expression for the partial molal entropy of a monatomic positive ion of charge, Z, and crystal radius, r

$$\bar{S}^0 = \frac{3}{2} R \ln M - 270 \frac{Z}{(r + 2.00)^2} + 37$$

For uranyl ion we should reduce the electrostatic contribution to the entropy (the second term on the right of the above expression) by the factor of 6/8 as stated above. The empirical equation for the partial molal entropy of UO_2^{++} is then

$$\bar{S}^0 = \frac{3}{2} R \ln 270 - \frac{6}{8} \times 270 \times \frac{3}{(0.89 + 2.00)^2} + 37 + S_{\text{int}}$$

Here we have inserted the mass of UO_2^{++} in atomic weight units, the equatorial radius, 0.89 Å., the effective charge at the equator, 3, and a term, S_{int}, to take care of the vibrational and rotational (or, more probably, librational) contributions to the entropy of the aqueous ion. The contribution of these modes to the entropy of UO_2^{++} would only be a few entropy units and to the accuracy of our calculation would not alter the fact that the calculated entropy, $-19 + S_{\text{int}}$, and the experimental entropy, -17 e.u., are in approximate agreement. In fact, the closeness of this agreement is doubtless fortuitous.

The sensitivity of the model to a change in the charge distribution is such that a shift of 0.1 of an electronic charge to each oxygen from the uranium would cause a decrease of 3 e.u. in the calculated entropy of UO_2^{++}. Therefore the charge distribution cannot be fixed with any great accuracy but it would appear that it approximates to $+4$ on the uranium and -1 on each oxygen.

The Relative Hydrolysis of PuO_2^{++} and UO_2^{++}.—Kraus and Dam[20] have found that uranyl ion appears to hydrolyze more extensively than plutonyl ion, although the complication of polymerization in the case of uranyl may make this conclusion incorrect. Kraus and Dam comment that the observed greater hydrolysis of uranyl seems anomalous since "Pu(VI) should be the smaller ion and thus have the larger acid constant."

Since the structural evidence shows that the six oxygen neighbors of uranyl ion (in $CaUO_4$, for example) are in contact with the oxygens of the uranyl group rather than in contact with the uranium, the fact that PuO_2^{++} is a smaller ion than UO_2^{++} does not follow from the expected actinide contraction. A calculation based on the packing of hard spheres about a uranyl group also composed of hard spheres shows that, in the case where the uranium cannot contact the six peripheral neighbors, a decrease in the radius of the uranium causes an increase in the uranium–peripheral oxygen distance. The relevant formula obtained by straightforward geometrical considerations is

$$a^2 = 4b^2 - \frac{(b + c)^2}{3}$$

where a is the uranium–peripheral oxygen neighbor distance, b is the radius of oxygen, c is the radius of uranium, and $b + c$ is the uranium–uranyl oxygen distance. Obviously then a will decrease as c is increased, and we must conclude that plutonyl behaves as a larger ion than uranyl toward oxygens or water molecules about the equator.

Provided that the charge distribution is not appreciably altered in going from uranyl to plutonyl one must then conclude that uranyl ion should indeed be more acidic than plutonyl ion.

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[20] K. A. Kraus and J. R. Dam, National Nuclear Energy Series, "The Transuranium Elements," Division IV, Volume 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, Part 1, pp. 528–549.

[CONTRIBUTION FROM KING COLLEGE AND THE OAK RIDGE NATIONAL LABORATORY]

Bispentanedione Diaquo Manganese(III) Compounds

BY G. H. CARTLEDGE

RECEIVED JUNE 7, 1952

Salts of a new cationic manganese(III) complex with 2,4-pentanedione have been prepared. The acidic ionization constant of the diaquo-ion previously reported has been confirmed. The equilibrium constant for the interconversion of the bis- and tris-complexes has been determined at different temperatures for the estimation of the ΔH and ΔS of the reaction.

In a previous paper[1] it was shown that trispentanedione manganese(III) resembles the trioxalato and trimalonato complexes in that one of the bidentate organic ligands may be reversibly replaced by two water molecules under proper conditions of acidity. The equilibrium constant was determined for the reaction $MnPn_3 + 2H_2O + H^+ \rightleftarrows MnPn_2(H_2O)_2^+ + HPn$, in which Pn^- is used to represent the anion of 2,4-pentanedione.

This reaction is of particular interest in that it produces a cationic complex. Previously only neutral or anionic complexes of tervalent manganese had been prepared, though Taube[2] had postulated the formation, in solution, of a monoöxalato manganese(III) cation, $MnC_2O_4^+$, in order to account for the catalytic effect of manganese in the oxidation of oxalic acid. The isolation and properties of a few salts of the bispentanedione diaquo ion will be described in this paper, together with a determination, at different temperatures, of the equilibrium constant of the reaction for its conversion to the tris-complex.

Preparation of the Complex Perchlorate.—The first attempt to isolate the complex salt was based upon the possibility that the large univalent cation might form a perchlorate of sparing solubility. The equilibrium measurements indicated that at a pH of 2 the trispentanedione complex is totally converted to the bis-ion, even in the presence of much free pentanedione. After a few experiments had demonstrated that the perchlorate has a surprisingly high solubility, a convenient method of preparation was developed as follows. Three grams of the tris-complex was tri-

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[1] G. H. Cartledge, THIS JOURNAL, **73**, 4416 (1951).

[2] H. Taube, *ibid.*, **69**, 1418 (1947); **70**, 1216, 3928 (1948).

turated in a mortar with 2 *F* perchloric acid in slightly less than the theoretical quantity for the reaction $MnPn_3 + HClO_4 + 2H_2O \rightarrow MnPn_2(H_2O)_2ClO_4 + HPn$. Additional 2 *F* perchloric acid was gradually added so that the *p*H was kept between 2 and 2.5. When the acidity no longer changed after about a minute of further grinding, the mixture was transferred to a separatory funnel with 20 ml. of ether to extract the major portion of the free pentanedione. The slurry was then filtered and washed with a very little acetone, followed by much ether, in which the salt is very sparingly soluble. The crystals were sucked as dry as possible on the filter and dried in air for 30 minutes. The yield of 2.3 g. represents 60% recovery, based on trihydrated perchlorate. The water content was found to decrease upon exposure to the atmosphere.

The salt soon hydrolyzes and gives a precipitate when added to water. The solution is stabilized against precipitation by sufficient free acid, though reduction to manganese(II) sets in at high acidity. It was found possible to make an analysis by the following procedure. A quantity of a cation exchange resin (Amberlite IR 100H-AG) was completely converted to the acid form by washing it with hydrochloric acid; the excess acid was washed out until the *p*H of the washings rose above 5. Two grams of this resin was placed in a small beaker and 3 g. put in a column of 1 cm. diameter. A weighed sample of complex salt was put in a dry beaker and 25 ml. of water was quickly added. Solution was almost instantaneous. One 5-ml. aliquot was added to sulfuric acid for a manganese analysis and a 10-ml. aliquot was transferred to the beaker containing the resin. Liberation of hydrogen ions and pentanedione by the resin took place before there was time for precipitation to begin.

The resin mixture was agitated until the solution became essentially colorless and then was poured through the column. One slow pass was found sufficient to remove all detectable manganese. The column was then washed with distilled water until the washings had a *p*H greater than 5.5. The solution was titrated electrometrically to differentiate perchloric acid from any pentanedione that might be liberated by the resin. It was found that at least 90% of the pentanedione contained in the complex could be found in the solution after the resin treatment. Hence perchloric acid was determined by noting the amount of standard alkali required to titrate to a *p*H of 4.00 and making a calculation for the slight additional quantity required to go to a *p*H of 7 if pentanedione were absent. An approximate determination of pentanedione was made by continuing the titration to a slight inflection at a *p*H of about 11, the Beckman blue electrode being used for this titration.

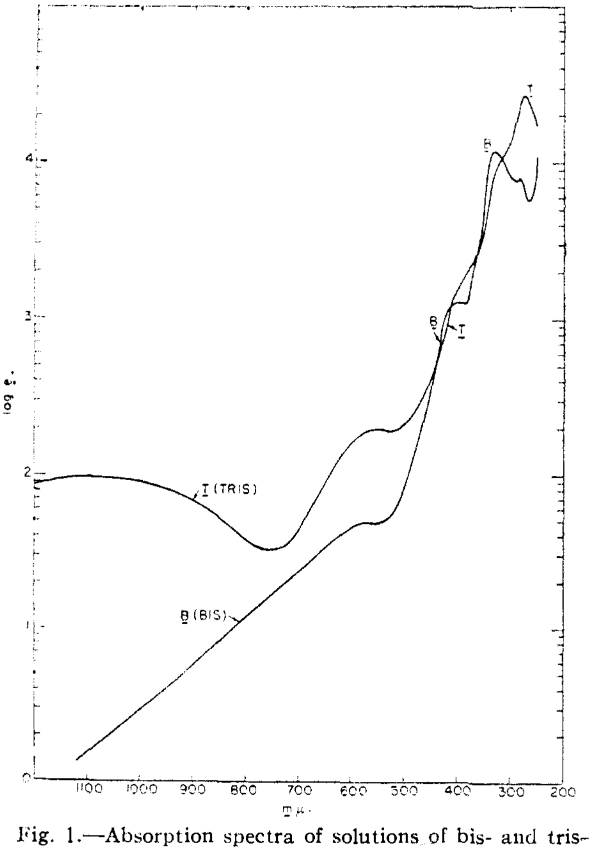

Fig. 1.—Absorption spectra of solutions of bis- and tris-pentanedione manganese(III) complexes. The solvent for the tris-compound was alcoholic 0.1 *F* pentanedione.

Manganese was determined by fuming the aliquot with sulfuric and nitric acids, taking up in sulfuric acid, diluting to volume, and oxidizing an aliquot to permanganate by potassium periodate for spectrophotometric determination.

Analysis of the preparation described above gave Mn 12.74, ClO_4 23.10%, or Mn:ClO_4 = 1:1.006. The percentages correspond to a formula $MnPn_2(H_2O)_2ClO_4 \cdot 2.5H_2O$; calculated, Mn 12.67, ClO_4 22.94. Analyses of other preparations gave similar results, with 85–91% of the theoretical amount of pentanedione found to be liberated by the resin. Tests on the resin showed that the manganese remained in the upper portion of the column, partly in the bivalent and partly in the tervalent condition.

Preparation of the Complex Chloride.—Following the trituration procedure used with perchloric acid, the tris-compound was ground in a mortar with 1 *F* hydrochloric acid until a permanent *p*H of 2 was attained. Transformation was rapid, and the slurry was extracted, filtered and washed as described above. Ether may be used in large quantities, since the salt is essentially insoluble. The chloride was dried in air for 15 minutes before being bottled.

Other preparations were made by the reaction $4MnCl_2 + KMnO_4 + 10HPn + 6H_2O \rightarrow 5MnPn_2(H_2O)_2Cl + KCl + 2HCl$. One-hundredth of a mole of potassium permanganate was dissolved in 50 ml. of water; 0.04 mole of $MnCl_2 \cdot 4H_2O$ (7.92 g.) was dissolved in 20 ml. of water. To the manganese(II) chloride solution 11 ml. of pentanedione (a slight excess) was added gradually with mechanical stirring, while the permanganate solution was run underneath the surface of the mixture from a buret. The reaction was conducted in an ice-bath, and stirring was maintained for about 15 minutes after the addition of permanganate was complete. The product was washed with a 1:1 acetone–water mixture containing 0.1% pentanedione, then stirred into ether and air-dried for about 15 minutes.

Analysis of products from both procedures gave comparable results, showing a slight chloride contamination in most cases. Typical analyses were: Mn, 15.30, 15.08, 14.97, 15.31; calcd. Mn, 15.23; Cl, 10.05, 10.03, 9.96, 9.80; calcd. Cl, 9.83. The calculated percentages are for the dihydrate, $MnPn_2(H_2O)_2Cl \cdot 2H_2O$. The manganese analyses were made spectrophotometrically; chloride was determined by both the resin procedure and direct titration by the adsorption indicator method, after reduction of manganese(III) to manganese(II) by hydrogen peroxide. Results from the two procedures were indistinguishable.

Properties.—The perchlorate and chloride are both of a dark olive-green color when well crystallized. Solutions in dilute aqueous pentanedione brought to a *p*H of approximately 2 by addition of a strong acid are yellowish green in color. Water alone quickly decomposes the salts with precipitation of manganese(III) hydroxide. Hydrogen peroxide rather rapidly reduces the acidified solution. Potassium ferrocyanide in weakly acid solution produces a creamy precipitate that is very difficultly filterable. No precipitate is given by potassium dichromate. Like all the manganese(III) complexes, the salt is rapidly converted to other complexes under appropriate conditions. Thus, pentanedione anions are displaced by addition of an oxalate, malonate, phosphate, pyrophosphate or cyanide. The sulfate and nitrate evidently have very high solubilities, as no solid is formed when the tris-complex is triturated with 1 *N* nitric acid or sulfuric acid.

The absorption spectrum of both the chloride and the perchlorate was measured in aqueous solution (containing 0.05 *F* pentanedione at *p*H 2.3) and also in 95% ethanol containing 0.05 ml. of pentanedione and 6 drops of 1 *N* sulfuric acid per 100 ml. Figure 1 shows the absorption spectrum, which was the same in both solvents, with the curve for tris-pentanedione manganese(III) for comparison. Too much significance cannot be attached to the exact value of the extinction coefficients at the extreme short-wave end of the spectrum, because of the instability of the very dilute solutions required even when an absorption cell of about 0.02

cm. length was used. The carbonyl band at approximately 270 mμ is clearly shown in both compounds. Bands common to both compounds are also found at approximately 330, 400 and 550 mμ. The radical difference between the two curves in the near infrared was utilized in the previous paper[1] in determining the equilibrium constant for the displacement of the third pentanedione ion. It is interesting to note that the trioxalato manganese(III) ion also has a similar broad band in the 1 μ region and that this band also disappears when one oxalate ion is displaced by water.

Measurement of the Acidic Dissociation Constant of the Aquo Ion.—In the former paper[1] it was shown that the spectrophotometric measurements required correction for an acidic dissociation of the aquo cation at the higher *p*H values, in accordance with the equation $MnPn_2(H_2O)_2^+ \rightleftarrows MnPn_2(H_2O)(OH) + H^+$. The dissociation constant 5 (±1) × 10^{-8} was derived. An attempt has been made to confirm this result by direct measurement of the acidity of a solution of the pure chloride in boiled distilled water. Such solutions soon become turbid, but since ionization reactions quickly come to equilibrium it was hoped that a reliable *p*H value might be obtained before complicating reactions set in.

Weighed samples of the salt were added to boiled water in a lipless beaker having a magnetic stirrer and protected from atmospheric carbon dioxide. *p*H readings were begun as quickly as the samples could be mixed, complete solution requiring less than 15 seconds. With 0.01 *F* complex chloride, the initial *p*H reading of 4.72 rose in 2 minutes to 4.90 and then decreased to 4.29 while a turbidity appeared. In other experiments, 0.02 *F* aqueous pentanedione was used as solvent for the salt. In this case the initial *p*H of 4.58 changed to 4.46 in 1 minute. The temperature was 25 ± 2°.

It is at once evident that the initial change in acidity makes the measurement of the dissociation constant by this method somewhat inexact. The initial readings in the simple aqueous solutions lead to a K_a value of 3.6 × 10^{-8}; the value obtained from measurements of the solutions containing pentanedione is 6.7 × 10^{-8} (the solvent pentanedione was taken into consideration in this computation). The instrumental uncertainty in reading *p*H and the unavoidable time lag are sufficient to account for the discrepancy between these numbers and the value 5 × 10^{-8} previously found, which may therefore be taken as substantially correct.

The experimental time–*p*H curves may be interpreted by assuming that additional replacement of pentanedione anions by water molecules occurs in the aqueous solution, but not in the pentanedione solution. This causes the initial rise in *p*H in the simple aqueous solution, which is then followed by a decrease in *p*H owing to further dissociation (hydrolysis) of the aquo ion to insoluble products.

Thermodynamics of the Bis–Tris Equilibrium.—A further study of the system $MnPn_3 + 2H_2O + H^+ \rightleftarrows MnPn_2(H_2O)_2^+ + HPn$ was made by determining the equilibrium constant between 14 and 38°. Higher temperatures were not used because of the instability of the solutions. Absorption spectra were measured at 1100 mμ, as in the previous work, using 0.500 *F* aqueous pentanedione as solvent, 0.005 *F* complex as solute, and adjusting the *p*H to the neighborhood of 5.5 by addition of a trace of sulfuric acid. A Beckman model G *p*H meter was used, the electrodes being kept at the different temperatures until no further drift could be detected. Calibration was based on 0.05 *F* potassium biphthalate as *p*H 4.00 at 10–30° and 4.02 at 30–40°.[3] Coleman buffer tablets were also checked at *p*H 10.00 at 30°, no difference from the phthalate calibration being found.

Calculation of the equilibrium constant was made as before. The same value of the extinction coefficient e_3 of the tris-compound was used at the three temperatures, since experiment showed that there was no change in the e_3 value with temperature in an alcoholic solution over a 10° range, after correction for the volume change. The results are shown in Fig. 2, the constants being as follows: 14.1°, 1.29 × 10^5; 21.4°, 1.24 × 10^5; 38°, 1.09 × 10^5. Previously the value 1.22 ± 0.05 × 10^5 was found for temperatures approximating 25°. The curve of log *K* *vs.* 1/*T* is seen to be essentially linear within the accuracy of the measurements. The slope of the curve gives $\Delta H = -1170$ cal. for the reaction as written above.

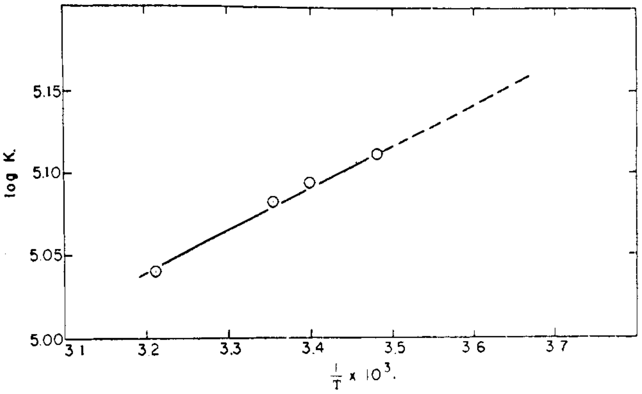

Fig. 2.—Temperature dependence of the equilibrium constant for the reaction $MnPn_3 + 2H_2O + H^+ \rightleftarrows MnPn_2(H_2O)_2^+ + HPn$.

In order to compute the heat and entropy changes for the reaction $MnPn_3 + 2H_2O \rightleftarrows MnPn_2(H_2O)_2^+ + Pn^-$ the dissociation constant of pentanedione at different temperatures is required. For this purpose, Eastman pentanedione was purified as previously described[1] in order to remove small amounts of acetic acid or anhydride. The importance of such purification may be judged from the observation that one commercial sample contained sufficient acid impurity to decrease the *p*H of a half-neutralized 0.1 *F* solution by 0.2 *p*H unit, as compared with the same specimen after purification. Simple distillation did not remove the impurity.

For the *p*H measurements, 0.100 *F* pentanedione was titrated potentiometrically with carbonate-free sodium hydroxide approximately 0.1 *F*, using Beckman universal electrodes with a model G meter and temperature control to 0.1°. The electrodes were stabilized to the different temperatures and calibrated as stated above. In other experiments, quantities of 0.500 *F* pentanedione were suitably diluted with boiled water and treated with an amount of standard sodium hydroxide sufficient to give half neutralization. These solutions were adjusted to temperature and measured quickly. No difference was found between the *pK* values obtained by the two procedures. From the titration curves obtained with 0.1 *F* solutions, the *pK* calculated did not vary significantly from 4 to 50% of complete neutralization. The maximum salt concentration at half neutralization was only 0.03 *F*, hence an approximate activity coefficient of 0.9 was assumed for the pentanedione anion. This correction for activity adds 0.04 to the *pK* value, which is only slightly more than the probable instrumental error.

The experimental values of log K_a are shown in Fig. 3. Between 11 and 30° the curve is strictly linear within the experimental error. The points at around 40° are definitely below the curve. This observation is in agreement with the determinations reported by Schwarzenbach, Suter and Lutz,[4] whose data cover the temperature range from 20 to 60°. Their pK_a value at 25° is 0.05 smaller than the value read from Fig. 3 and may indicate a small amount of acetic acid in their material, since there is no statement regarding any special purification. The triangles in Fig. 3 represent a portion of their data and show an increasing discrepancy at the higher temperatures.

In order to determine the effect of hydrolytic splitting of pentanedione into acetone and sodium acetate under the conditions of these experiments, a 0.100 *F* solution was prepared from some pentanedione that had been kept at laboratory temperature for eleven weeks since purification. A portion was

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[3] D. A. MacInnes, D. Belcher and T. Shedlovsky, THIS JOURNAL, **60**, 1094 (1938).

[4] G. Schwarzenbach, H. Suter and K. Lutz, *Helv. Chim. Acta*, **23**, 1191 (1940).

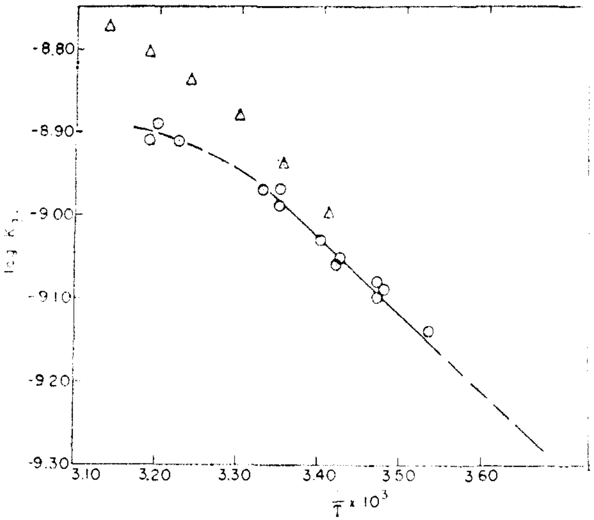

Fig. 3.—Temperature dependence of the ionization constant of 2,4-pentanedione. Circles are author's results, triangles from Schwarzenbach, Suter and Lutz.

half neutralized and the *p*H of the mixture measured 8.79 at 32°. The measurement was repeated after the sample had been warmed to 45° for 50 minutes. The *p*H value decreased 0.08 unit during this time. It is evident that such splitting will be significant after a very few minutes at the higher temperatures. The Schwarzenbach results are therefore probably low in numerical value by a few hundredths of a *pK* unit at temperatures above 35°.

Below 30° both sets of data agree closely in the free-energy change for the ionization of pentanedione. In this temperature range the log K_a *vs.* $1/T$ graph is essentially linear and the ΔH value calculated from the data of the present paper is 4200 cal.[5]

The thermodynamic results calculated for the reactions A, B and C may be summarized as follows for 25°:

	Reaction	ΔH^0	ΔF^0	ΔS^0
A	$MnPn_3 + 2H_2O + H^+ \rightleftarrows$ $MnPn_2(H_2O)_2^+ + HPn$	−1170	−6950	19.4
B	$HPn \rightleftarrows H^+ + Pn^-$	4200	12300	−27.2
C	$MnPn_3 + 2H_2O \rightleftarrows$ $MnPn_2(H_2O)_2^+ + Pn^-$	3030	5350	− 7.8

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(5) The Schwarzenbach results between 20 and 35° can also be considered linear within their 0.5 millivolt error; such a linear graph leads to a ΔH value of about 4800 cal. This is also the value these authors derive for 25° from the differentiation of their parabola expressing the temperature-dependence of pK_a. The parabola ΔH's vary from 5610 cal. at 20° to 3825 cal. at 35°. It is to be noted, however, that extrapolation of their parabola to 0° leads to a ΔH value which, when combined with an extrapolated K value for reaction C, makes the ΔS for this reaction positive, which appears unreasonable.

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Structures and Properties of Some Metal Derivatives of Azo and Azomethine Dyes[1]

BY JOHN C. BAILAR, JR., AND CLAYTON F. CALLIS

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Cobalt lakes of the mono-*o*-hydroxyazo dye, benzeneazo-β-naphthol and cobalt, chromium and zinc lakes of the di-*o*-hydroxyazomethine dye, 2′-hydroxybenzal-2-hydroxy-5-chloroaniline have been studied. The results indicate that these can be fitted into a general pattern that will permit predictions as to the types of azo dye complexes that certain metals may be expected to form. The oxidation state of the cobalt was found to be +3 in the monoortho dye lakes, and either +2 or +3 in the diortho dye lakes. The lakes of trivalent cobalt can be prepared by replacement reactions using cobalt(III) ammine complexes as the source of the trivalent cobalt. The lakes of divalent cobalt and of zinc are analogous in composition, as are those of trivalent cobalt and of chromium. The experimental evidence indicates that a monoortho substituted azo dye can satisfy one primary valence and two secondary valences of the metal atom. Diortho substituted dyes are capable of satisfying three secondary valences and two primary valences of the metal atom.

The fact that the metallic lakes of the azo dyes are true coördination compounds is becoming more generally realized, and the nature of the bonds between the metallic ion, the azo-nitrogen atoms, and the substituents in the aromatic nuclei have elicited much interest. Several authors[2] have postulated the formation of a ring structure involving these groups. In an earlier paper[3] it was pointed out that Drew and his co-workers,[4] in studying the reactions of azo compounds with several metals (Cu, Ni, Zn, Fe, Cr, Al, V), concluded that these lakes are typical Werner type coördination compounds, that both the coördination number of the metal ion and its valence must be satisfied, and that the azo group occupies one coördination position.

Morgan and Main Smith[5] and Drew and Landquist[6] recognized that lakes prepared from azo compounds containing two substituents such as hydroxy, carboxy, amino or other donor groups ortho to the azo-nitrogen atoms are more stable than lakes prepared from monoortho azo compounds. If a mono-*o*-hydroxy- or carboxyazo dye forms a chelate ring with a metal ion, it will satisfy one primary valence and two secondary valences of the metal. With a diortho substituted molecule three secondary valences and two primary valences

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(1) Abstracted from a portion of the doctorate thesis of Clayton F. Callis, University of Illinois, 1948.

(2) A. Werner, *Ber.*, **41**, 1062 (1908). O. Baudisch, *Z. angew. chem.*, **30**, 133 (1917). G. T. Morgan and J. D. Main Smith, *J. Chem. Soc.*, **125**, 1731 (1924). O. Charrier and A. Beretta, *Gazz. chim. ital.*, **56**, 865 (1926). G. B. Crippa, *ibid.*, **57**, 20 (1927). A. Cremonini, *ibid.*, **58**, 372 (1928). Marjorie Elkins and Louis Hunter, *J. Chem. Soc.*, 1598 (1935).

(3) Clayton F. Callis, Niels C. Nielsen and John C. Bailar, Jr., THIS JOURNAL, **74**, 3461 (1952).

(4) H. D. K. Drew, *et al.*, *J. Chem. Soc.*, 292 (1938); 823 (1939); 603, 608, 1064 (1940).

(5) G. T. Morgan and J. D. Main Smith, *ibid.*, **125**, 1731 (1924).

(6) H. D. K. Drew and J. K. Landquist, *ibid.*, 292 (1938).