TABLE III

LATTICE DIMENSIONS OF HEXAGONAL BRONZE COMPOSITIONS

Compn	Lattice parameters, Å a	c	Ref
$Rb_{0.27}MoO_3$	7.321	7.683	*a*
$Rb_{0.27}WO_3$	7.38	7.36	*b*
K_xReO_3	7.318 ± 0.0001	7.485 ± 0.002	*c*

[a] See ref 2. [b] A. Magneli, *Acta Chem. Scand.*, **1**, 315 (1953). [c] This work.

conveniently handled in air without oxidation or hydration, (2) are relatively stable to grinding and heating under the proper conditions of applied external pressure to minimize the rapid evolution of nitrogen at and above their decomposition temperature, (3) are commercially available or can readily be prepared and purified, (4) are a source of alkali metals in a finely divided and highly reactive state, (5) are a convenient source of high-purity nitrogen which can be used for nitride formation or as a protective atmosphere during reaction of the alkali metal, (6) are readily soluble in water for easy removal from the reaction product, and, finally, (7) decompose quantitatively to the metal and nitrogen at relatively low temperatures.

High pressures were used to prepare $NaWO_3$ and molybdenum, rhenium, and cubic K_xWO_3 bronze derivatives. These products are not necessarily high-pressure phases, for molybdenum bronzes with low alkali content and monoclinic structures have been prepared[9] at atmospheric pressure.

The preparation of cubic tungsten bronzes (Na_xWO_3 and K_xWO_3), where $x = 0.90–1.00$, was achieved at the highest reactant ratios of alkali azide to tungsten(VI) oxide and at the highest pressures. As the reactant ratio decreased and the pressure and temperature remained constant, the cubic cell edge decreased until the tetragonal bronze appeared as the primary product. Variations in the temperature or pressure for a given azide to metal oxide ratio also yielded different phases. The three parameters—reactant ratio, temperature, and pressure—therefore can be varied in the preparation of different bronze products.

The isolation of bronzes with high alkali content has been greatly facilitated by the use of these high-pressure techniques. Cubic K_xWO_3, as well as cubic or tetragonal rhenium and molybdenum bronzes, has not yet been prepared at atmospheric pressure.

Several cubic sodium tungsten bronzes were isolated that appeared on the basis of a cell edge *vs.* composition plot to have an x value slightly greater than the theoretical limit of 1.00. These values, however, all fall within the standard deviation (±0.007 Å) given by Brown and Banks[6] for the composition–unit cell equation. Support of this equation was recently presented by Wechter, Shanks, and Voigt[10] from thermal neutron activation analyses on the cubic Na_xWO_3 derivatives.

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A 3:1 8-Hydroxyquinoline-5-sulfonic Acid–Zinc Ion Complex[1a]

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The bidentate ligand 8-hydroxyquinoline-5-sulfonic acid (L) has been reported to form 1:1 and 2:1 complexes with zinc ions.[2–5] At temperatures of 20–25° and ionic strengths of 0–0.1, the stabilities obtained were $\log K_1 = 7.54–8.70$, and $\log K_2 = 6.7–7.5$. In the course of a recent investigation of the removal of zinc by L from the bacterial enzyme alkaline phosphatase the existence of a 3:1 complex of L with ionic zinc seemed indicated, leading to a reexamination of this system. The present data demonstrate the occurrence of a 3:1 complex, similar to those previously observed for both cobalt(II) and iron(II).[5–7]

Zinc was obtained as the "SpecPure" sulfate salt from the Johnson Matthey Co., and L was obtained from the Eastman Chemical Co. All other chemicals were reagent grade and were further purified by dithizone extraction to remove trace metal contaminants.[8] Absorption spectra were obtained with a Cary Model 15 recording spectrophotometer. Potentiometric titrations were carried out using a Radiometer pH meter and titration cell assembly, under a nitrogen atmosphere at 20.0°. The titrant was added with a micrometer buret of the syringe type. All experiments were performed at an ionic strength of 0.5 M (NaCl). In those experiments where buffering was necessary, 0.01 M N-2-hydroxyethylpiperazine-N′-2-ethanesulfonic acid (HEPES), pH 7.0, was utilized.

Addition of zinc to L at pH 7.0 generates a new absorption spectrum with a maximum at 370 mμ. When a constant amount of ligand is titrated with increasing

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amounts of metal, the absorptivity increases until the ratio of ligand to metal is 3:1 and then remains constant up to equimolar proportions of zinc and ligand (Figure 1). Similarly, application of the method of Job[9] to the determination of the stoichiometry of this interaction demonstrates the presence of a complex with 3 mol of chelating agent per mole of metal (Figure 2). In both instances the extinction at 370 mμ of the 3:1 complex of L with zinc is found to be 1.1×10^4 M^{-1} cm^{-1}.

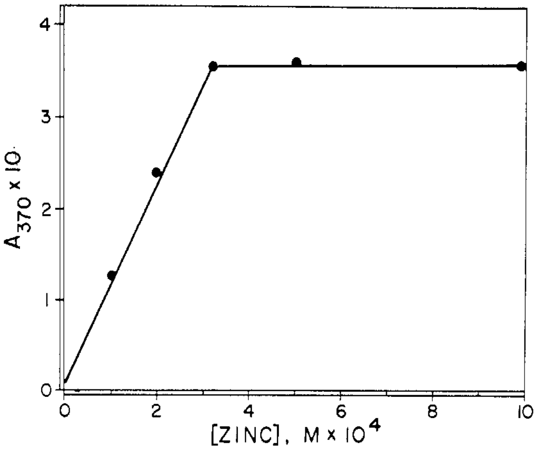

Figure 1.—Titration of L with ionic zinc. Solutions contained 10^{-3} M L in 0.01 M HEPES and 0.5 M NaCl, pH 7.0. Zinc was present as indicated on the abscissa. Spectra were recorded in 1.00-mm cells, and the absorbance at 370 mμ is plotted. The reference cell contained L without zinc.

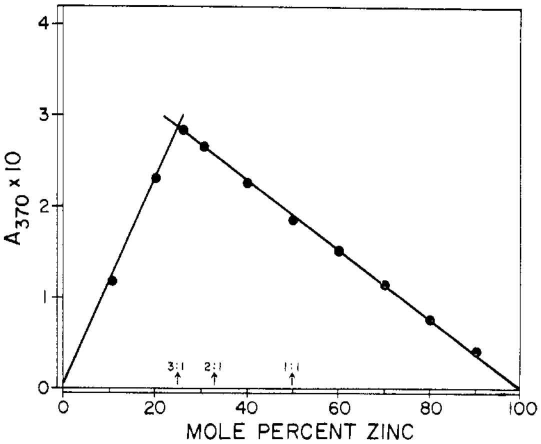

Figure 2.—Job's curve for interaction of zinc with L. The total concentration of L plus metal was 10^{-3} M in 0.01 M HEPES and 0.5 M NaCl, pH 7.0. Spectra were determined in 1.00-mm cells *vs.* a reference containing L without zinc.

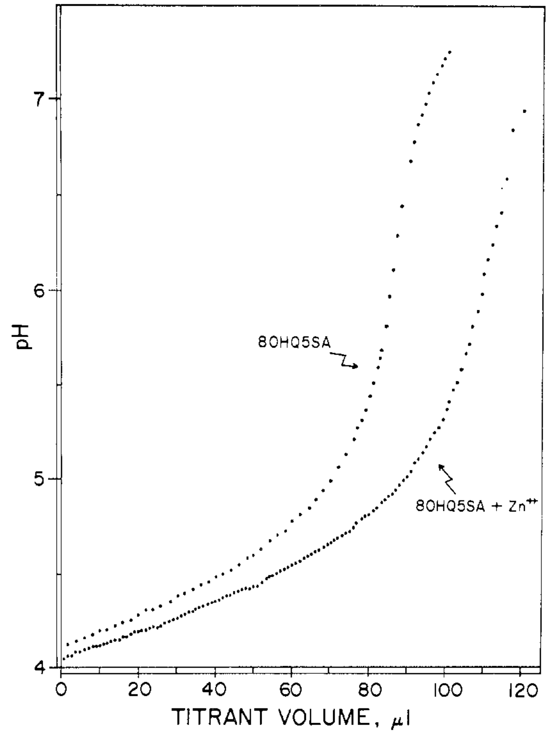

Figure 3.—Potentiometric titration of L in the presence and absence of zinc. A solution of 20 ml of 10^{-3} M L in 0.5 M NaCl was titrated in the presence and absence of 5×10^{-5} M Zn^{2+}. The titration was performed at 20° under a nitrogen atmosphere with a titrant of 0.11 N NaOH.

Potentiometric titration of a 10^{-3} M solution of ligand with and without 5×10^{-5} M Zn^{2+} results in the titration curves presented in Figure 3. Throughout the pH range investigated the curve for ligand plus metal lies below that for ligand alone demonstrating the occurrence of complex formation. A plot of n, the number of moles of ligand bound per Zn^{2+}, *vs.* pL^-, the negative logarithm of the concentration of ionized ligand, obtained using a pK for the ligand of 8.35[5] fails to reveal any distinct inflection points. The three individual stability constants were, therefore, evaluated by solution of the simultaneous equations for the three stability constants as proposed by Block and McIntyre,[10] using ten sets of different triplets of data points. The values obtained were $\log K_1 = 7.46 \pm 0.11$, $\log K_2 = 7.18 \pm 0.05$, and $\log K_3 = 5.86 \pm 0.07$.

Three different approaches demonstrate the occurrence of a 3:1 complex of L with zinc ions. (A previously reported complex of Zn^{2+} with the related chelating agent, 8-hydroxyquinoline (HOx), having a 3:1 composition, has been shown to be a 2:1 chelate with a third mole of HOx present as an adduct, *i.e.*, $Zn(Ox)_2 \cdot HOx$.[11]) In view of the finding that the stability constant for binding of a third mole of L is nearly two orders of magnitude lower than those for the first and second moles, the failure to observe the 3:1 complex in earlier studies, performed at lower total L + Zn^{2+} concentrations, and lower L:Zn^{2+} ratios, is not surprising. When studied under conditions which favor the formation of higher order complexes, it is apparent that zinc, as well as cobalt(II) and iron(II), can coordinate with 3 mol of this ligand.

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