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New Lithium, Ammonium, and Tin Hexagonal Tungsten Bronzes Prepared Hydrothermally

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The hexagonal tungsten bronzes M_xWO_3 (maximum $x = 0.33$) containing the alkali metals K, Rb, and Cs were prepared by Magnéli[1] using a melt-fusion technique. He described their hexagonal, open tunnel-type structure and metallic conductivity, and Sweedler, *et al.*,[2] have demonstrated that these materials show superconductivity. In contrast, the remaining alkali metal tungsten bronzes containing Li or Na usually adopt a perovskite-related or a tetragonal tunnel-type structure depending upon stoichiometry.[1,3] The formation of hexagonal Na_xWO_3 in a melt reaction carried out at 65 kbars pressure has only recently been described.[4] We wish to report the synthesis and superconductivity of the hexagonal tungsten bronzes Li_xWO_3 and $(NH_4)_xWO_3$, thus completing the series of alkali metal M_xWO_3 compositions having this structure (NH_4^+ is considered to belong to this group). In addition, we wish to report the preparation of hexagonal and tetragonal Sn_xWO_3.

Experimental Section

These hexagonal bronzes were prepared hydrothermally in sealed gold tubes with a volume of 7–9 cm³ under an external argon pressure of 3000 atm. Amounts of reactants, as well as reaction times and temperatures, are given individually below. Stoichiometries were determined by chemical analyses. Single-crystal data (precession photographs) on both the Li_xWO_3 and $(NH_4)_xWO_3$ compositions were compatible with space group $P6_3/mcm$ as reported by Magnéli[1] for $Rb_{0.29}WO_3$. Powder patterns were obtained with either Debye–Scherrer or Hägg–Guinier cameras. The cell dimensions were refined by least-squares with the Nelson–Riley function as a parameter for Debye–Scherrer data. Resistivity was determined by a standard four-probe technique[4] on single crystals, and superconductivity was measured magnetically by the Meissner effect in which the self-inductance of a coil containing the sample was observed.[5]

Li_xWO_3.—In a typical preparation of hexagonal Li_xWO_3, the reaction of 0.8 g of a WO_3–W–LiOH mixture in a 1:3:2 mole ratio in 1.5 ml of H_2O at 700° for 9 hr gave purple crystals, some rod-shaped with hexagonal cross sections and up to 1 mm in length. Metallic-type conduction was observed (Table I). A unit cell volume calculated from the hexagonal cell dimensions (Table I) and a measured density of 6.496 g/cm³ gave a formula weight equating to the composition $Li_{0.30}WO_3$. *Anal.* Calcd for $Li_{0.30}WO_3$: Li, 0.89; O, 20.5. Found: Li, 0.85; O, 22.6. An alternative possibility is $(Li\cdot H_2O)_{0.29}WO_3$. *Anal.* Calcd for $(Li\cdot H_2O)_{0.29}WO_3$: Li, 0.84; O, 22.0; density, 6.64 g/cm³. Found: Li, 0.85; O, 22.6; density, 6.50 g/cm³.

TABLE I

M_xWO_3	Cell dimensions,[a] Å		Resistivity, ohm-cm		Superconductivity, range of T_c, °K
	a	c	4.2°K	298°K	
Alkali Metal Hexagonal Tungsten Bronzes					
$Li_{0.30}WO_3$	7.405	7.554	4.5×10^{-5}	3.4×10^{-4}	2.2–<1.3
Na_xWO_3	7.38	7.55			5.4–<1.3
$K_{0.31}WO_3$[b]	7.37	7.54	(powder)[b]	5×10^{-2}	5.7–0.5[c,d]
$(NH_4)_{0.33}WO_3$	7.395	7.525			3.2–1.4
$Rb_{0.32}WO_3$[e]	7.386	7.54		6.3×10^{-5}	6.6–1.9[c,d]
$Cs_{0.30}WO_3$[b]	7.38	7.59	(powder)[b]	7×10^{-2}	4.8–1.1[c,d]
Group IVa Tungsten Bronzes[f]					
Hexagonal					
$Sn_{0.21}WO_3$ (H)	7.428	7.581			No T_c to 1.3°K
$Sn_{0.24}WO_3$ (H)	7.430	7.581	8×10^{-5}	1.5×10^{-4}	No T_c to 1.3°K
Sn_xWO_3 (ST)	7.453	7.565			No T_c to 1.3°K
Tetragonal					
$Sn_{0.19}WO_3$ (ST)	12.241	3.774			No T_c to 1.3°K
$Pb_{0.17}WO_3$ (ST)[g]	12.163	3.767		6×10^{-4}	No data

[a] Standard deviation (Li, NH_4, Sn bronzes) ±0.001 Å or less. [b] See ref 1. [c] See ref 10. [d] See ref 2. [e] M. J. Sienko and S. M. Morehouse, *Inorg. Chem.*, **2**, 485 (1963). [f] Synthesis: H, hydrothermal; ST, sealed tube. [g] See ref 9.

$(NH_4)_xWO_3$.—The NH_4^+ cation, which is formally considered as a member of the alkali metal ion series, is similar in size to Rb^+. Hexagonal $(NH_4)_xWO_3$ was readily prepared by reaction of 1.2 g of a WO_3–W mixture (1:1 mole ratio) in 1 ml of concentrated NH_4OH at 700° for 9 hr. Acicular, purple microcrystals were isolated which corresponded to the composition $(NH_4)_{0.33}WO_3$. *Anal.* Calcd for $(NH_4)_{0.33}WO_3$: N, 1.94. Found: N, 1.89, 1.95.

The reaction of 0.52 g of $(NH_4)_2W_2O_7$ in 2 ml of H_2O under the same conditions gave a similar product of comparable small crystallite size. The thermal stability of $(NH_4)_xWO_3$ is lower than that of Rb_xWO_3 (prepared at 1050° [1]). Thus, reaction of 1.3 g of a WO_3–W mixture in a 2:1 mole ratio in 1 ml of concentrated NH_4OH at 900° for 5 hr gave the oxide $W_{18}O_{49}$ rather than the bronze.

Na_xWO_3.—Efforts were made to prepare hexagonal Na_xWO_3 by the above hydrothermal technique, but the known cubic perovskite form, with varying Na content, was obtained instead. The reaction of 6 g of an $Na_2WO_4\cdot 2H_2O$–W (5-mil foil) mixture in a 2:1 mole ratio in 4 ml of H_2O at 700° for 9 hr gave golden, cube-shaped crystals with a cell dimension $a = 3.863 \pm 0.001$ Å and resistivities of 6×10^{-7} and 1×10^{-5} ohm-cm at 4.2 and 298°K, respectively. Extrapolation from the data of Brown and Banks[6] of unit cell size *vs.* Na concentration for cubic Na_xWO_3 indicates the composition $Na_{0.96}WO_3$. By comparison with the electrical measurements of Ellerbeck, *et al.*,[7] for a cubic Na_xWO_3 series, the low resistivity of this metallic-type conductor also indicates a very high Na content. Bronzes approximating this $Na_{0.96}WO_3$ composition appear to have the highest Na content reported.[7,8] In contrast to the superconducting hexagonal alkali metal tungsten bronzes, Sweedler, *et al.*,[2] have detected no superconductivity down to

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(1) A. Magnéli, *Acta Chem. Scand.*, **5**, 372 (1951); **7**, 315 (1953).
(2) A. R. Sweedler, C. J. Raub, and B. T. Matthias, *Phys. Letters*, **15**, 108 (1965).
(3) A. S. Ribnick, B. Post, and E. Banks, Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, paper 23, p 246.
(4) T. A. Bither, J. L. Gillson, and H. S. Young, *Inorg. Chem.*, **5**, 1559 (1966).
(5) P. E. Bierstedt, T. A. Bither, and F. J. Darnell, *Solid State Commun.*, **4**, 25 (1966).
(6) B. W. Brown and E. Banks, *J. Am. Chem. Soc.*, **76**, 963 (1954).
(7) L. D. Ellerbeck, H. R. Shanks, P. H. Sidles, and G. C. Danielson, *J. Chem. Phys.*, **35**, 298 (1961).
(8) F. Kupka and M. J. Sienko, *ibid.*, **18**, 1296 (1950).

about 0.1°K for cubic tungsten bronzes. Similarly, no superconductivity was observed in this $Na_{0.96}WO_3$ phase down to 1.3°K, the lower limit of our measurement.

Sn_xWO_3.—The group IVa metal tungsten bronze Pb_xWO_3 with tetragonal structure has been prepared by the melt–fusion technique.[9] Hexagonal Sn_xWO_3 was obtained hydrothermally by the reaction of 2 g of an $SnO–WO_3–W$ mixture in a 3:9:1 mole ratio in 3 ml of H_2O at 400° for 8 hr. Blue-black microcrystals of composition $Sn_{0.21}WO_3$ (Calcd: Sn, 9.71. Found: Sn, 9.72) were formed. Reaction of 5.8 g of an $SnO–WO_3–W$ mixture in a 3:1:1 mole ratio in 1 ml of H_2O at 700° for 10 hr gave single crystals of hexagonal $Sn_{0.24}WO_3$ (Calcd: Sn, 10.94. Found: Sn, 11.10) of sufficient size to demonstrate their metallic-type conduction (Table I). These Sn_xWO_3 compounds showed no superconducting transition, T_c, down to the lowest measured temperature of 1.3°K, even after an etch with strong acid which has been demonstrated to increase T_c.[10]

Hexagonal Sn_xWO_3 was also obtained as very small blue-black crystallites by the solid-state reaction of 5 g of an $SnO–WO_3–W$ mixture in a 3:9:1 mole ratio in a sealed, evacuated silica tube at 1000° for 24 hr. Crystals of WO_2 contaminated this phase. Again, no superconductivity was noted to 1.3°K. When the same reactants were heated for 5 days at 1000°, purple needles of Sn_xWO_3 having the tetragonal bronze structure (tunnel-type) as in Pb_xWO_3 rather than the hexagonal type were obtained. After extraction with hot 40% H_3PO_4, a composition $Sn_{0.19}WO_3$ (Calcd: Sn 8.86. Found: Sn, 8.95) was obtained. As with the hexagonal Sn bronzes, no superconductivity was observed to 1.3°K.

Results and Disscusion

Cell dimensions and electrical properties of the complete group of alkali metal tungsten bronzes are summarized in Table I for comparative purposes. The near equivalence of these metallic materials reflects the importance of the WO_6 octahedral framework in establishing their basic properties. Goodenough[11] has proposed that if the coordination of oxygen is less than four, a π^* band may be formed using the metal d orbitals and oxygen orbitals with π^*-bonding symmetry. Since oxygen atoms are coordinated by two tungsten atoms in all of the tungsten bronze structure types, this band is possible. The band is empty in WO_3 but has electrons donated to it, *e.g.*, by an alkali metal, in the various tungsten bronzes.

Transitions to the superconducting state in the range 1–6°K have now been observed in hexagonal tungsten bronzes containing all of the alkali metals, as well as the group IIa and IIIa metals Ca, Sr, Ba, In, and Tl.[5] The absence of a similar transition in the analogous metallic, hexagonal Sn_xWO_3 compositions of group IVa thus seems unusual. Since our lower limit of measurement is approximately 1.3°K, we cannot rule out superconductivity occurring in these Sn bronzes at some lower temperature.

The existence of Li_xWO_3 with the hexagonal tungsten bronze structure is unusual in that Li would appear to be too small to be held in the large hexagonal tunnels. These tunnels would seem best suited for cations larger than ~1 Å in radius while Li is much smaller than this ($R_{Li} \sim 0.68$ Å). Other sites are available in the hexagonal tungsten bronze structure. The largest of these would be trigonal prisms capped on all rectangular faces. If the Li were at one end of a prism, its coordination to oxygen could be six or even three. Jamieson, *et al.*,[12] have suggested that Li occupies sites of this type in $K_{1-x}Li_xNbO_3$ ($x \sim 0.4$) compounds which have the tetragonal tungsten bronze structure.[13] Graham and Wadsley[14] have shown that the presence of large cations in the hexagonal tunnels is not structurally necessary since $MoW_{11}O_{36}$ and $MoW_{14}O_{45}$ both have the hexagonal tungsten bronze structure with these tunnels being completely empty.

Since Li_xWO_3 was prepared hydrothermally, it is also possible that hydrated Li is present in the hexagonal tunnels.

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Fluorinated Derivatives of Azodiformamidine

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It was recently reported that the stirred, solid fluorination of guanidine monohydrofluoride produced the novel compound pentafluoroguanidine, $(NF_2)_2C{=}NF$.[1] We wish to report that when azodiformamidine dinitrate was allowed to react with very dilute fluorine in the presence of sodium fluoride, a series of new highly fluorinated azo compounds was formed. The most abundant of these was difluorotetrakis(difluoramino)-azomethane, $(NF_2)_2CFN{=}NCF(NF_2)_2$, a faintly yellow liquid which boiled at 81°. Also isolated were two isomers of [bis(difluoramino)fluoromethylazo]trifluoroformamidine, $(NF_2)_2CFN{=}NC({=}NF)NF_2$, IIa and b, and three isomers of hexafluoroazodiformamidine, $NF_2C({=}NF)N{=}NC({=}NF)NF_2$, IIIa, b, and c.

The colors of the unsaturated compounds varied from yellow-orange to red, owing to the effect of conjugation of the fluorimino group with the azo chromophore. Pertinent spectroscopic properties and probable stereochemical configurations for these materials are summarized in Table I. It should be pointed out that for

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(1) R. A. Davis, J. L. Kroon, and D. A. Rausch, *J. Org. Chem.*, **32**, 1662 (1967).