The complete name would be *a*-oxo-*b*:*c*,*d*:*e*-bis(2,4-pentanedionato)-5*B*-vanadium.

Although this designation system has been developed specifically for coordination compounds, it appears to be extensible to other classes of compounds. For example, if the locant designators of some of the reference structures are replaced by corresponding numbers (a by 1, b by 2, etc.), the resulting designation patterns are almost identical with the enumeration system for cage boranes recently suggested by the boron nomenclature subcommittee.[6] In addition, the reference-structure approach may be applicable in the description of the structure of other inorganic compounds such as heteropoly acids. Furthermore, the system is not restricted to application in nomenclature. The table of reference structures has proved to be particularly valuable in the development of a linear notation system for coordination complexes.[2]

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(6) R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

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The Reactivity of Metal Chelates of 8-Quinolinol-5-sulfonic Acid[1]

Sir:

In a preliminary report on a study of the effect of metal ions on the kinetics of iodination of 8-quinolinol-5-sulfonic acid,[2] the results suggested that the observed decrease in rate might be attributed to the decrease in concentration of the quinolinolate anion (the reactive species). By using lower pH values and higher metal: ligand ratios, we were able to reduce the concentration of ligand anion to sufficiently low values to permit the observation of the iodination of the metal chelates themselves.

Reagents.—Eastman White Label 8-quinolinol-5-sulfonic acid was recrystallized twice from de-ionized water to give long yellow needles and dried at 90° (corrected m.p. 319–321°). Its purity was checked by an iodometric titration: equiv. wt. found, 225.6; calcd., 225.3.

Kinetic Data.—Rate data were obtained by the following titrimetric method. An aqueous solution of iodine was added to the solution and aliquots were withdrawn for titration at appropriate time intervals. The buffer, together with a solution of reagent, and metal ion, if necessary, were diluted to 90 ml. in a 125-ml. glass-stoppered flask immersed in a constant-temperature bath. After the solution had reached the desired temperature, 10 ml. of a solution containing iodine and iodide at the same temperature was added. A timer was started when the iodinating solution had half-emptied into the flask. The stopper was replaced and the contents of the flask mixed. Aliquots (10 ml.) were withdrawn at intervals, quenched in an acidic solution of iodide, and titrated with a 10^{-3} *M* thiosulfate solution to the starch end point. On the basis of the titer at infinite time it was found that 1 mole of iodine reacted with each mole of ligand in every experiment.

TABLE I

EFFECT OF METAL IONS ON THE RATE OF IODINATION OF 4.54×10^{-4} *M* 8-QUINOLINOL-5-SULFONIC ACID IN WATER IN 0.1 *M* ACETATE BUFFER AND 0.02 *M* KI AT 20° AT pH 5.0

Metal ion	Metal: ligand ratio	k_{obsd}, l. mole^{-1} sec.$^{-1}$ [a]
None	...	0.159
Zn(II)	0.50	0.088
	1.00	0.055
	2.00	0.029
	4.00	0.022
	10.0	0.018
	20.0	0.018
	50.0	0.016
	100	0.015
	200	0.011
	500	0.0098
Mn(II)	10.0	0.097
	100	0.049
	500	0.033
Co(II)	10.0	0.014
	100	0.013
Ni(II)	10	0.014
	100	0.012

[a] k_{obsd} calculated from $-d[B^-]/dt = k_{\text{obsd}}[B^-][I_2]$.

Results and Discussion.—The rate of iodination of 8-quinolinol-5-sulfonic acid was found to be first order in both 8-quinolinol-5-sulfonic acid and iodine.

Second-order rate constants (k_{obsd}) calculated on this basis were found to fit the experimental data for most of the reaction range (20–80%) to within 3%.[3] Although the precision of these results is not as good as that obtained with the coulometric method,[4] the calculated rate constants are in accord.

In the earlier work describing the effect of metal ions on the reaction kinetics at pH 7.0 and 9.0, only stoichiometric metal: ligand ratios (1:2), were used in order to avoid precipitation due to metal ion hydrolysis. By working at pH 5.0, it was found possible to raise the metal: ligand ratio and thus check on the hypothesis that the reduction in rate observed previously could be attributed solely to the unchelated ligand.

From the data in Table I it may be seen that the rate of iodination does not decrease upon increasing the metal ion concentration in a manner that is consistent with the above hypothesis. The drop in the concentration of free ligand which decreases by several hundredfold in the case of Zn(II), for example, is ac-

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(1) This work was supported by a grant from the National Institutes of Health.

(2) C. Bostic, Q. Fernando, and H. Freiser, *Inorg. Chem.*, **2**, 232 (1963).

(3) C. R. Bostic, Ph.D. Thesis, University of Arizona, 1963.

(4) G. S. Kozak and Q. Fernando, *J. Phys. Chem.*, **67**, 811 (1963).

companied by a decrease in the rate constant by less than a factor of ten. Obviously, then, the metal chelate species are involved in the reaction. At metal:ligand ratios of less than 10:1 the values of k_{obsd} decrease with increasing metal ion concentration, which might be due in part to the presence of mixtures of the intermediate and fully formed zinc(II) chelate. At metal:ligand ratios ranging from 10:1 to 100:1 the values of k_{obsd} are relatively constant, although the calculated free ligand concentration decreases by a factor of ten. Thus if the free ligand rather than the metal chelate is being iodinated, k_{obsd} would have decreased by this same factor of ten in this range. At metal:ligand ratios higher than 100:1 a further small decrease in k_{obsd} was noted, but this may well reflect the change due to the greatly increased ionic strengths involved in these higher ratios. Further, there is very little effect of the nature of the metal ion on the rate constant. These factors probably result from the complex nature of the mechanism of the iodination reaction. This iodination reaction is therefore probably not suitable as a diagnostic means of elucidating the effect of metal ions on the reactivity of metal chelates. For this purpose reactions with simpler mechanisms must be sought.

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Book Reviews

Preparative Inorganic Reactions. Volume I. Edited by WILLIAM L. JOLLY. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1964. ix + 271 pp. 15 × 22.5 cm. $9.

This book, the first of a projected series, contains chapters dealing with preparative aspects of ten types of inorganic compounds: coordination polymers (J. C. Bailar, Jr.); optically active coordination compounds (S. Kirschner); metal derivatives of ketimine and aldimine compounds (D. F. Martin); metal carbonyls (J. C. Hileman); halide and oxyhalide complexes of the titanium, vanadium, and chromium subgroups (G. W. A. Fowles); anhydrous metal nitrates (C. C. Addison and N. Logan); halogen and halogenoid derivatives of the silanes (A. G. MacDiarmid); saline hydrides (C. E. Messer); sulfur–nitrogen–fluorine compounds (O. Glemser); and hypohalites and compounds containing the –OX group (S. M. Williamson).

The various discussions emphasize the principles involved in the preparative procedures and relatively few detailed recipes are given. The generally complete and up-to-date literature coverage gives the reader ready access to such recipes. For some of the compound types where the experimental techniques are not ordinary, *e.g.*, the metal carbonyls and the saline hydrides, there are excellent descriptions of the apparatus requirements. On the whole the approach to the consideration of the synthetic procedures has been critical rather than indiscriminate.

As would be expected from the diversity of compound types covered, there is no common mode in the presentation of introductory material leading to the synthetic procedures. The reviewer found all of the introductions to be thoroughly adequate and some to be of particular excellence in that the treatment of the special compound types goes beyond purely synthetic implications.

The book contains both author and subject indexes. The latter appears to be fairly complete and the former is especially good, since it not only gives the page number on which an author's name is to be found but also the literature reference number at the end of the chapter.

Finally, it should be noted that the book with its major emphasis on the principles of synthesis does not compete with Brauer's excellent volumes on preparative inorganic chemistry or with the *Inorganic Syntheses* series. Rather, it is a useful complement to these works.

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Inorganic Ion-Exchange Materials. (Topics in Inorganic and General Chemistry, Volume 2). By C. B. AMPHLETT. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York 17, N. Y. 1964. x + 141 pp. 14.5 × 21.5 cm. $6.50.

In this little volume the author has skillfully summarized the present knowledge of inorganic ion exchangers. The first chapter contains an historical development and a brief introduction to the quantitative expression of the equilibrium ion-exchange properties. Chapter 2 is devoted to the ion-exchange properties of clay minerals. Included are discussions on the structures of the clay minerals with respect to their ion-exchange behavior, the exchange on montmorillonite, attapulgite, mica, vermiculite, kalonite, and organic derivatives of clay minerals, the thermodynamics of the systems including the problem of determining the activity coefficients in the solid phase, and the problem of swelling in clay minerals. Chapter 3 is devoted to the properties of zeolites. After taking up the structural features and the composition of these compounds, the molecular sieve properties for gaseous species are considered. The ionic sieve properties of the zeolites are then illustrated, followed by a reasonably detailed discourse on the thermodynamic equilibrium properties, exchange isotherms, activity coefficients in the solid phase, and the kinetics of exchange. There is also a short section on zeolites containing two channels, each of different dimensions. The properties of nonsilicic inorganic ion exchangers are discussed in the last two chapters. Chapter 4 is devoted entirely to ion exchange in heteropoly acids. Here the exchange properties are considered in relation to the structure of the compounds, and specific consideration is given to ammonium phosphomolybdate, both in the column separation of alkali metals and in paper chromatography. This chapter also contains sections on the separation of cesium from fission product waste solutions, and separations involving polyvalent cations. Chapter 5, dealing with hydrous oxides and insoluble salts, contains data for zirconium oxide and zirconium phosphate; the exchange properties of hydrous metals oxides in general, and other insoluble phosphates, molydates, and tungstates, are dealt with briefly. The effects of structure, drying times, and temperatures in relation to the sieve and exchange properties are considered, as are the kinetics and thermodynamics of exchange. The practical application of these materials to water purification systems and in ion-exchange membranes completes the chapter. The book is neatly produced, although an occasional broken letter and misalignment mar the otherwise acceptable product.

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