complexes)[18] and at 364 cm^{-1} for the complex $[(C_2H_5)_4N]_3Cr(NCS)_6$.[19] As has been pointed out,[20] the frequency of a metal–ligand vibration will be highest for the most basic ligand. The ligands used in this study are weakly basic compared to ammonia, and thus the ν_{MN} vibration would be expected at a lower frequency.

Weak bands are found in the ~280-cm^{-1} region. The δ_{NMN} and the δ_{MOM} vibration would be expected to occur at lower frequency than the ν_{MO} or ν_{MN} stretching vibrations. Assignments for these compounds are presented in Table I.

The assignment for ν_{CrO} in the compound $K_4[(C_2O_4)_2CrOH]_2 \cdot 3H_2O$ and for the ν_{CoO} vibration in $K_4[(C_2O_4)_2CoOH]_2 \cdot 3H_2O$ is made with less assurance, for other vibrations occur in the same general region (Table I).

Iron Complexes.—Assignments for the hydroxy-bridged iron complexes are made in Table I. The ν_{FeO} vibration in the hydroxy-bridged ring is assigned at 500–550 cm^{-1}. The ν_{FeN} vibration is suggested at 270–290 cm^{-1}. For both vibrations several bands are observed. The ligands are free of absorption in these regions. Similar behavior of the ligand bands to that observed for the chromium compounds is noted as complexation occurs.

It should be indicated that the complexity of these compounds prevents any possible normal coordinate treatment from being made to make more quantitative assignments of the frequencies. Similarly, O^{18} or N^{15} analogs are difficult to prepare, and it is questionable as to how valuable the infrared results of these substances would be. Our assignments, therefore, must be considered to be tentative.

A comparison of the ν_{MO} and ν_{MN} data for the Cr(III), Fe(III), and Cu(II)[2,3] compounds is made in Table II.

TABLE II

COMPARISON OF ν_{MO} AND ν_{MN} VIBRATIONS FOR Cr(III), Fe(III), AND Cu(II)

	ν_{MO}, cm^{-1}	ν_{MN}, cm^{-1}
Cr(III)	547–567	343–378 (A and B ligands)[a]
Fe(III)	506–550	260–294 (A and B ligands)
Cu(II)	480–490[2]	270[2] (A ligand)
	500–515[3]	300[2] (B ligand)

[a] A = 2,2′-bipyridyl; B = 1,10-phenanthroline.

The decrease in frequency for ν_{MO} as one goes from Cr(III) to Fe(III) to Cu(II) is the expected behavior for these transition metals and has been observed for other complexes.[21,22] A comparison of the hydroxy-bridged oxalato complexes of Cr(III) and Co(III) shows that the suggested assignment for the ν_{MO} vibration (stretching modes to oxalate plus hydroxyl) is at 565 cm^{-1} for Co(III) and at 547 cm^{-1} for Cr(III). The predominantly M–O stretching mode[21] is found at 447 cm^{-1} for Co(III) and at 411 cm^{-1} for Cr(III). This is similar to the trends observed for the oxalato complexes of the trivalent transition metals.[21]

---

(18) T. Shimanouchi and I. Nakagawa, *Inorg. Chem.*, **3**, 1805 (1964).

(19) A. Sabatini and I. Bertini, *ibid.*, **4**, 959 (1965).

(20) R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

(21) J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 324, 331 (1962).

(22) K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066, 1272 (1961).

CONTRIBUTION FROM THE GOVERNMENT RESEARCH LABORATORY,
ESSO RESEARCH AND ENGINEERING COMPANY,
LINDEN, NEW JERSEY 07036

Lanthanum and Yttrium Tungsten Bronzes

BY BARRET BROYDE[1]

Received January 23, 1967

Two new tungsten bronzes, one containing lanthanum and the other yttrium, have been prepared and characterized in this laboratory. These materials have a cubic perovskite-type structure, are acid resistant, and are electrically conductive.

Experimental Section

The tungsten bronzes were prepared by thoroughly mixing the required proportions of the transition metal oxide powder with tungsten metal powder and tungsten trioxide powder to give the desired stoichiometry. The mix was pelletized and sealed into a quartz tube under 5 × 10^{-4} torr. The tubes were heated in either a Leco or a Lindberg tube furnace at 1100° for 72 hr. They were cooled under ambient conditions to room temperature. This took about 20 min. In some cases the pellets were ground and pressed again every 24 hr but it was found that this did not change the results. The pellets remained intact during the heating. Less than 25 mg was lost from the pellets during the preparation, indicating that the resulting stoichiometry was quite close to that of the mix. Preparations normally were made in 9–10-g batches.

Reagents.—The yttrium and lanthanum oxides were obtained from the Rare Earth Division of the American Potash and Chemical Corp. and were at least 99.999% pure. Tungsten metal (0.70 μ) and tungsten trioxide (Grade TO-1) were obtained from the Chemical and Metallurgical Division of Sylvania Electric Products, Inc. Scandium oxide was 99.95% pure and was purchased from Leico Industries, Inc.

The scandium group oxides were ignited for 4 hr at 1000° prior to use.

X-Ray Investigation.—The products of the above preparations were examined for homogeneity both by microscopy and by X-ray powder methods. No materials were obtained that showed inhomogeneity in one method of examination but not the other. X-Ray studies were made with a Norelco X-ray diffractometer, Type 12045-6, modified for use with an Advanced Metals Research Corp. curved crystal focusing monochromator, Model 3-202. The copper Kα lines were detected with a Norelco scintillation counter attachment, Type 52245.

Results and Discussion

A homogeneous cubic perovskite-type structure is found for La_xWO_3 when x is between 0.08 and 0.19. Powder X-ray diffraction data show that the cubic lattice parameter increases in a nonlinear manner with x from 3.829 to 3.845 A in this region. Below x = 0.08 a tetragonal structure also appears, and at x = 0.02 it occurs as a pure form with lattice parameters of a = 7.52 and c = 3.89 A. Above x = 0.19 two additional phases are present. One has the same X-ray pattern as $La_2W_3O_{12}$,[2a] while the other gives an X-ray diffraction pattern similar to WO_2.[2b]

Y_xWO_3 also exists in tetragonal and cubic forms. The range of x yielding homogeneous cubic structures

---

(1) Western Electric Engineering Research Center, Princeton, N. J. 08540.

(2) (a) H. J. Borchardt, *J. Chem. Phys.*, **39**, 504 (1963); (b) ASTM X-Ray Powder Diffraction Card 5-0431.

is narrower for this material than for lanthanum tungsten bronze. Above $x = 0.15$, WO_2 appears. No yttrium tungstate structure[2a,3] could be detected even when the stoichiometric value of x was 0.2. Below $x = 0.09$ a tetragonal form appears. It has the same lattice parameters as the tetragonal form of the lanthanum tungsten bronze. The cubic lattice parameter varies from 3.800 A at $x = 0.09$ to 3.815 A at $x = 0.15$. Scandium does not form a tungsten bronze under the preparative conditions employed here. A mixture of $W_{18}O_{49}$[4] and $W_{20}O_{58}$[5] was found by X-ray examination.

Tungsten bronzes containing the rare earths have recently been described.[6,7] In the cases reported, a tetragonal form was found at low concentrations of the rare earths while at higher concentrations a cubic perovskite-type structure was found for all of the readily available rare earth elements. Magnetic studies[6] showed that the rare earth was present in a trivalent form. It would appear that both yttrium and lanthanum also form tungsten bronzes in their trivalent states. This is to be expected as these elements normally exist in a trivalent state and further have essentially the same radii as the rare earths in the 12-coordinated position of the perovskite lattice. Geller[8] has found that relative radii of Y^{3+}, Eu^{3+}, and La^{3+} in the A position of perovskites to be 1.281, 1.304, and 1.346 A, respectively. The cubic lattice parameters for the corresponding tungsten bronzes are in the same order. $Y_{0.1}WO_3$ has a parameter of 3.802 A and $Eu_{0.1}WO_3$ was found to have a lattice constant of 3.815 A[6] while $La_{0.1}WO_3$ prepared here has a cubic parameter of 3.834 A.

The color of La_xWO_3 varies from green at $x = 0.02$ to blue at $x = 0.10$ and finally to red-purple at $x = 0.19$. A yellow form such as is found in the sodium tungsten bronzes at high sodium concentrations[9] does not appear here.

Electrical conductivity measurements on pressed powders of the materials synthesized here indicate that all the phases prepared, with the possible exception of $La_{0.02}WO_3$, have specific conductivities greater than 100 mhos/cm. The tungsten bronzes were not attacked by 3.7 M sulfuric acid at 90° even after 16 hr. The intense, lustrous color, the high electrical conductivity, the resistance to attack by acid, and the range of chemical composition of these materials characterize them as bronzes.[10]

Acknowledgment.—We wish to thank the U. S. Army Electronics Command, Fort Monmouth, N. J., for supporting this research under Contract DA 36-039 AMC-03743(E). The author is indebted to Professor E. Banks for many stimulating discussions, to Mr. J. T. Allen, Jr., for his aid in obtaining the X-ray data, and to Mr. J. T. Pavlovcak for his help in preparing the materials.

---

[3] K. Nassau, H. J. Levinstein, and G. M. Loiacono, *J. Phys. Chem. Solids*, **26**, 1805 (1965).

[4] ASTM X-Ray Powder Diffraction Cards 5-0392 and 5-0393.

[5] ASTM X-Ray Powder Diffraction Cards 5-0386 and 5-0387.

[6] W. Ostertag, *Inorg. Chem.*, **5**, 758 (1966).

[7] C. V. Collins and W. Ostertag, *J. Am. Chem. Soc.*, **88**, 3171 (1966).

[8] S. Geller, *Acta Cryst.*, **10**, 248 (1957).

[9] M. J. Sienko, Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, paper 21.

[10] S. Anderson and A. D. Wadsley, *Acta Cryst.*, **15**, 201 (1962).

CONTRIBUTION FROM THE RESEARCH LABORATORIES,
XEROX CORPORATION, ROCHESTER, NEW YORK 14603

The Crystal Structure of Trigonal Selenium[1]

BY PAUL CHERIN AND PHYLLIS UNGER

Received January 31, 1967

Because of the intensified interest in trigonal selenium in recent years, an investigation of the Se–Se bond length, bond angle, and interchain separation was undertaken, using modern techniques of collecting and analyzing data. Elemental selenium can exist in several solid modifications: two monoclinic (α and β), a trigonal, a vitreous, and a cubic modification. Under normal conditions of temperature and pressure, only the trigonal phase is stable; the others, being metastable, slowly convert to the trigonal form. A previous crystal structure determination of trigonal selenium was completed by Bradley,[2] who used powder photography techniques.

Experimental Section

Crystals were grown by slowly cooling a saturated solution of amorphous selenium in hot aniline. The resulting needle crystals were mounted parallel to their long axis, which was parallel to the c axis of the hexagonal cell. Those which were relatively strain free and with regular hexagonal cross sections (diameters were about 0.2 mm) were selected for further study. Two-dimensional $hk0$ data were collected using a General Electric XRD-5 unit equipped with a quarter-circle Eulerian cradle goniostat, a scintillation counter, and a pulse-height discriminator. Both Cu Kα and Mo Kα radiation (filtered with Ni and Zr, respectively) were used.

Determination and Structure

The stationary crystal–stationary counter method was used to record the reflections. This was related to integrated intensity in the usual manner.[3] Difficulties were encountered owing to high and rapidly changing background.

For convenience, the unit cell is generally treated as hexagonal. The hexagonal cell dimensions, determined by Swanson, Gilfrich, and Ugrinic,[4] are $a = 4.3662$ and $c = 4.9536$ A. The space group is either $P3_121$ or $P3_221$. There are three atoms per unit cell, lying on twofold axes; the position of the asymmetric atom in the hexagonal cell can be described by one parameter. The usual Lorentz and polarization corrections were made. An absorption correction was

---

[1] Presented at the 7th International Congress and Symposium of the International Union of Crystallography, Moscow, July 12–21, 1966.

[2] A. J. Bradley, *Phil. Mag.*, **48**, 477 (1924).

[3] L. E. Alexander and G. S. Smith, *Acta Cryst.*, **15**, 983 (1962).

[4] H. E. Swanson, N. T. Gilfrich, and G. M. Ugrinic, National Bureau of Standards Circular 539, Vol. 5, U. S. Government Printing Office, Washington, D. C., 1955, p 54.