepared crystals of the compound $CsTaO_3$ from a melt at 1400°C. The unit cell showed monoclinic symmetry with

$$a=12{\cdot}90,\ b=7{\cdot}51,\ c=14{\cdot}81,\ \beta=105^\circ\,.$$

The system Li_2O–Pa_2O_5

At 700°C we obtained products corresponding to the compositions $LiPaO_3$ and Li_3PaO_4 in this system. The complex powder pattern of $LiPaO_3$ is similar to that obtained by Keller, Koch & Walter (1965) and could not be indexed. Attempts to prepare the compound Li_3PaO_4 by starting with a mixture of carbonate and oxide in the ratio of 3:1 resulted in the formation of $LiPaO_3$ and a new phase. The powder diffraction lines of the new phase could be indexed on the basis of the tetragonal unit cell having $a=4{\cdot}52\pm0{\cdot}01$ and $c=8{\cdot}48\pm0{\cdot}01$ Å reported by Keller (1965*b*) while our work was in progress. It is likely that the compound Li_3PaO_4 slowly decomposes at the temperature of the experiment, leading to the formation of $LiPaO_3$ (and presumably Li_2O) as in the corresponding compound Li_3NbO_4, though the decomposition temperature of the latter is of the order of 1300 °C (Whiston & Smith, 1965).

Products richer in Pa_2O_5 than $LiPaO_3$ gave powder patterns indicative of a cubic phase similar to cubic

Pa_2O_5 with

$$a = 5{\cdot}358 \pm 0{\cdot}007 \text{ Å}$$

and presumed to be the solid solution limit of Li_2O in Pa_2O_5.

The system Na_2O–Pa_2O_5

Two compounds $NaPaO_3$ and $NaPa_3O_8$ were identified in this system. We obtained $NaPaO_3$ at 850 °C with a rhombohedrally distorted perovskite structure with

$$a = 2 \times (4{\cdot}182 \pm 0{\cdot}007) \text{ Å}, \ \alpha = 90{\cdot}8° .$$

The doubling of the cell edge was necessary to index the weak lines on the pattern. The powder pattern obtained by us was different from that reported by Keller (1965*b*) for this compound. Our product may be another form of $NaPaO_3$. Possible deviation from stoichiometry also cannot be ruled out as our reaction temperature was much higher than that (500 °C) used by Keller, volatilization of Na_2O being possible.

The compound $NaPa_3O_8$ was obtained at 700 °C. The powder pattern was indexed on the basis of a hexagonal unit cell with

$$a = 6{\cdot}282 \pm 0{\cdot}005, \ c = 8{\cdot}243 \pm 0{\cdot}005 \text{ Å} .$$

As with the lithium system, solid solutions were obtained from compositions rich in Pa_2O_5. The cell constant was $a = 5{\cdot}399 \pm 0{\cdot}007$ Å.

This product was also obtained by heating $NaPaO_3$ at 950 °C for 48 hours.

The system K_2O–Pa_2O_5

Our attempt to prepare $KPaO_3$ at 950 °C resulted in a product which was not isostructural with either $LiPaO_3$ or $NaPaO_3$, as described above, nor with the $KPaO_3$ prepared by Keller (1965*b*) at 500 °C. It is likely that the product obtained by us is richer in Pa_2O_5 than $KPaO_3$. The powder pattern of the compound is given in Table 2.

Table 2. *X-ray powder pattern of the product* ($K_2CO_3 + Pa_2O_5$) *at* 950 °C

I	*d*	*I*	*d*
4	3·433 Å	2*B*	1·118 Å
1	3·096	*VW*	1·103
VW	2·735	2	1·082
1	2·112	2	1·070
2	2·001	*VWB*	1·052
1	1·871	*VW*	1·011
6	1·709	1	0·970
7*B*	1·658	1	0·964
VW	1·608	6	0·952
VW	1·439	6	0·942
VW	1·407	*VW*	0·895
8	1·356	2	0·885
2	1·293	1	0·875
10	1·274	3	0·851
2*B*	1·241	*VW*	0·847
VW	1·166	1	0·837
1	1·145		

VW – very weak; *B* – broad line.

The ionic radius of Pa^{5+}

In the ABO_3 compounds formed by protactinium, $KPaO_3$ and $RbPaO_3$ can have the ideal cubic perovskite structure (Keller, 1965*a*). The important interatomic distances in perovskite structures are *A*–O and *B*–O equal to $r_A + r_O$ and $r_B + r_O$ respectively. The compounds $KPaO_3$ and $RbPaO_3$ have cell constants $a = 4{\cdot}34 \pm 0{\cdot}01$ and $a = 4{\cdot}36 \pm 0{\cdot}01$ Å respectively and one formula unit per cell. These give $r_{Pa} + r_O = 2{\cdot}17$ Å in $KPaO_3$ and 2·18 Å in $RbPaO_3$. The Goldschmidt ionic radius for O^{2-} (1·32 Å) then gives 0·86 Å for the ionic radius of Pa^{5+} in perovskite type compounds. The value reported by Zachariasen (1950) is 0·90 Å.

The tolerance factor '*t*' for APaO$_3$ compounds

The tolerance factor '*t*' (Goldschmidt, 1926) has been extensively used in predicting whether a given ABO_3 compound could be expected to show a perovskite-like or some other structure (*e.g.* Megaw, 1946). Of the five $A^{I}Pa^{V}O_3$ compounds reported, $NaPaO_3$ has a distorted perovskite structure, and $KPaO_3$ and $RbPaO_3$ have the ideal cubic perovskite structure and $LiPaO_3$ and $CsPaO_3$ have unknown structures. The ionic radius of protactinium derived above and the ionic radii of alkali-metals corrected for twelvefold coordination have been used to calculate the tolerance factor '*t*' for all the APaO$_3$ compounds and are given in Table 3. Goldschmidt's radii have been used.

Table 3. *Tolerance factors*

Ion	Ionic radii corrected for twelvefold coordination	Tolerance factor '*t*'
Li^+	0·84 Å	0·70
Na^+	1·06	0·77
K^+	1·44	0·90
Rb^+	1·61	0·95
Cs^+	1·78	1·00

An ilmenite-type structure should be expected for $LiPaO_3$ by analogy with $LiNbO_3$ and $LiTaO_3$ and from the tolerance factor value. From the powder pattern, it appears that the structure is different from those of $LiNbO_3$ and $LiTaO_3$. As expected from the tolerance factor value the compound $NaPaO_3$ has a distorted perovskite structure while $KPaO_3$ and $RbPaO_3$ have ideal cubic structures. A tetragonal distorted perovskite structure should have been found for $CsPaO_3$ from the tolerance factor value. The powder pattern of this compound reported by Keller (1965*a*) suggests lower symmetry than this, and it is doubtful whether this compound possesses a perovskite structure at all. It may be that the Cs ion is too large to fit in the hole between the oxygen octahedra. The effect of such a large ion in the *A* position pushes the oxygen atoms apart, leaving the *B* ion to 'rattle' in the octahedral hole. Hence the structure collapses around the *B* ion and a structure with a smaller coordination number for *B* or a larger coordination number for *A* would result.

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The Crystal Structure of Tetraphenylphosphonium Trichloro-(*cis*-but-2-en-1,4-diol)platinum(II)

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Tetraphenylphosphonium trichloro(*cis*-but-2-en-1,4-diol)platinum(II), $(C_6H_5)_4P^+.[PtCl_3(C_4H_8O_2)]^-$, forms yellow monoclinic crystals, $a=13\cdot665$, $b=7\cdot471$, $c=27\cdot402$ Å, $\beta=102\cdot00°$, space group $P2_1/c$, with four formula units in the unit cell. The structure has been solved by standard methods and refined by the block-diagonal matrix least-squares methods, using 1899 photographic observations, to a final R value of 0·085. The $[PtCl_3(C_4H_8O_2)]^-$ anion is a π-complex and the platinum atom is square coordinated with the three chlorine atoms and the double bond of the olefinic diol. Two centrosymmetrically related anions interact through two O–H···O hydrogen bonds. The $(C_6H_5)_4P^+$ cation has almost $\bar{4}$ point symmetry. Intramolecular bond distances are normal.

During the investigation of the thermodynamics of the formation of platinum(II)-π-complexes with functionally substituted olefins, the X-ray crystal structure determination of some of them was undertaken. The purpose was to determine the mode of bonding of the substituted olefins and the effect of the substituents on the bonding to the metal.

Papers dealing with the structure of π-complexes of platinum(II) with unsaturated amines have been published by Spagna, Venanzi & Zambonelli (1970*a*, *b*).

In this article, the structure of tetraphenylphosphonium trichloro(*cis*-but-2-en-1,4-diol)platinum(II) is reported.

Experimental

Preparation

The compound $(C_6H_5)_4P^+.[PtCl_3(C_4H_8O_2)]^-$ was synthesized in the following manner. Commercial *cis*-but-2-en-1,4-diol (b.p. 102–107°/2·5–3 mmHg; dibenzoate, m.p. 65–66°C from ethanol) (0·5 g) in 2*N*-hydrochloric acid (7–8 cm^3) was added to potassium tetrachloroplatinate (1 g) in 2*N*-hydrochloric acid (7–8 cm^3). The solution was heated (70°C) until it became yellow, then cooled and filtered. The stoichiometric amount of tetraphenylphosphonium chloride was added to the solution, and the compound precipitated as a light yellow powder. Transparent yellow crystals suitable for single-crystal X-ray analysis were grown from dichloromethane–benzene solutions; m.p. 173–174°C (found Pt, 26·7%; $C_{28}H_{28}Cl_3O_2PPt$ requires Pt, 26·8%).

Crystal data

Crystals of $(C_6H_5)_4P^+.[PtCl_3(C_4H_8O_2)]^-$ are stable in air and to X-rays. Preliminary X-ray and optical examinations of the crystals indicated that they belong to the monoclinic system. The space group, $P2_1/c$ (No. 14), was assigned on the basis of the systematic absences ($h0l$, $l=2n+1$; $0k0$, $k=2n+1$). Unit-cell dimensions at about 23°C are: $a=13\cdot665\pm0\cdot002$, $b=7\cdot471\pm0\cdot001$, $c=27\cdot402\pm0\cdot003$ Å, $\beta=102\cdot00\pm0\cdot02$; these were determined by a least-squares refinement of seventy-six 2θ values measured on $0kl$ and $h0l$ Weissenberg photographs calibrated with superimposed ZnO powder lines, using Cu $K\alpha$ radiation ($\lambda=1\cdot5418$ Å).

The measured density (by flotation in a $ZnCl_2$ solution) of $1\cdot77\pm0\cdot01$ g.cm^{-3} agrees very well with the value of 1·769 g.cm^{-3} calculated for 4 units $(C_6H_5)_4P.[PtCl_3(C_4H_8O_2)]$ of formula weight 728·95 in the cell volume of 2736·26 Å^3.

The X-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken, at room-temperature, about the a (9