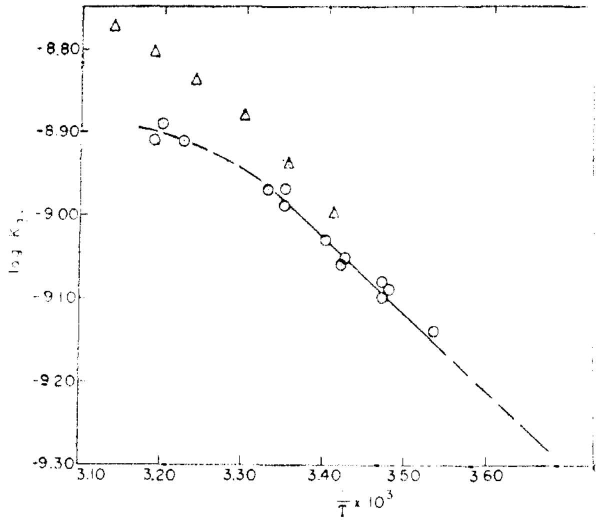

Fig. 3.—Temperature dependence of the ionization constant of 2,4-pentanedione. Circles are author's results, triangles from Schwarzenbach, Suter and Lutz.

half neutralized and the pH of the mixture measured 8.79 at 32°. The measurement was repeated after the sample had been warmed to 45° for 50 minutes. The pH 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

RECEIVED JULY 14, 1952

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).

of the metal are satisfied if the metal combines with both of the ortho-substituted groups.

The cobalt lakes present some interesting theoretical problems because the cobalt can be stabilized in either the +2 or the +3 state. The cobalt(III) lake of a bifunctional organic molecule will carry a +1 charge if the dye:metal ratio is 1:1, but a −1 charge if this ratio is 2:1.

The purpose of this investigation was to study the cobalt lakes of some very simple azo and azomethine dyes, to extend our knowledge of structures of these molecules with regard to the valence state of the metal, the ratios in which the constituents combine, and the importance of coördinating groups that may be points of attack in the decomposition of the lakes.

Cobalt lakes of the mono-*o*-hydroxyazo dye, benzeneazo-β-naphthol, and of the di-*o*-hydroxyazomethine dye, 2′-hydroxy-benzal:2-hydroxy-5-chloroaniline, have been studied. It has been shown previously[3] that the azomethine group forms the same sort of coördinate link with a metal atom as does the azo group. Magnetic susceptibility measurements combined with other analytical data have shown that the oxidation state of cobalt is +3 in the monoortho dye lakes and may be either +2 or +3 in the lakes of the di-*o*-hydroxy dyes. The lakes of trivalent cobalt can be prepared by replacement reactions in 2 *N* ammonium hydroxide using hexammine cobalt(III) chloride, bisdiethylenetriamine cobalt(III) chloride or sodium hexanitrocobaltate(III) as the source of the cobalt. Lakes of divalent zinc and trivalent chromium were also studied. The properties and compositions of these lakes are summarized in Table I.

Experimental

Analytical Methods. Cobalt.—Cobalt was determined with 8-hydroxyquinoline by a procedure adapted from directions given by Mellan.[7] The sample was digested with concentrated sulfuric acid containing 15% by volume of concentrated nitric acid until the hot solution turned a deep blue. The solution was heated an additional two hours to destroy all of the excess nitric acid. After cooling, the solution was made basic with sodium hydroxide, and the resultant precipitate was dissolved in glacial acetic acid. Small amounts of sodium bisulfite and sodium acetate were added, the solution was filtered and then heated. 8-Hydroxyquinoline was added and the precipitate was collected, dried and weighed.

Chromium was determined by oxidation with perchloric acid and titration of the resulting dichromate solution with standard ferrous iron.[8]

Magnetic Susceptibility Measurements.—The magnetic measurements were made on the modified Curie and Cheveneau magnetic balance used by Driggs and Hopkins[9] in the determination of the composition of rare earth fractions. This method is a comparative one, in which the attraction or repulsion of a permanent magnetic field on a weighed specimen is compared with the attraction or repulsion on a standard substance whose susceptibility is known. The instrument was calibrated with pure Mohr salt. The susceptibility values, in units per gram, were converted into Bohr magnetons by the relation[10]

$$\mu_{\mathrm{EFF}} = 2.84\sqrt{X_{\mathrm{m}}T}$$

where μ_{EFF} = the effective moment in Bohr magnetons, X_{m} = the susceptibility per mole, T = the absolute temperature.

Equivalent Conductance.—The resistance of the solution of known concentration was measured in a calibrated cell on a Shedlovsky-type Wheatstone bridge.

Preparation of the Lakes.—The lakes were prepared by modifications of several different methods.

(**A**).—An excess of the metal salt was dissolved in 95% alcohol, heated on the steam-cone and mixed with a solution of the dye in the same solvent. After the mixture cooled, the lake which had precipitated was filtered, washed with 95% alcohol and water and dried in an Abderhalden drier with toluene reflux. When $Co(C_2H_3O_2)_2 \cdot 4H_2O$ was used as the metal salt, the reaction was carried out in an atmosphere of nitrogen as well as in air.

(**B**).—The same method as A, with sodium acetate added to buffer the solution.

(**C**).—The same method as A, but the lake was isolated from the filtrate by evaporation to a small volume in a stream of air.

(**D**).—A slight excess of the metal salt dissolved in 50% alcohol was mixed with a solution of the dye in 50% alcohol and refluxed two hours on the steam-cone. The lake was filtered from the solution, washed with water and dried in the oven at 80°.

(**E**).—An excess of the metal ammine dissolved in 2 *N* ammonium hydroxide was heated on the steam-cone and mixed with a solution of the dye in 2 *N* ammonium hydroxide. Heating on the steam-cone was continued for 30 minutes with occasional stirring. After cooling, the lake which had formed was collected on sintered glass, washed with water and dried in the Abderhalden.

(**F**).—Same method as (E), but the filtrate was evaporated to dryness, and the residue was triturated with absolute alcohol. This step was repeated, and the residue was dissolved in absolute alcohol. The solution was filtered into a large volume of benzene. Final purification was achieved by recrystallizing from a 75% benzene–alcohol mixture.

(**G**).—Same method as (E), except the solutions were not heated, and after mixing were allowed to stand 20–24 hours without heating.

Discussion of Results

Lakes of Monoortho Substituted Dyes.—In all of the important cases of complex formation between metals and dye molecules, the structure of the organic molecule is such that the metal can combine with it by replacing a hydrogen from a functional group and accepting an electron pair donated by an oxygen or a nitrogen atom. With the azo compounds, such a chelate ring is formed only when the functional group is in the ortho position to the azo group. Hydroxyl groups in the meta or para positions have been found to have little or no effect.[6]

In a previous communication[3] it is reported that the main product obtained with cobaltous acetate and benzene-azo-β-naphthol is a 3:1 dye:metal complex containing trivalent cobalt even when prepared in the absence of an oxidizing agent. The coördination number of six of the metal and its ionic charge of three are balanced by three molecules of dye. In the present investigation, the same 3:1 dye:metal complex was prepared from hexammine cobaltic chloride. Apparently all of the ammonia was liberated and the six coördination positions filled by the dye molecules.

The product obtained in the reaction with sodium cobaltinitrite and benzene-azo-β-naphthol could not be identified. If all the nitro groups are replaced from the coördination sphere, the same 3:1 dye:metal complex should be formed. However, if only two dye molecules are held by the cobalt atom, the third primary valence could be satisfied

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[7] I. M. Mellan, "Organic Reagents in Inorganic Analysis," The Blakiston Company, Philadelphia, Pa., 1941, p. 326.

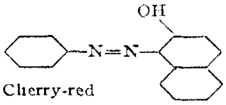
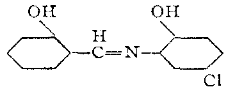
[8] J. J. Lichtin, *Ind. Eng. Chem., Anal. Ed.*, **2**, 129 (1930).

[9] F. H. Driggs and B S. Hopkins, THIS JOURNAL, **47**, 363 (1925).

[10] Selwood, "Magneto-Chemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 29.

TABLE I

COMPOSITION AND PROPERTIES OF THE LAKES

Ident. no.	Dye	Metal salt	Method of preparing lake	Color of lake	Ratio of dye:metal (based on C)	Composition of lake	Analyses, % Metal Found	Analyses, % Metal Calcd.
I		$[Co(NH_3)_6]Cl_3$	D	Purple-red	2.91 (based on N)	Co·Dye_3	7.6	7.4
II	Cherry-red	$Na_3Co(NO_2)_6$	D	Dark purple-red	....	Not identified[a]	8.8	
III		$Co(OAc)_2·4H_2O$	A	Yellow-brown	1.01	Co·Dye	19.3	19.4
IV		$Co(OAc)_2·4H_2O$	C	Red-brown	3.05	$Co(Dye)_3$	7.3	7.4
V	Yellow-brown recrys. from 50% alcohol	$[Co(NH_3)_6]Cl_3$	E	Brown	3.03:2	$Co_2Dye_3(NH_3)_3$	13.1	13.0
VI		$[Co\ dien_2]Cl_3$	F	Reddish-brown	0.97	[Co dien dye]Cl	13.6	13.3
VII		$[Co(NH_3)_5SCN]Cl_2$	E	Brown	3.03:2	$Co_2Dye_3(NH_3)_3$	12.8	13.0
VIII		$Na_3Co(NO_2)_6$	G	Brown	2.97:2	$Co_2Dye_3(NH_3)_3$	13.25	13.0
IX		$[Cr(NH_3)_6](NO_3)_3$	E	Brown	3.09:2	$Cr_2Dye_3(NH_3)_2H_2O$	11.3	11.7
X		$Zn(OAc)_2·2H_2O$	A	Yellow	1.03	Zn·Dye	20.6	21.0
XI		$ZnCl_2$	B	Yellow	1.03	Zn·Dye	20.9	21.0

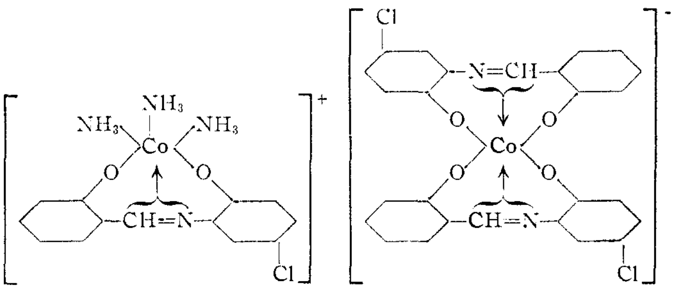
[a] Results are intermediate between those for $[Co(Dye)_3]$ and $[Co(Dye)_2NO_2H_2O]$.

by a nitro group and the coördination sphere completed with a molecule of water. Actually, analysis of the material obtained indicated that it had a composition intermediate between those demanded by the two compounds indicated.

Lakes of Diortho Substituted Dyes.—Dyes of the diortho substituted type form coördination compounds with metals more readily than do the monoortho substituted dyes, and the resultant complexes are considerably more stable. Drew and Landquist[6] are of the opinion that this phenomenon can best be explained by assuming that the metal combines with both of the ortho-substituted groups and with the azo or azomethine group to form a fused-ring system.

Magnetic measurements on the product isolated indicated that the reaction of cobaltous chloride in ammoniacal alcoholic solution with 2′-hydroxybenzal:2-hydroxy-5-chloroaniline, in air, gave a mixture of lakes of both di- and trivalent cobalt. Trituration of the brown material with 95% alcohol gave a paramagnetic yellow-brown residue with a 1:1 metal:dye ratio (divalent cobalt complex). A red-brown 3:1 dye:metal complex was isolated from the dark-colored filtrate (trivalent cobalt complex). In order to formulate a structure for this lake, it must be assumed that one of the hydroxyl groups is not attached to the cobalt. This preparation was repeated by mixing the constituents in an atmosphere of nitrogen; the same products were isolated, but when the nitrogen atmosphere was used, a much higher yield of the cobaltous 1:1 dye:cobalt complex was obtained, and a lower yield of the red-brown cobaltic complex. The filtrate from the reaction carried out in the nitrogen atmosphere was evaporated in a stream of air to obtain the cobaltic complex.

A 2:3 cobalt(III):dye complex with the structure given below was obtained in a series of replacement reactions with 2′-hydroxy-benzal-2-hydroxy-5-chloroaniline, using hexammine cobalt(III) chloride, and thiocyanatopentammine cobalt(III) chloride as sources of cobalt. The coördination sphere of the cobalt atom in the positively charged group is completed with three molecules of ammonia. A similar 2:3 metal:dye complex was prepared from hexammine chromic ion and the same dye. In this case, two molecules of ammonia and a molecule of water are present in the coördination sphere of the positively charged group.



The mode of formation of these lakes can be illustrated by the reaction involving hexammine cobalt(III) ion. The reaction takes place stepwise, each molecule of dye replacing three molecules of ammonia. The product of the first step is the cation $[Co\ dye\ (NH_3)_3]^+$, while the product of the second step is the anion $[Co\ dye_2]^-$. As fast as any of this anion is formed, it combines with the complex cation to form an insoluble salt. It was obtained in soluble form, however, by allowing the dye to displace the nitro groups from the hexanitrocobaltate(III) ion, $[Co(NO_2)_6]^{---}$. In order to keep the dye in solution, the reaction was carried out in ammonia, and the main product was the 3:2 dye:metal lake. The very dark colored filtrate, upon treatment with a solution of *trans* $[Coen_2Cl_2]$Cl, gave a poor yield of a compound which is formu-

TABLE I (*Continued*)

Analyses, %									
Chlorine		Carbon		Nitrogen					
Found	Calcd.	Found	Calcd.	Found	Calcd.	Solubility of lake	Yield, %	Magnetic susc. (Bohr magnetons)	Oxidation state of cobalt
				10.5	10.5	Sol. in alcohol Insol. in water	30	Diamagnetic	+3
		69.2				Sol. in alcohol Insol. in water	2.1 g. from 3 g. dye	Diamagnetic	+3
		51.6	51.2	4.9	4.6	Insol. in H_2O Insol. in 95% alc.	Air-17 N_2-48	5.1(35.2 $\times 10^{-6}$ units/gm.) 4.9(33.1 $\times 10^{-6}$ units/gm.)	+2
13.1	13.3	59.6	58.6	6.1	5.3	Sol. in 95% alc. Insol. in water	Air-33 N_2-21	(1.05 $\times 10^{6}$ units/gm.) (1.29 $\times 10^{-6}$ units/gm.)	+3
		52.6	51.7	8.9	9.3	Mod. sol. in acetone and abs. alc. Gives yellow-brown coloration to H_2O	66	Diamagnetic	+3
8.2 (ionic)	8.0 (ionic)	45.7	46.1	4.8	4.7	Easily sol. in water and alcohol. Insol. in benzene and ether	31	Diamagnetic	+3
						Same as V	62	Diamagnetic	+3
		52.1	51.7	9.2	9.3	Same as V and VII	43	Diamagnetic	+3
11.4	11.9	52.4	52.4	7.8	7.8	Mod. sol. in acetone and abs. alc. Gives yellow-brown color to H_2O	67		
11.3	11.4	50.6	50.3	2.9	2.6	Sl. sol. in abs. alc. Insol. in water	86		
						Same as X	65		

lated as $[Coen_2Cl_2]$ $[Codye_2]$. (Found: Co, 14.2; C, 44.8. The proposed structure requires Co, 14.75; C, 45.1.)

It was not possible to obtain the cation $[Co(NH_3)_3$ dye$]^+$ in soluble form because of the ease with which the ammonia molecules are displaced to form the anion $[Co\ dye_2]^-$. However, a water soluble compound [Co(diethylenetriamine) (dye)]Cl was prepared from the same dye and bisdiethylenetriamine cobaltic chloride. Each molecule satisfies three coördination positions, and the three primary valences of the metal are taken up by the bifunctional dye molecule and the ionic chlorine. The equivalent conductance, measured at a dilution of 1 mole in 1024 liters, indicates that this water-soluble material gives two ions in solution.

With divalent zinc and diortho substituted azomethine dye, 2′-hydroxy-benzal-2-hydroxy-5-chloroaniline, a 1:1 dye:metal lake was obtained. Both primary valences of the metal atom are satisfied by one dye molecule. Higher yields were obtained when the solution was buffered with acetate ion.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

Stability of Metal Chelates. III. Iminopropionic-acetic and Aspartic Acids

BY S. CHABEREK, JR.,[1] AND A. E. MARTELL

RECEIVED MAY 12, 1952

The acid dissociation constants of iminopropionic-acetic and aspartic acids, and the first and second chelate stability constants of the corresponding anions with Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2} and Cd^{+2} ions are reported. Comparisons are made with the stabilities of analogous compounds, iminodiacetic and iminodipropionic acids, and the trends observed are interpreted in the light of the probable structures of these chelate compounds.

The stability constants of some transition metal chelates of iminodiacetic (IMDA) and iminodipropionic (IMDP) acids have been reported in a recent paper.[1a] It was shown that an increase in the size of the chelate rings from five members to six members results in a substantial decrease in the magnitude of the stability constants of the metal chelates. Iminopropionic-acetic acid and aspartic acid, an isomer of iminodiacetic acid, are of interest because they represent structural forms intermediate to those of iminodiacetic and iminodipropionic acids. The production of a 1:1 complex would require the formation of five- and six-membered chelate rings within the same structure as opposed to two five-membered rings with iminodiacetic acid and two six-membered rings with iminodipropionic acid.

Although the behavior of aspartic acid with the alkaline earth metals has been investigated,[2-4]

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(1) F. C. Bersworth Postdoctoral Fellow, Clark University.

(1a) S. Chaberek, Jr., and A. E. Martell, THIS JOURNAL, **74**, 5052 (1952).

(2) S. Miyamoto and C. L. A. Schmidt, *J. Biol. Chem.*, **99**, 335 (1933).

(3) A. C. Batchelder and C. L. A. Schmidt, *J. Phys. Chem.*, **44**, 893 (1940).

(4) R. Lumb, Ph.D. Dissertation, Clark University, 1951.