[CONTRIBUTION FROM THE UNIVERSITY OF MISSOURI, SCHOOL OF MINES AND METALLURGY, DEPARTMENT OF METALLURGY]

The Lithium Tungsten Bronzes[1]

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Introduction

Pure sodium tungsten "bronze" $NaWO_3$ is cubic[2] and can absorb more than 80% by weight of tungsten(VI) oxide under lattice contraction and formation of solid solutions without changing its cubic symmetry.[2] The "bronze" and the resulting solid solutions are, of course, not bronzes. This name was applied by Wöhler, because the bronzes have metallic properties.[3] Due to the shortness of the expression, it will be used throughout this paper.

Since lithium has a smaller ionic radius than sodium, it was thought that a series of cubic lithium tungsten bronzes could be formed. The present investigation was undertaken to determine the region of stability of lithium tungsten bronzes and to describe their structure and properties.

The lithium tungsten bronzes were first mentioned by Hallopeau[4a] and Brunner.[4b] The dark blue to steel blue crystalline compounds consisting of microscopic plates and prisms were found to correspond in composition to the formulas $Li_2W_4O_{12}$, $Li_2W_5O_{15}$ and $Li_2W_7O_{21}$. The bronzes were prepared by electrolysis or by reducing fused lithium paratungstate with tin.

Experimental

Preparation.—For the present work an improved method previously described was applied.[3] It was first assumed, as in the case of sodium bronze, that the following reaction would take place at 800°

$$3Li_2WO_4 + 2WO_3 + W = 6LiWO_3 \qquad (1)$$

However, X-ray and chemical analyses of the brown product obtained showed the formation of tungsten dioxide. Efforts to obtain the pure $LiWO_3$ by varying the experimental conditions of temperature, composition, annealing and cooling proved to be without effect. It was concluded that a compound with the composition of $LiWO_3$ does not form under these experimental conditions, while a sodium compound can be prepared without difficulty.[3]

The experiments were continued on the basis of eq. (1) but the amounts of tungsten(VI) oxide were increased. The amount of tungsten(IV) oxide decreased and the quantity of blue bronze increased. When the composition W, 0.2 + WO_3, 2.32 + Li_2WO_4, 1.60 (anhydrous) = 4.12 g. was reached, tungsten(IV) oxide was no longer observable in the reaction product. It showed a deep blue color throughout. A sample was obtained from the mixture by heating it *in vacuo* at 900° for four hours.

The reaction product was washed and boiled in distilled water to remove the unreacted lithium tungstate, treated with hot sodium hydroxide solution to remove excess free tungstic oxide, washed thoroughly with water, treated with hot diluted hydrochloric acid, rewashed, and dried on a hot-plate. The resulting powders were subjected to microscopic and X-ray examination in order to determine the crystal form and the homogeneity of these blue products with the lowest possible tungsten(VI) oxide content. Chemical analyses of the homogeneous products were made.

Structure and Formula of the Blue Compound.—The X-ray powder diffraction patterns of the compound with the lowest possible tungsten(VI) oxide content showed at once that it was almost identical with that of the cubic sodium tungsten bronze,[3] but that the lattice constant was smaller. Cobalt radiation and the asymmetric method of lattice constant determination were applied.[5] All possible diffraction lines were present, indicating a simple cubic structure. Five samples at approximately 25° gave an average value for the lattice constant as 3.7143 ± 0.0002 kX. or 3.7218 Å. The lattice constant of nearly pure sodium tungsten bronze was 3.8520 kX. or 3.8598 Å.

Because the chemical and physical properties of the blue lithium tungsten bronze resemble in all points the sodium bronze containing free tungstic oxide in solid solution, it was supposed that the structures of the two compounds were identical.

Assuming that the atomic positions would be the same as in the case of the sodium tungsten bronze (perovskite type, $CaTiO_3$), namely

$$Li^+ - 000$$
$$W^{5+} \text{ or } W^{6+} - \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2} \text{ and}$$
$$O^{2-} - 0\tfrac{1}{2}\tfrac{1}{2},\ \tfrac{1}{2}0\tfrac{1}{2} \text{ and } \tfrac{1}{2}\tfrac{1}{2}0$$

the intensities of the lines of the powder pattern were calculated. The observed and calculated intensities (I) of all lines are shown in Table I; Σh^2 is the sum of squares of the indices. The observed and calculated intensities coincide for many planes and run parallel for others.

TABLE I

OBSERVED AND CALCULATED INTENSITIES OF LINES OF LITHIUM TUNGSTEN BRONZE OF LOWEST POSSIBLE TUNGSTEN(VI) OXIDE CONTENT, CU $K\alpha$ RADIATION

Σh^2	Plane	$I_{\text{obsd.}}$	$I_{\text{calcd.}}$	Σh^2	Plane	$I_{\text{obsd.}}$	$I_{\text{calcd.}}$
1	100	st	m	12	222	w	vw
2	110	st	st	13	320	m	w
3	111	w	w	14	321	st	m
4	200	m	w	15	...	...	...
5	210	st	st	16	400	vw	vw
6	211	st	m	17	410	st	st
7	...	...	..	18	330	st	m
8	220	m	w	19	331	m	w
9	300	st	m	20	420	m	m
10	310	m	w	21	421	vst	vst
11	311	w	w	22	332	st	st

It was concluded, therefore, that the structures of the sodium and lithium tungsten bronzes were identical and that the latter also represented solid solutions of the general formula[2,3]

$$LiW^{V}O_3(W^{VI}O_3)_x \quad (2) \text{ or } Li_{1/(1+x)}WO_3 \qquad (3)$$

That is, tungsten(VI) oxide is dissolved in the hypothetical $LiWO_3$ which is stable only in such a solid solution,

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[1] Based on a thesis submitted by S. S. Hsu to the Graduate School of the University of Missouri, School of Mines and Metallurgy in partial fulfillment of the requirements for the Master's Degree.

[2] Hägg, *Z. physik. Chem.*, **B29**, 192 (1935).

[3] Straumanis, THIS JOURNAL, **71**, 679 (1949).

[4] (a) Hallopeau, *Ann. chim. phys.*, **19**, 117 (1900); (b) Brunner, "Beitrage zur Kenntnis der Wolframbronzen," Dissertation, Zurich, 1903.

[5] Straumanis, *J. Appl. Phys.*, **20**, 726 (1949)

unlike the sodium tungsten bronzes, of which the $NaWO_3$ is stable independently.

Brunner determined the specific gravities of solid solutions corresponding to the formulas $Li_2W_4O_{12}$ and $Li_2W_5O_{15}$: 7.501 resp. 7.465.[4] As the lattice constant of the mentioned solid solutions could be read from Fig. 1 and the number of molecules in the unit cell was one, the molecular weight M_x of the solutions could be calculated roughly from the X-ray data.[6] The following results were obtained

	M_x	M_{chem}	%
$Li_2W_4O_{12}$ really $Li_{0.5}WO_3$	233.21	235.39	−0.9
$Li_2W_5O_{15}$ really $Li_{0.4}WO_3$	233.0	234.7	−0.7

This proved the correctness of the X-ray work.

Since no precision density data of the bronze with lowest tungsten(VI) oxide content were available, chemical analyses were made in order to evaluate the factor x of the formulas (2) and (3). The factor was calculated from the lithium content and from the ratio Li : WO_3 in the bronze.

The chemical analyses, especially those of lithium, were difficult. To determine the tungsten(VI) oxide, the samples were decomposed by fusing them with sodium carbonate and sodium peroxide. The melt was dissolved in water and the tungstic acid precipitated by evaporating the liquid with perchloric[2] or other acids.[7,8,9] To determine the lithium (as sulfate), the bronze samples were decomposed by boiling them with a mixture of concd. sulfuric acid and ammonium sulfate.[7]

It was found that a sample of 0.4000 g. of lithium bronze (with lowest tungstic(VI) oxide concentration) contained 0.00659 g. of lithium (average of 3 determinations) and 0.3825 g. of WO_3 (average of 5 determinations, the weight of oxygen caused by the oxidation of W(V) being subtracted). From these data the amount of tungsten(VI) oxide in solid solution was calculated on the basis of (2).

from Li alone	43.3% WO_3 by weight
from Li:WO_3 = 1:1.74	41.8% WO_3
Average	42.6 ± 2% WO_3 in solid solution

Using this average value, the formula of the blue bronze on the basis of (2) and (3) was

$$LiW^{V}O_3(W^{VI}O_3)_{0.77} \text{ or } Li_{0.56}WO_3 \qquad (4)$$

With x being 0.77, the compound had the lowest possible tungsten(VI) oxide content and decomposed when the content was made lower.

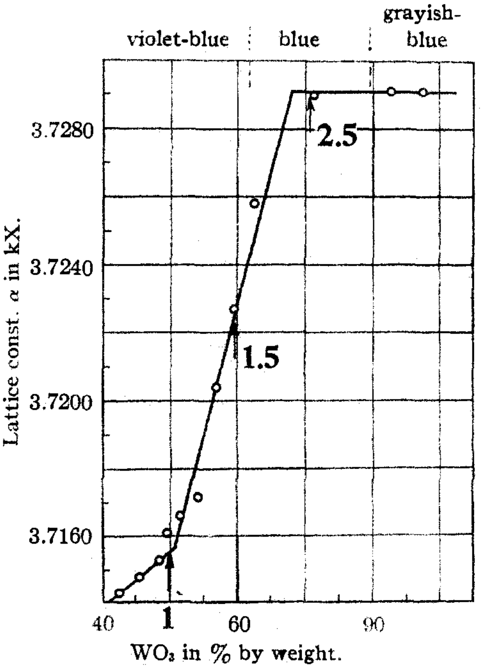

Fig. 1.—Lattice constants of blue lithium tungsten bronze *versus* tungstic oxide content in solid solution. The solubility limit is at 68% by weight of tungstic oxide at 900°: 1 is $LiWO_3(WO_3)$; 1.5, $LiWO_3(WO_3)_{1.5}$; 2.5 $LiWO_3(WO_3)_{2.5}$.

The Solubility of Tungstic Oxide in the Blue Lithium Bronze.—Tungsten(VI) oxide is easily absorbed by the bronze with the composition represented by formula (4) at elevated temperatures. To determine the solubility limit (at 900°), lattice constants were calculated for a series of solid solutions. The products were prepared by mixing the calculated amounts of bronze and tungsten(VI) oxide and placing the mixture in a quartz bulb. After the air was removed from it, the bulb was sealed and heated at 900°. In two hours the tubes were removed from the furnace and cooled in air. Each sample was then prepared to determine the lattice constants. The doublet No. 17$\alpha_1\alpha_2$ (410, cobalt radiation) was used in making the measurements.[10] The results are summarized in Fig. 1.

The lattice of lithium tungsten bronze expands with the increasing tungsten(VI) oxide content, while that of sodium bronze contracts. Two of the compounds described by previous investigators[4] are within the solubility range; $Li_2W_7O_{21}$ is just outside the solubility limit. The curve shows that the blue bronze absorbed up to 25% tungstic oxide to give a total amount of 68%.

The formation of solid solutions can be explained easily by the fact that the dimensions of the anion WO_3^- (with pentavalent tungsten) were similar to that of WO_3.[3] The latter could, therefore, be absorbed by the bronze lattice and could be located in positions for tungsten and oxygen while the 000-positions of Li^+ remained open. The solid solutions shown in Fig. 1 all belong to the same type of anionic substitutional mixed crystals. The distribution of WO_3^- and WO_3 is random throughout the crystals because superstructure lines could not be observed. The changes in color that prevailed when the concentration of tungstic oxide was increased are also given in Fig. 1.

Solid Solutions with a Higher Tungsten(VI) Oxide Content.—The X-ray powder photographs of samples that contained more than 68% tungstic oxide showed the presence of new spacings while the lines of the cubic bronze became weaker and weaker with the increasing tungsten(VI) oxide content. It is very probable that the new phase was tetragonal; however, no further investigations concerning this were made. The color of the samples changed from blue to dark olive-green.

For samples containing 99% tungstic oxide and more, the X-ray diffraction patterns were the same as those of pure tungstic oxide. Their color was olive-green and finally greenish-yellow.

Properties of the Cubic Lithium Bronzes

Chemical Properties.—The reaction between metallic lithium and tungstic oxide was so violent at elevated temperatures that no bronze could be obtained in this way. But if the vapor pressure of lithium was reduced, the blue bronze became a reaction product. Pure tungstic oxide and the cubic lithium tungsten bronze were placed in separate partitions of a combustion boat and heated at 900° for two hours. After the heating, the tungstic oxide had assumed the color of the bronze. This could be explained only by assuming that an equilibrium was established in the bronze crystals

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(6) Straumanis, *Acta Crystallogr.*, **2**, 82 (1949); *Z. Physik*, **126**, 49 (1949).

(7) Treadwell and Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 234–236.

(8) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, pp. 551–555.

(9) Treadwell and Hall, *ibid.*, pp. 227–228.

(10) Straumanis, *Z. Kristallogr.*, **104**, 173 (1942).

$$\mathrm{LiW^{V}O_3(W^{VI}O_3)_x} \rightleftarrows \mathrm{Li^\circ} + (1 + x)\mathrm{WO_3} \qquad x = 0.77 \qquad (5)$$

The lithium vapor then reacted with the tungstic oxide in the adjacent compartment of the boat and the formation of the blue bronze resulted

$$\mathrm{Li} + (1 + y)\mathrm{WO_3} = \mathrm{LiWO_3(WO_3)}y$$

When a mixture of blue bronze and metallic lithium was heated in a vacuum, lithium tungstate, metallic tungsten and some blue bronze with a slightly smaller lattice constant than the original bronze were formed.

The reaction (5) can also be made to proceed from left to right in the presence of other lithium acceptors. Thus, the blue bronze, when heated in vacuum with iodine, was converted into a product with a higher tungstic oxide content and the presence of lithium iodide in the reaction product was verified.

In the case of sodium tungsten bronze, the reaction corresponding to (5) could be reverted from right to left by heating with sodium iodide at 800° in vacuum.[3] Because lithium iodide was too powerful as a reducing agent, tungsten dioxide and tungsten were obtained instead of bronze.

$$\mathrm{LiI} \rightleftarrows \mathrm{Li} + \mathrm{I}$$

$$2\mathrm{WO_3} + 2\mathrm{Li} \longrightarrow \mathrm{W} + \mathrm{WO_2} + 2\mathrm{Li_2O}$$

$$\mathrm{Li_2O} + \mathrm{WO_3} \longrightarrow \mathrm{Li_2WO_4}$$

Iodine condensed in the cooler part of the sealed quartz tube. The presence of all other products was verified by X-ray analyses.

The resistance of the cubic lithium tungsten bronzes against attack by acids and bases was even greater than in the case of the sodium bronzes. Acids, even boiling concentrated hydrofluoric or nitric acids, did not attack the compound. The mixture of both acted very slowly and formed tungstic acid. Boiling concentrated sulfuric acid oxidized the compound only in the presence of ammonium sulfate. Bases, even when concentrated and hot did not attack the compound but the bronze dissolved slowly if sodium peroxide was added. The reaction was similar to that in the case of sodium bronze.[3] Finely divided lithium bronzes produced colloidal solutions when the electrolytes were removed by washing. Such solutions were violet to grayish-blue in transmitted light.

Physical Properties.—Crystals of the lithium tungsten bronze consisted of regular cubes with a violet-blue or bluish-gray color. Occasional thin plates showed a reddish-yellowish color in transmitted light. The crystals were brittle and of good cleavage parallel to (100).

The crystals or crystal conglomerates had high electrical conductivity. The resistance of the conglomerates increased continuously in air at room temperature and decreased in vacuum or while heated, etc.[11]

The resistance measurements were carried out with the purified bronze powders and the sintered samples made of powders of the composition mentioned under Preparation. The experimental arrangement was the same as previously described,[11] except that the glass tube was replaced by a quartz tube because the lithium bronze reacted with the sodium of the glass at elevated temperatures.

The specific resistance (σ) of a sintered specimen of lithium tungsten bronze was about 0.63 ohm at a temperature of 435 to 440° in vacuum; on cooling, the resistance (σ) increased up to 4.2 ohm. In air it rapidly increased even more. Of course, this resistance did not represent that one of pure lithium bronze.[11]

Purified powders with the lowest possible tungstic oxide (not sintered) were used for further work. Eight series of measurements at different temperatures in vacuum were made with one sample. In Table II the results of 4 runs and the average of 6 runs are given. A further series of measurements gave similar results.

The data of Table II show several differences in behavior between the lithium and sodium tungsten bronzes: (1) with decreasing temperature, the conductivity appears to rise slightly at first (negative temperature coefficient, $-\mathrm{d}\kappa/\mathrm{d}t$) then to decrease (positive $\mathrm{d}\kappa/\mathrm{d}t$), while the sodium tungsten bronze showed $-\mathrm{d}\kappa/\mathrm{d}t$ throughout. (2) The conductivity of the lithium bronze at room temperature ($\kappa = 23$) was considerably lower than that of pure sodium bronze ($\kappa = 350$). The reproductivity of such measurements was fairly good, the resistance of the sample decreased slightly with every run.

TABLE II

THE SPECIFIC RESISTANCE (σ) AND CONDUCTIVITIES (κ) OF LITHIUM TUNGSTEN BRONZE OF THE COMPOSITION $\mathrm{LiWO_3(WO_3)_{0.77}}$ AT DIFFERENT TEMPERATURES IN VACUUM

Temp., °C.	σ of 4 experiments				σ av.[a] in ohm	κ in ohm^{-1}
450–455	0.027	0.027	0.011	0.006	0.019	53
410–415	.016	.021	.007	.004	.012	83
370–375	.016	.021	.009	.006	.014	71
320–325	.021	.021	.011	.010	.016	63
270–275	.027	.027	.015	.014	.020	50
225–230	...	.032	.019	.018	.023	43
180–185	.032	.032	.024	.022	.029	34
125–130	.032	.032	.027	.027	.030	33
80–85	...	.037	.031	.031	.034	29
25–30	.037	.042	...	.036	.043	23
20–25	.037	...	.037	.036	.044	23

[a] Average of 6 runs: lowest σ at 410°, 0.0042 ohm, highest κ 238 ohm^{-1}; lowest σ at room temp., 0.036 ohm or 28 ohm^{-1}.

The lithium bronzes of higher tungsten(VI) oxide content had a considerably lower conductivity. The average resistance of a bronze with 54% tungstic oxide was 36.7 at about 20° and 6.8 at about 450° (in vacuum). The coefficient $\mathrm{d}\kappa/\mathrm{d}t$ was therefore positive. The reproducibility of the measurements decreased if the bronzes contained still more tungstic oxide.

The conclusion can be made that bronzes with lowest tungsten(VI) oxide content (43%) possess ionic conductivity (because $\mathrm{d}\kappa/\mathrm{d}t$ is positive).[12,13] Metallic conductivity also may exist. In lithium bronzes with higher tungstic acid content only, ionic conductivity could be established.

It is believed that the reasons for changes in conductivity caused by moist air and the restoration of conductivity by vacuum or elevated temperatures are the same as recently discussed in the case of sodium tungsten bronzes.[11]

Discussion

The cubic lithium tungsten bronzes differ from the sodium bronzes in three respects: (1) The lattice of the lithium bronze expands with absorption of tungstic oxide. (2) The pure $\mathrm{LiWO_3}$ does not exist. (3) The lithium bronzes show ionic conductivity and may have some electronic conductivity.

All three differences can be explained on the basis of the structure of the lithium bronze. The sodium tungsten bronze consists of a lattice built up of the large oxygen ions (r = 1.37 Å.), the centers of which are placed at the corners of octahedra (positions $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$). The whole is held together by the small $\mathrm{W^{6+}}$ (r = 0.57 Å.) located in the centers of the octahedrons (positions $\frac{1}{2}\frac{1}{2}\frac{1}{2}$) and by the $\mathrm{Na^+}$ (r = 0.95 Å.) between the octahe-

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[11] Straumanis and Dravnieks, THIS JOURNAL, 71, 683 (1949).

[12] Meyer, *Z. Elektrochem.*, 50, 276 (1944).

[13] Justi, "Leitfähigkeit und Leitungsmechanismus fester Stoffe," Vandenhoeck, Göttingen, 1947, pp. 25 and 169.

dra (positions 000). It must be assumed that the withdrawal of Na^+ (vacant sites remaining) causes the expansion of the lattice, but the process $W^{5+} \rightarrow W^{6+}$ ($W^{5+} + Na^+ = Na^\circ + W^{6+}$) or absorption of tungstic oxide causes the contraction of the lattice. Since there is enough space for the sodium ions, their removal causes only a slight expansion of the lattice, which is surpassed by the contraction involved by the W^{6+}. The lattice thus contracts with increasing tungstic oxide concentration C ($\mathrm{d}a/\mathrm{d}C = -8.3 \times 10^{-4}$ Å. per weight % WO_3).

The small lithium ions (r = 0.6 Å.) contract the whole lattice appreciably, so that the radius of the oxygen ions is only 1.32 Å. When the lithium ions are removed from the lattice, the expansion becomes larger than the contraction. The solution of tungstic oxide in the bronze is associated with the formation of vacant sites (in the places of lithium ions) and the highly contracted lattice therefore expands ($\mathrm{d}a/\mathrm{d}C = 4 \times 10^{-4}$ Å. per 1% WO_3 for the middle part of the curve, Fig. 1).

Figure 1 shows that a lithium tungsten bronze with a content less than 43% by weight of tungstic oxide would have a still smaller lattice constant. But this is evidently impossible, because the radius of the oxygen ions in this case must be smaller than 1.32 Å., which is already a very low value. The pure $LiWO_3$, therefore, cannot exist, at least not in the same lattice type.

The lithium ions can slip through the openings between the octahedra, having a width of 0.54 Å., because of their small size (r = 0.6 Å.). Therefore, the lithium tungsten bronzes are also ionic conductors already at 450°. Sodium ion (r = 0.95 Å.) cannot slip through and up to 450° the sodium bronze shows only electronic conductivity.

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Summary

It has been proven that the blue lithium tungsten bronze consists of $LiWO_3$, in which at least 42.6 ± 2% by weight tungsten(VI) oxide has been dissolved. Its composition may be represented by the formula $LiW^{V}O_3(W^{VI}O_3)_{0.77}$. The pure lithium tungsten bronze ($LiWO_3$) could not be obtained.

The bronze with 42.6% tungstic oxide is cubic (a = 3.7218 Å.) and possesses the perovskite ($CaTiO_3$) type structure.

The bronze can dissolve up to 68% tungstic oxide (at 900°) under expansion of the lattice, without changing the structure type. An anionic substitutional solid solution results.

The chemical behavior of the bronze can be explained on the basis of the reversible reaction $LiW^{V}O_3(W^{VI}O_3)_x \rightleftarrows Li^\circ + (1 + x)WO_3, x = 0.77$. Li can easily be bound by iodine or tungstic oxide.

The electric conductivity of the blue bronze (with 43% WO_3) in vacuum above 450° varies around 53 ohm^{-1}. At room temperature the conductivity is about 23 ohm^{-1}.

The temperature coefficient of conductivity is positive at lower temperatures. Conductivity is therefore ionic. Electronic conductivity may also exist.

The conductivity decreases with increasing concentration of tungsten(VI) oxide in the bronze.

The changes in conductivity caused by moist air are very similar to those of the sodium tungsten bronzes.

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Exchange Studies with Complex Ions. I. The Exchange of Radiocyanide with Certain Heavy Metal Complex Cyanides[1]

BY ARTHUR W. ADAMSON, JOAN P. WELKER[2] AND MILTON VOLPE[3]

Early studies in the field of complex ions have yielded a degree of understanding of the descriptive chemistry and structural relationships of these compounds such that, in recent years, increased attention is being directed toward the more difficult problem of determining the mechanism of their formation and reaction. The group of complex cyanides constitute an important example of this point. These complex ions have been described in terms of methods of synthesis, composition, appearance and their simple reactions. The structure of a number of them has been established[4] and thermodynamic

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(1) Presented in part in the Symposium on Tracers at the San Francisco Meeting of the American Chemical Society, March-April, 1949.

(2) This paper is based on a portion of a thesis to be submitted by Joan P. Welker in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Southern California.

(3) The work on potassium hexacyanoferrate(II) described in this paper is taken from a thesis to be presented by Milton Volpe to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the degree of Master of Science.

(4) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945.