cis-$Mo(CO)_3[P(OCH_3)_3]_3$ was prepared by the method previously described by Dobson.[33]

All other compounds were prepared by the method previously reported.[34]

Infrared Spectra.—All infrared spectral measurements were made on a Beckman IR-7 spectrophotometer, calibrated using water vapor. The spectrophotometer was equipped with a linear absorbance potentiometer. Spectroscopic grade hexane was used without further treatment. Calibrated 1-mm sodium chloride cells were employed in the measurements. Instrumental conditions were as previously described.[7,35]

The area under the bands was determined by the weighing technique and was comparable to that obtained with a planimeter. Overlapping bands were separated by graphical procedures, assuming symmetric band shapes. The spectra were integrated over an interval of 30–40 cm^{-1} on either side of the band maximum or about 8 times the half-intensity width. Intensities were determined at a number of concentrations and extrapolated to zero concentration.[36] An example of such a plot is shown in Figure 4 for $(C_2H_5O)_3PMo(CO)_5$. Slopes were always negative, in general increasing in magnitude with decreasing half-intensity band widths. All data were analyzed by least-squares methods.

Electronic Spectra.—Electronic spectra were recorded on a Cary 14RI spectrophotometer using matched 1.0-cm or 1.0-mm cells. Spectroscopic grade hexane was employed in the measurements without further treatment. In the cases in which the ligand possesses a phenyl ring which absorbs strongly in the ultraviolet region attempts were made to compensate for its absorption using the free ligand as reference. This technique rests on the assumption that the absorptions in the free ligand are not perturbed greatly upon complexation. Spectra were recorded from 4500 to 2000 Å.

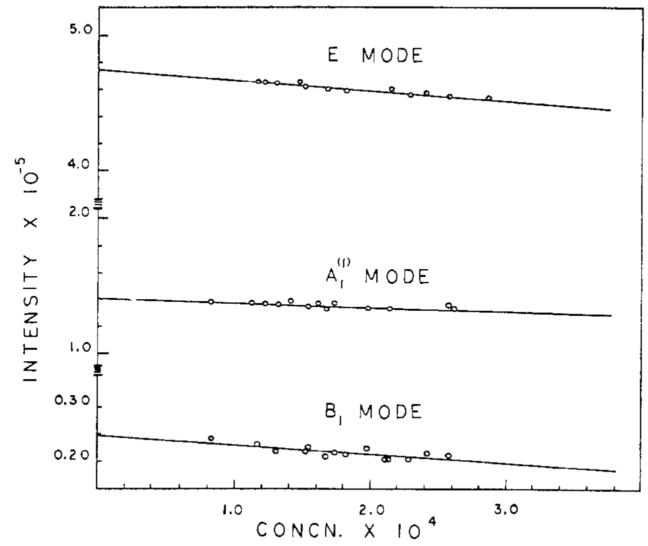

Figure 4.—Intensity *vs.* concentration for the CO modes in $Mo(CO)_5P(OC_2H_5)_3$.

Calculations.—Frequencies for the normal modes and the *L* matrix elements were calculated in the cases cited using a computer program written by Schachtschneider[37] for the IBM-7090 computer and modified for use on the IBM-7094 computer at the University of Illinois.

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[33] G. R. Dobson and L. W. Houk, in press.

[34] T. D. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Am. Chem. Soc.*, **83**, 3200 (1961).

[35] Slightly different instrumental conditions were needed for the amine complexes. It was found that with a scan rate of 20 cm^{-1}/min and a shorter pen response time, good spectra were obtained with decomposition less than 2%.

[36] D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952). Method II, but not including wing corrections.

[37] J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules. III," Technical Report No. 263-62, Shell Development Co., Emeryville, Calif.

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The Solution of Lithium in Hexagonal Potassium Tungsten Bronze[1]

By E. Banks and A. Goldstein

Received August 1, 1967

It has been found that lithium may be dissolved readily in the hexagonal phase of potassium tungsten bronze K_xWO_3 ($0.13 \leq x \leq 0.33$). This introduction of Li initially causes a very small expansion in the "*a*" direction and a large expansion in the "*c*" direction, followed by a very slight expansion in both directions. A number of compositions of $K_xLi_yWO_3$ in the hexagonal region have been prepared. Hexagonal bronzes with x as low as 0.13 and $x + y$ as high as 0.51 have been obtained.

Introduction

The tungsten bronzes M_xWO_3,[2] which have metallic properties over a wide range of compositions, have received considerable attention as metallic conductors with a wide range of electron concentrations. Most studies of electrical properties have concentrated on the cubic sodium and lithium bronzes, with some attention to specific compositions in other structural modifications. This work was done in order to attempt to extend the electron concentration range in the hexagonal potassium bronze structure by incorporating lithium into sites too small to accommodate sodium or potassium.

Potassium tungsten bronzes were prepared by Laurent[3] by reduction of K_2WO_4–WO_3 mixtures with hydrogen. Later preparation methods included reduction of

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[1] Abstracted in part from a dissertation to be submitted in partial fulfillment of the requirements for the Ph.D. degree in chemistry at the Polytechnic Institute of Brooklyn.

[2] See, for example, R. Ward, Ed., "Nonstoichiometric Compounds," Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, pp 224–253.

[3] A. Laurent, *Ann. Chem. Phys.*, **67**, 215 (1838).

K_2WO_4–WO_3 with tin,[4] electrolysis of fused K_2WO_4,[5] reduction of K_2WO_4–WO_3 with WO_2,[6] and reduction of K_2WO_4–WO_3 with elemental tungsten.[7] The potassium bronzes K_xWO_3 have been found to be tetragonal in the range 0.40–0.57 and hexagonal in the range 0.13–0.31. (Magnéli's[8] and Jacobs'[9] lattice constants for the hexagonal structure are compared with the present results in Table I.)

TABLE I

LATTICE PARAMETERS OF HEXAGONAL K_xWO_3

Composition, x	a, Å	c, Å	c/a
		Magnéli	
0.27	7.40	7.56	1.022
0.31	7.37	7.54	1.023
		Jacobs	
0.13	7.378 7.361	7.499 7.510	1.016
0.26	7.376 7.373	7.542 7.535	1.023
		This investigation	
0.13	7.370	7.515	1.020
0.265	7.397	7.543	1.020
0.30	7.394	7.550	1.021

The crystal structure of hexagonal potassium tungsten bronze was found by Magnéli to contain six formula units of K_xWO_3 per unit cell. The hexagonal crystal structure as reported by Magnéli is shown in Figure 1. He described the structure as built up of WO_6 octahedra connected by having corners in common and arranged in layers normal to the hexagonal axis, forming three- and six-membered rings of octahedra. The theoretical upper limit of potassium in the formula A_xWO_3 is 0.33. As indicated in the diagram, the potassium atoms fall between two six-membered oxygen rings. There remain sites at the centers of the polyhedral defined by the triangles formed by three corner-sharing octahedra. These sites have a coordination number of 9 and trigonal symmetry. Assigning radii for oxygen and lithium according to Pauling's[10] values, these polyhedra were calculated to be of a size which would accommodate the lithium ion reasonably well.

On the basis of these calculations, it was decided to study the extent of solution of lithium in the hexagonal potassium tungsten bronze. The theoretical limit for these hexagonal tungsten bronzes would be $K_{0.33}$-$Li_{0.66}WO_3$, if all interstices were filled. The results of the attempts to approach these limiting values are given below.

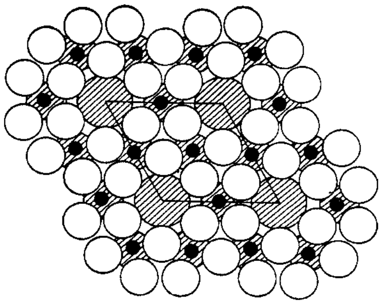

Figure 1.—A layer of the structure of the hexagonal tungsten bronzes. WO_6 octahedra having corners in common form three- and six-membered rings.[8]

Experimental Section

Preparation and Materials.—Powders of varying compositions of the formula $K_xLi_yWO_3$ were prepared by solid-state reaction under vacuum at elevated temperature (500° for 500 hr). The compositions were in the ranges $x = 0.10$–0.32 and $y = 0.0$–0.40. Samples were prepared according to

$$(x/2)K_2WO_4 + (y/2)Li_2WO_4 + [(x + y)/6]W + [1 - {}^2/_3(x + y)]WO_3 \longrightarrow K_xLi_yWO_3.$$

All samples were dried, ground and mixed prior to reaction. The samples were introduced into $^3/_8$-in. i.d. medium-wall silica tubes, which were evacuated for 1 hr, flushed with helium, re-evacuated, and heat sealed using an oxyhydrogen torch.

The sealed tubes were placed in a nichrome-wound furnace and maintained at a temperature of 500° for a period of 500 hr. At the end of this time the tubes were cooled to room temperature over a period of 6 hr. It was noted that samples containing high concentrations of lithium tungstate (Li_2WO_4) attacked the wall of the quartz tubes. There was some indication that these samples may have sintered during the reaction since some of the powder samples formed a solid porous block in the tube. The powders were removed from the quartz tubes and ground so that they would pass through a 200 mesh silk screen. All of these samples were deep blue.

All samples were then washed in a platinum dish according to the procedure: (1) 48% HF to remove any silica powder from the reaction tube; (2) distilled water; (3) 5% Na_2CO_3 to remove unreacted WO_3; (4) distilled water to remove all remaining soluble material. The samples were then dried at 200° for a period of 2 hr.

Potassium tungstate (K_2WO_4) and lithium tungstate (Li_2WO_4) were obtained from the Jarrell Ash Co. These materials were heated to 200° to remove all traces of water and then desiccated until used. Tungsten metal of 99.99% purity was obtained from Fansteel Corp. Tungsten trioxide (WO_3) was obtained from the Fisher Scientific Co. This material was also heated to 200° to remove water and then desiccated prior to use.

Chemical Analysis.—The tungsten bronzes were heated in an open platinum dish for a period of 4 hr at a temperature of 700°. This was done in order to oxidize the bronze to potassium tungstate (K_2WO_4), lithium tungstate (Li_2WO_4), and tungsten trioxide (WO_3). Samples of approximately 2 g were used. By weighing the samples before and after oxidation a measurement of the oxygen pickup was obtained

$$K_xLi_yWO_3 + [(x + y)/2]O_2 \longrightarrow (x/2)K_2WO_4 + (y/2)Li_2WO_4 + [1 - ((x + y)/2)]WO_3 \quad (1)$$

The oxidized sample was then boiled with 50 ml of concentrated nitric acid

$$K_2WO_4 + 2HNO_3 \longrightarrow 2KNO_3 + WO_3 + H_2O \quad (2a)$$

$$Li_2WO_4 + 2HNO_3 \longrightarrow 2LiNO_3 + WO_3 + H_2O \quad (2b)$$

The solution was boiled down to a volume of 15 ml and then diluted to 100 ml with distilled water in order to precipitate WO_3. The solution was filtered through ashless filter paper using ashless filter-aid to retain the tungsten trioxide. The precipitate was washed with distilled water to remove all soluble nitrates. The precipitate and filter paper were then heated to 500° in a

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(4) G. von Knorr, *J. Prakt. Chem.*, **27**, 49 (1883).

(5) E. Zettnow, *Pogg. Ann.*, **130**, 240 (1867).

(6) O. Brunner, Dissertation, Zurich, 1903.

(7) E. O. Brimm, J. C. Brantley, J. H. Lorenz, and M. H. Jellinek, *J. Am. Chem. Soc.*, **73**, 5427 (1951).

(8) A. Magnéli, *Acta Chem. Scand.*, **7**, 315 (1953).

(9) G. L. Jacobs, M.S. Thesis, Polytechnic Institute of Brooklyn, 1959, unpublished.

(10) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p 346.

partially closed porcelain crucible to drive off the water and burn off the paper. The precipitate was weighed and the concentration of tungsten trioxide in the original sample was thus obtained. The measured tungsten concentration agreed very closely with the tungsten content of the initial mixtures, indicating that essentially all of the free tungsten and the tungsten in the oxide and the tungstates were incorporated into the bronze.

The filtrate was evaporated to dryness and weighed to determine the concentration of potassium and lithium nitrates. From these steps it was possible to determine the concentrations of potassium, lithium, and tungsten trioxide in the original sample

$$\text{wt of bronze} - \text{wt of WO}_3 = \text{wt of K} + \text{Li} \qquad \text{(3a)}$$

$$\text{wt of oxidized bronze} - \text{wt of bronze} = \text{oxygen pickup} \qquad \text{(3b)}$$

$$x + y = \text{moles of oxygen pickup} \qquad \text{(3c)}$$

$$\left.\begin{aligned} x\text{KNO}_3 + y\text{LiNO}_3 &= \text{wt of nitrates} \\ 101.1x + 68.95y &= \text{wt of nitrates} \end{aligned}\right\} \qquad \text{(3d)}$$

Equations 3c and 3d can be solved for x and y.

X-Ray Determination.—Lattice parameters were obtained from the tungsten bronze powders on a Norelco diffractometer running at 0.2°/min using Cu Kα radiation.

Density Measurements.—Densities were measured pycnometrically, using distilled water as the pycnometric liquid. Only those samples whose X-ray patterns showed a single hexagonal phase were measured. The pycnometer was equilibrated in a constant-temperature bath at 25°. Before equilibration, the water was gently boiled in contact with the sample in the pycnometer, to remove any trapped gases. No powder remained floating. As shown in Table II, the measured and calculated densities agree within about 0.015 g/cm^3. This is within the experimental error, which is estimated to be about 0.02–0.03 g/cm^3 The good agreement is taken as strong evidence that the true compositions of the samples are very close to the values obtained by analysis.

Table II

Data for $K_xLi_yWO_3$

Analyzed		Density	
x	y	Measd	Calcd
0.13	0	6.665	6.678
0.18		6.699	6.712
0.20		6.714	6.728
0.215		6.728	6.739
0.24		6.745	6.758
0.265		6.753	6.766
0.30		6.777	6.788
0.13	0.05	6.640	6.651
0.14	0.07	6.641	6.654
0.14	0.14	6.651	6.665
0.13	0.18	6.625	6.635
0.14	0.26	6.635	6.648
0.18	0.08	6.673	6.687
0.18	0.11	6.660	6.672
0.17	0.21	6.661	6.672
0.17	0.34	6.682	6.696
0.23	0	6.735	6.747
0.24	0.03	6.725	6.736
0.22	0.04	6.602	6.616
0.24	0.08	6.715	6.728
0.24	0.11	6.715	6.727
0.24	0.15	6.725	6.735
0.23	0.22	6.725	6.738
0.28	0.08	6.761	6.776
0.27	0.12	6.750	6.760

Discussion

X-Ray analysis of hexagonal potassium tungsten bronzes prepared in this investigation was correlated with the work done by Magnéli and by Jacobs. The "a" lattice parameter was found to fall between the values obtained by Magnéli and Jacobs (Table I). The low end of the hexagonal bronzes corresponds fairly closely with Jacobs' work while the high end was similar to that obtained by Magnéli but did not indicate a decrease in the "a" direction when approaching the upper limit of x = 0.33.

Table III

Data for $K_xLi_yWO_3$

Nominal		Analyzed				
x	y	x	y	a, Å	c, Å	c/a
0.13	0.0	0.13	0.0	7.370	7.515	1.020
0.20	0.0	0.18	0.0	7.374	7.529	1.021
0.25	0.0	0.20	0.0	7.377	7.529	1.021
0.25	0.0	0.215	0.0	7.382	7.533	1.020
0.275	0.0	0.24	0.0	7.383	7.538	1.021
0.30	0.0	0.265	0.0	7.390	7.543	1.021
0.33	0.0	0.30	0.0	7.394	7.550	1.021
0.15	0.05	0.13	0.05	7.374	7.547	1.023
0.15	0.10	0.14	0.07	7.380	7.550	1.023
0.15	0.15	0.14	0.14	7.382	7.554	1.023
0.15	0.20	0.13	0.18	7.388	7.567	1.024
0.15	0.25	0.14	0.26	7.393	7.571	1.024
0.20	0.10	0.18	0.08	7.384	7.555	1.023
0.20	0.15	0.18	0.11	7.390	7.566	1.024
0.20	0.25	0.17	0.21	7.393	7.568	1.024
0.20	0.40	0.17	0.34	7.394	7.570	1.024
0.25	0.01	0.23	0.0	7.380	7.538	1.021
0.25	0.03	0.24	0.03	7.384	7.563	1.024
0.25	0.05	0.22	0.04	7.385	7.564	1.024
0.25	0.10	0.24	0.08	7.390	7.570	1.024
0.25	0.15	0.24	0.11	7.391	7.570	1.024
0.25	0.20	0.24	0.15	7.391	7.570	1.024
0.25	0.30	0.23	0.22	7.391	7.570	1.024
0.30	0.10	0.28	0.08	7.388	7.568	1.024
0.30	0.15	0.27	0.12	7.394	7.571	1.024

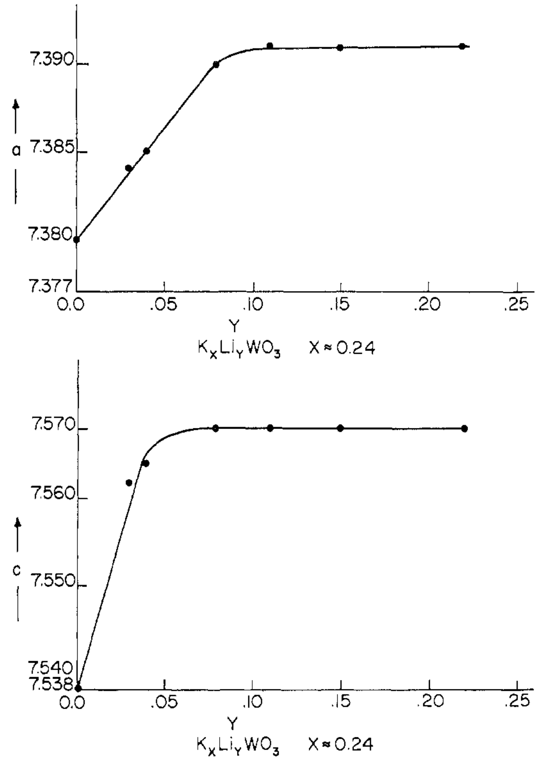

Figure 2.—Lattice parameters *vs.* lithium concentration at constant potassium concentration (x = 0.24).

This work covered the range obtained by Magnéli and Jacobs for the lattice parameters in the "*c*" direction.

On the basis of the crystal structure of hexagonal potassium tungsten bronze, it is apparent that a compound of the formula $K_{0.33}Li_{0.66}WO_3$ could be prepared, if all of the interstices could be filled. However, as indicated in Table III, the maximum total concentration of $x + y$ obtained was 0.51. Since the large holes for potassium could readily contain lithium ions as well, it is possible to prepare samples of the mixed bronze in which the smaller sites are not used at all, *i.e.*, $x = 0.15$ and $y = 0.10$. In such a case, one would not expect the lattice to expand with the addition of lithium. In fact, a contraction might be expected, as found in the cubic lithium bronzes.[11] If the lithium ions are occupying the "triangular" holes, one would expect to observe an expansion of the lattice. This is certainly indicated in the lattice expansion in the "*c*" direction as shown in Table III.

As the concentration of alkali metal in the hexagonal bronze becomes substantial ($x = 0.35$), the structure tends to stabilize with respect to expansion in the "*c*" direction as lithium is added (Table III). Apparently, at higher potassium concentrations, the expansion due to increases in the lithium ion concentration tends to reach a maximum in the "*a*" direction ($a = 7.391$ Å) and "*c*" direction ($c = 7.570$ Å). This is shown in Figure 2. No phases, other than hexagonal, were discernible in these samples.

Adding lithium to the hexagonal potassium tungsten bronze has permitted the extension of the homogeneity range of the hexagonal phase to increased metal concentrations, up to $x + y = 0.51$. This increase in concentration of carriers should yield a substantially greater conductivity for the material. The catalytic activity of the powders for ortho–parahydrogen conversion[12] and other reactions should also be increased.

Systems which might be expected to show similar behavior would be the rubidium and cesium hexagonal bronzes, the sodium tetragonal bronzes, and possibly the potassium tetragonal bronzes, since there are a substantial number of sites available for the introduction of other ions.

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[11] M. E. Straumanis and S. S. Hsu, *J. Am. Chem. Soc.*, **72**, 4027 (1950).

[12] F. T. Jones, Dissertation, Polytechnic Institute of Brooklyn, 1960, unpublished.

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Hexagonal Indium Tungsten Bronze

By R. J. BOUCHARD and J. L. GILLSON

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The electrical resistivity of single crystals of hexagonal In_xWO_3 ($x = 0.21$–0.27) has been measured both perpendicular to and parallel with the *c* axis. Nearly isotropic metallic behavior was found. Seebeck voltages were small and negative, while magnetic susceptibility measurements showed isotropic diamagnetism. These results are consistent with covalent t_{2g}–pπ bonding and the formation of a π^* band.

Introduction

At least three possible mechanisms have been proposed to explain the metallic conductivity in the cubic tungsten bronzes A_xWO_3 (A = alkali metal): (a) direct A–A overlap,[1] (b) direct W–W overlap,[2] and (c) covalent pπ–dπ interactions[3,4] with the formation of a π^* band. Several difficulties are associated with the first of these models, and the W–W separation in these materials is probably too great for the second. The work of Ferretti, Rogers, and Goodenough[5] provides convincing evidence that the third mechanism, involving the formation of π^* bands *via* t_{2g}–pπ covalent interactions, is responsible for the observed properties of these materials. If this is the case, the framework of WO_6 octahedra is the most important property-determining feature of the metallic bronzes and the particular bronze structure should be secondary. Therefore, metallic hexagonal bronzes would be expected to exhibit isotropic conductivity even though their crystal structures are highly anisotropic.

Sienko and Morehouse[6] measured resistivities on single crystals of K_xWO_3 and Rb_xWO_3 hexagonal bronzes, but only in the direction parallel with the *c* axis. Hexagonal $In_{0.11}WO_3$ was prepared earlier in this laboratory[7] as a powder by hydrothermal reaction. A subsequent study revealed that single crystals of the general formula In_xWO_3 could be easily prepared by solid-state techniques and vapor-transport reactions. It was therefore considered a good candidate to test the above ideas.

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[1] A. R. Mackintosh, *J. Chem. Phys.*, **38**, 199 (1963).

[2] M. J. Sienko, Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p 224.

[3] J. B. Goodenough, *Bull. Soc. Chim. France*, **4**, 1200 (1965).

[4] See also the brief statement on p 226 of ref 2, where the possibility of π-molecular orbital formation is mentioned in passing.

[5] A. Ferretti, D. B. Rogers, and J. B. Goodenough, *J. Phys. Chem. Solids*, **26**, 2007 (1965).

[6] M. J. Sienko and S. M. Morehouse, *Inorg. Chem.*, **2**, 485 (1963).

[7] P. E. Bierstedt, T. A. Bither, and F. J. Darnell, *Solid State Commun.*, **4**, 25 (1966).