allows sp³ hybridization of the metal orbitals with one of the orbitals occupied by a lone pair of electrons, it is not too surprising to find that a triphosphate complex is apparently formed without appreciable formation of a diphosphate species. Other systems of tin(II) complexes have previously been shown to exhibit this behavior.[14]

At the pH of these experiments the predominant phosphate species, in the absence of tin, are H_3PO_4 and $H_2PO_4^-$. Even though it is impossible to specify, without a measure of the acid dependence of the quotients q_1 and q_3, the acid dissociation constants of the tin phosphate complexes, it is fair to say that these complexes must be stronger acids than $H_2PO_4^-$. If we then assign the formulas $SnHPO_4$ and $Sn(HPO_4)_3^{4-}$ to the respective complexes, we calculate formation constants for them of $\beta_{11} = (6.7 \pm 1.5) \times 10^7$ and $\beta_{33} = (1.1 \pm 0.3) \times 10^{10}$. These values do not seem unreasonable and provide an estimate of the interaction between tin(II) and orthophosphate.

(14) J. D. Donaldson, "A Review of the Chemistry of Tin(II) Compounds," Tin Research Institute, Columbus, Ohio, 1964.


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Preparation of Tungsten Bronzes from Metal Halides[1]

By Lawrence E. Conroy and George Podolsky

Tungsten bronzes, M_xWO_3 (M is a metal and $0 < x < 1$), containing alkaline earth metals (Ba and Sr) were first prepared by Conroy and Yokokawa,[2] utilizing the reaction of the corresponding alkaline earth chloride with mixtures of tungsten trioxide and tungsten dioxide at 900–1000°
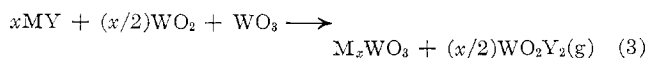
$$xMCl_2 + xWO_2 + WO_3 \longrightarrow M_xWO_3 + xWO_2Cl_2 \quad (1)$$
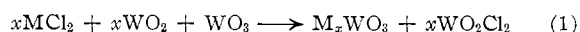
Tungsten metal may also serve as the reducing agent at such temperatures

$$xMCl_2 + (x/3)W + [1 + (2x/3)]WO_3 \longrightarrow$$
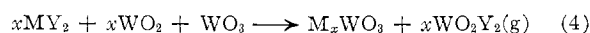$$M_xWO_3 + xWO_2Cl_2(g) \quad (2)$$
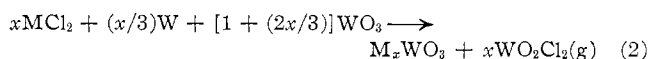
Further experiments have shown that this type of reaction, utilizing the volatilities of the tungsten oxyhalides, will function with the corresponding bromides or iodides in place of the chlorides. The method is of general utility for the preparation of tungsten bronzes from either monohalides or dihalides. The

assumed stoichiometry for monohalides with WO_2 and WO_3 is then

$$xMY + (x/2)WO_2 + WO_3 \longrightarrow$$
$$M_xWO_3 + (x/2)WO_2Y_2(g) \quad (3)$$

and for dihalides

$$xMY_2 + xWO_2 + WO_3 \longrightarrow M_xWO_3 + xWO_2Y_2(g) \quad (4)$$

where Y is Cl, Br, or I.

Experimental Section

Materials.—LiCl, NaCl, NaBr, NaI, KCl, KBr, KI, $MgCl_2$, $MgBr_2$, $CaCl_2$, $CaBr_2$, CaI_2, $SrCl_2$, $BaCl_2$, and $PbCl_2$ were reagent grade. LiBr, LiI, MgI_2, $SrBr_2$, $BaBr_2$, BaI_2, $PbBr_2$, and TlCl were obtained from City Chemical Corp. in Purified or USP grades. CsCl and CsI were BDH 99%. BrCl was Alfa Inorganics, Inc., 96+%. Nd_2O_3 was Lindsay Rare Earth Chemicals Code 217. WO_3 was Sylvania Chemical and Metallurgical Division Grade TO-2, and tungsten was A. D. Mackay, Inc., 99.99%. WO_2 was prepared by the reaction of W and WO_3 at 950° under purified argon. Commercial grade argon was purified in a reduction column described previously.[2] Solid chemicals were dried 3 hr at 400° and 10^{-2} torr.

Nd_2O_3 was converted to $NdCl_3$ by heating with excess NH_4Cl for 3 hr at 320°.

Preparations.—Mixtures of the halide, WO_3, and WO_2 were prepared employing an excess of the halide and using the WO_2-limiting reactant to limit x. The reactants were ground together, packed into recrystallized alumina combustion boats, and heated in Vycor tubes under vacuum (10^{-5} torr) or under purified argon. The reaction tube was situated in the tube furnace with at least one-fourth of the length extending from the furnace, so that this cool portion served as a condenser for the volatilized tungsten oxyhalides. The temperature of the hot zone was raised slowly past the melting point of the halide to some arbitrary maximum temperature. The reactants were held at the maximum temperature for at least 3 hr, and then were allowed to cool rapidly to room temperature. The products were purified by successively heating in water, dilute HCl, and dilute NH_3, in the case of the alkali metal preparations, and by heating in 10% oxalic acid solution for 6 hr, followed by leaching with dilute NH_3, in the case of the other compounds. Silica was removed by washing with 48% aqueous HF.

Chemical Analysis.—The alkali metal and alkaline earth bronzes were analyzed by heating in a stream of dry HCl-air mixture to volatilize tungsten and oxygen as the oxychloride, leaving a residue of the metal halide in the combustion boat.[2,3] The metal content of the chloride residue was determined by flame or atomic absorption spectrophotometry for all but the magnesium chloride residues. Magnesium was determined gravimetrically as the 8-hydroxyquinolinate. All of the chloride residues were checked for purity by determining chloride using the Volhard method. For all of the alkali metal and alkaline earth metal bronzes, tungsten was determined from the weight loss following the volatilization of the oxychloride.

The lead content in that bronze was determined by precipitating the very insoluble $PbWO_4$. A similar method was employed as an independent analysis for the alkaline earth metals. The bronze was fused with a 3:1 weight mixture of Na_2CO_3–$NaNO_3$ at red heat in a porcelain crucible. The cooled fusion cake was dissolved in water and made acid with HCl. After heating to expel CO_2 the solution was made basic with NaOH to dissolve any WO_3. The precipitate of MWO_4 was then filtered off, washed, dried at 750°, and weighed. The tungsten remaining in solution was determined as the trioxide by the nitric acid–cinchonine precipitation.[4] The thallium bronze was determined by the

method of Sienko.[5] In all of the above analyses, oxygen was determined by difference, and these analyses yielded $W:O$ ratios averaging 3.1 ± 0.2. The neodymium bronze composition was estimated from the magnetic susceptibility.[6]

X-Ray Diffraction Data.—X-Ray powder diffraction data were recorded by both photographic and diffractometer methods, using copper radiation.

Results and Discussion

Reaction of each halide was evident by the appearance of a yellow "smoke" of the tungsten oxyhalide that eventually deposited in the cool portion of the reaction tube. Such evidence usually appeared within 100° below the melting point of the pure halide. The data for the various reactions are summarized in Table I. Temperatures below 500° could not be determined with the recording apparatus used in these preparations.
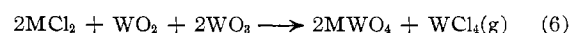
TABLE I

Halide	Mp, °C	Initial reaction temp, °C	Max temp, °C	Max x in M_xWO_3	Bronze-type structure
LiCl	614	585	700	0.3	Perovskite
LiBr	552	540	700	0.3	Perovskite
LiI	440	<500	900[a]	0.3	Perovskite
NaCl	800	780	950	0.8	Perovskite
NaBr	747	740	950	0.8	Perovskite tetragonal I[b]
NaI	662	650	950[a]	0.8	Perovskite
KCl	770	600	900	0.4	Hexagonal
KBr	742	730	900	0.4	Hexagonal
KI	682	670	900[a]	0.3	Tetragonal I
RbI	638	<500	900[a]	0.3	Hexagonal
CsCl	642	620	900	0.4	Hexagonal
CsI	621	<500	900[a]	0.3	Hexagonal
MgCl₂	712	540	950	0.2	Complex
MgBr₂	711	<500	700	0.2	Complex
MgI₂	dec	<500	700[a]	0.1	Complex
CaCl₂	782	550	700	0.1	Complex
CaBr₂	760	550	700	0.2	Complex
CaI₂	740	<500	700[a]	0.1	Complex
SrCl₂	872	850	950	0.2	Complex or tetragonal I
SrBr₂	653	620	700	0.1	Complex or tetragonal I
SrI₂	507	<500	600[a]	0.1	Complex or tetragonal I
BaCl₂	960	930	950	0.1	Tetragonal I
BaBr₂	847	800	850	0.1	Tetragonal I
BaI₂	740	640	700[a]	0.1	Tetragonal I
TlCl	427	~400	900	0.3	Tetragonal I
PbCl₂	498	<500	900	0.3	Tetragonal I
PbBr₂	497	<500	900	0.3	Tetragonal I
NdCl₃	760	650	1050	0.1	Perovskite

[a] Some decomposition to I_2. [b] A. Magneli, *Nova Acta Regiae Soc. Sci. Upsaliensis*, **14**, 3 (1950).

Products of the reactions were typically small needle crystals with metallic luster. The colors displayed by the crystals of known tungsten bronzes showed the same dependence upon composition as has been observed in samples prepared by other methods. Lithium bronzes ranged from violet to blue, sodium bronzes from yellow to blue, potassium bronzes from red to blue, and rubi-

dium and cesium bronzes were blue. The alkaline earth metal bronzes ranged from red-violet to blue, while the lead and thallium bronzes were always blue. The neodymium bronze was blue-violet. Even though all preparations contained an excess of the halide and quantities of WO_2 corresponding to x values from 0.3 to 0.9, the upper limits for x in the products, as shown in Table I, were always less than these numbers. The crystal structures were in general the same as those observed for the corresponding bronze in previously reported preparations. However, in the cases of the Mg, Ca, and some of the Sr preparations, a different structure appeared. We were unable to index this structure completely but the powder patterns were all similar to the tungsten oxide phase variously characterized as W_2O_5, W_4O_{11}, and labeled $W_{18}O_{49}$ by Wells.[7,8] All of the bronzes prepared by this method exhibited chemical properties similar to the sodium tungsten bronze system which is notable for its resistance to all common reagents except strongly alkaline solutions or melts. The new Mg, Ca, and Sr phases have high electrical conductivities similar to the other bronzes. The specific resistivity of a pressed powder sample was <0.1 ohm-cm at room temperature.

This halide method appears to have quite general utility for the preparation of tungsten bronzes and is, thus far, the only method capable of preparing the alkaline earth metal bronzes at atmospheric pressures. A usual by-product of these preparations was the corresponding orthotungstate compound, which was seperable from the bronze by water or oxalic acid solution. The orthotungstate may result from the reactions

$$MCl_2 + WO_2 + WO_3 \longrightarrow MWO_4 + WOCl_2(g) \quad (5)$$

$$2MCl_2 + WO_2 + 2WO_3 \longrightarrow 2MWO_4 + WCl_4(g) \quad (6)$$

Both of these side reactions are indicated by the colors of the volatile reaction products, but neither has been definitely established. At temperatures above 1200° the alkaline earth and lead halides produce a disproportionation reaction with tungsten dioxide[2]

$$MCl_2 + 3WO_2 \longrightarrow MWO_4 + W + WO_2Cl_2(g) \quad (7)$$
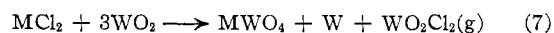
Thus 1200° seems to be the effective upper limit for this method with the group II metals and lead. Although the method described above yields only very small crystals, there is evidence that it may be adaptable to the growth of larger crystals by employing vapor-phase WO_3 as a reactant.

(5) M. J. Sienko, *J. Am. Chem. Soc.*, **81**, 5556 (1959).
(6) W. Ostertag, *Inorg. Chem.*, **5**, 758 (1966).
(7) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, Oxford, 1962, p 468.
(8) A. Magneli, *Arkiv Kemi*, **1**, 223 (1949).