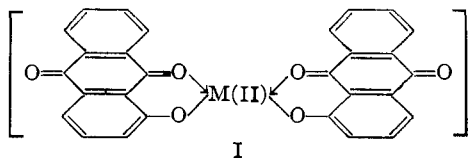


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Preparation and Properties of Some Peri-Hydroxyquinone Inner Complexes¹BY BRADFORD P. GEYER² WITH GEORGE MCP. SMITH

Little work has been done on the preparation and characterization of simple inner complexes of compounds containing the C,C,C-O,OH chelating group.³ Such inner complexes are of interest because of their structural relationship to the color lakes derived from alizarin and related substances. Because of the remarkable difference in color of these inner complexes compared to the color of the quinone and the metal ion involved, the preparation of several inner complexes of some peri-hydroxyquinones was undertaken with a view to determining, by absorption spectra, the relationship between color and structure.

1. 1-Hydroxyanthraquinone Inner Complexes.—Only three inner complexes of 1-hydroxyanthraquinone (9,10-anthracenedion-1-ol) have been described. Machemer⁴ has prepared the cobalt(II) and copper(II) complexes of this quinone. Pfeiffer and co-workers⁵ have made the dipyridinonickel(II) compound. We have prepared the four-coördinate cobalt(II), copper(II), magnesium, manganese(II), nickel(II), diaquo-nickel(II), and uranyl inner complexes of 1-hydroxyanthraquinone, with the general structure I.



Starting Material.—1-Hydroxyanthraquinone was prepared by a method similar to that of Roemer.⁶ To 10 g. of 1-aminoanthraquinone in 500 ml. of glacial acetic acid, a cold solution of 3.5 g. of sodium nitrite in 25 ml. of 36 *N* sulfuric acid was added gradually. After forty-two hours the solution was concentrated, a large volume of cold water added, and the solid filtered off after nine hours. By treating the crude acetoxy compound with 100 ml. of 3 *N* sodium hydroxide under reflux for three hours and then acidifying with 6 *N* hydrochloric acid, 1-hydroxyanthraquinone was obtained. Sublimation of the product yielded 4.6 g. (46%) of pure yellow-orange hydroxyquinone; m. p. 193-

194°. A sample of the crude 1-acetoxyanthraquinone, recrystallized from chloroform, formed pale-yellow crystals; m. p. 175-176°.

Inner Complexes: 9,10-Anthracenedion-1-olato-cobalt(II).—A cold, filtered solution of 0.25 g. of Co(OAc)₂·4H₂O in 50 ml. of methanol was added to a hot, filtered solution of 0.45 g. of 1-hydroxyanthraquinone in 200 ml. of methanol. The dark red mixture was heated under reflux for one-half hour, the solid filtered off when cool, washed with hot methanol, and dried at 100° to a brown powder.

9,10-Anthracenedion-1-olato-copper(II).—A cold solution of 0.40 g. of Cu(OAc)₂·H₂O in 100 ml. of water was added to 400 ml. of a warm 95% ethanol solution of 0.90 g. of 1-hydroxyanthraquinone. The solid was filtered off after twelve hours, washed with ethanol and water, and dried at 105°. It was purified by extraction with 95% ethanol for seven hours, followed by extraction with water, and dried at 105° to a bright brownish-red powder.

9,10-Anthracenedion-1-olato-magnesium.—To a warm solution of 0.90 g. of 1-hydroxyanthraquinone in 400 ml. of ethanol was added 100 ml. of a cold, water solution of 0.43 g. of Mg(OAc)₂·4H₂O. Six *N* ammonium hydroxide was added dropwise until a definite precipitate persisted. After standing overnight, the excess 1-hydroxyanthraquinone was removed by decanting the reheated solution from the solid. This solid was washed with hot ethanol, followed by hot water, dried at 100°, and extracted with 95% ethanol. This inner complex is a deep red powder.

9,10-Anthracenedion-1-olato-manganese(II).—A cold solution of 0.98 g. of Mn(OAc)₂·4H₂O in 50 ml. of methanol was mixed with a warm solution of 0.90 g. of 1-hydroxyanthraquinone in 300 ml. of ethanol. The solution was concentrated under reduced pressure. After cooling, the solid formed was collected by filtration, washed with cold water and ethanol, and dried at 105°. To remove excess quinone, the solid was heated for one hour under vacuum in a drying pistol at 205°. The compound was obtained as a dark olive-brown powder.

9,10-Anthracenedion-1-olato-nickel(II).—The four-coördinate nickel complex was prepared exactly as was the cobalt compound, using identical quantities. The unsolvated complex is an orange-brown powder.

Diaquo-9,10-anthracenedion-1-olato-nickel(II).—The six-coördinate diaquo nickel complex was prepared by the method used for the copper(II) complex, using 0.50 g. of Ni(OAc)₂·4H₂O, the other quantities being the same; red-violet powder.

9,10-Anthracenedion-1-olato-uranyl.—One hundred ml. of a warm methanol solution of 1.70 g. of UO₂(OAc)₂·2H₂O was added slowly to 300 ml. of a warm methanol solution of 0.90 g. of 1-hydroxyanthraquinone. After several days, the crystals were removed, washed with cold methanol, and dried at 105°. The complex was heated in the drying pistol at 204° for one hour; purple-brown crystals.

These compounds are stable at high temperatures, highly colored, insoluble in water, and in the common organic solvents at room temperature. Strong acids de-

(1) This paper represents an abstract of a portion of a thesis presented by Bradford P. Geyer to the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Present address: Shell Development Company, Emeryville, Calif.

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(4) Machemer, *J. prakt. Chem.*, **127**, 109 (1930).

(5) Pfeiffer, Breith, Lübke and Tsumaki, *Ann.*, **503**, 84 (1933).

(6) Roemer, *Ber.*, **15**, 1793 (1882).

TABLE I
ANALYTICAL AND SPECTRAL DATA FOR THE INNER COMPLEXES

Inner complex	Formula	Percentage of Metal		Yield, %	Maximum $m\mu$	
		Calcd.	Found			
9,10-Anthracenedione-1-olato-Cu(II)	$C_{28}H_{14}O_6Cu$	11.7	11.5	86	410, 480	6080, 3190
9,10-Anthracenedione-1-olato-Cu(II)	$C_{28}H_{14}O_6Cu$	12.5	12.3	91	400, 500	4830, 940
9,10-Anthracenedione-1-olato-Mg	$C_{28}H_{14}O_6Mg$	5.2	5.0	57	400, 500	3160, 1440
9,10-Anthracenedione-1-olato-Mn(II)	$C_{28}H_{14}O_6Mn$	11.0	10.9	14		
9,10-Anthracenedione-1-olato-UO ₂	$C_{28}H_{14}O_6UO_2$	33.2	33.8	80	410, 510	13900, 2020
9,10-Anthracenedione-1-olato-Ni(II)	$C_{28}H_{14}O_6Ni$	11.6	11.7	51	400, 500	8100, 6990
Diaquo-9,10-anthracenedione-1-olato-Ni(II)	$C_{28}H_{14}O_6Ni \cdot 2H_2O^a$	10.8	10.9	86		
2-Acetoxy-9,10-anthracenedione-1-olato-Cu(II)	$C_{32}H_{18}O_{10}Cu$	10.2	9.7	89	400, 530	2380, 2810
3-Nitro-9,10-anthracenedion-2(1)-ol-1(2)-olato-Cu(II)	$C_{28}H_{12}O_{12}N_2Cu$	10.1	10.8	57	500	3720

^a H₂O calcd.: 1:2. Found: 1:2.1; 1:1.9.

compose the complex with liberation of the quinone. The analytical data for the complexes are in Table I.

2. **1-Acetylalizarin Inner Complexes.**—It has been reported⁷ that alizarin, 1,2-dihydroxyanthraquinone, upon direct interaction with metal acetates, forms normal salts. Acetylation of the more active 2-hydroxy group should permit chelation through the other, or 1-hydroxy, group. As was expected, 2-acetylalizarin (2-acetoxy-9,10-anthracenedion-1-ol) did form an inner complex with copper(II) ion. The complex was similar in color and behavior to the corresponding complex of 1-hydroxyanthraquinone.

Starting Material.—2-Acetylalizarin was prepared according to Perkin⁸; m. p. 197–198°.

Inner Complex: 2-Acetoxy-9,10-anthracenedion-1-olato-copper(II).—A warm solution of 0.20 g. of $Cu(OAc)_2 \cdot H_2O$ in 30 ml. of absolute alcohol was added dropwise to a warm solution of 0.56 g. of 2-acetylalizarin in 20 ml. of nitrobenzene, with stirring. After five hours, the solid was filtered off, washed with hot ethanol, then with ether, and dried. The dry powder was heated for six hours in the drying pistol at 210°, followed by extraction with chlorobenzene and reheating at 210°; red-brown powder.

3. **3-Nitroalizarin Inner Complexes.**—The hydrogen bonding of peri-hydroxyquinones⁹ and of *o*-nitrophenols would suggest the possibility of inner complex formation through either of the two chelating groups in 3-nitroalizarin (3-nitro-9,10-anthracenedion-1,2-diol). This proved to be the case, for a copper(II) compound, which exhibited typical inner complex behavior, was prepared from the nitro compound.

Starting Material.—Crude 3-nitroalizarin was recrystallized from glacial acetic acid; m. p. 244–245°, with decomposition.

Inner Complex: 3-Nitro-9,10-anthracenedion-2(1)-ol-1(2)-olato-copper(II).—A cold solution of 0.20 g. of $Cu(OAc)_2 \cdot H_2O$ in 100 ml. of absolute alcohol was added slowly to a suspension of 0.57 g. of 3-nitroalizarin in 100 ml. of cold, absolute alcohol contained in a 3-neck flask fitted with mercury-seal stirrer, condenser with anhydrous-filled drying tube, and dropping funnel. The mixture was stirred and heated under reflux for seven hours, and while

still hot was filtered. The solid was washed with cold ether, air-dried, and then heated for ninety minutes in the drying pistol at 255° to give purplish-brown microcrystals.

Absorption Spectra

The absorption of these inner complexes was measured in the visual range following the same procedure as in our earlier publication.¹⁰ In the case of the inner complexes of 1-hydroxyanthraquinone, absorption occurs over one narrow band in the violet and another narrow, but less intense, band in the blue-green. As in the phthiocol series of inner complexes previously described¹⁰ the intensity of absorption is dependent upon the metal present. The absorption curves for the four-coordinate 1-hydroxyanthraquinone complexes are all similar in shape. Table I shows the wave lengths at which maximum absorption occurs and the corresponding molecular extinction coefficients.

From 370–410 $m\mu$, the absorption of the cobalt(II), copper(II), magnesium, and nickel(II) inner complexes show the same relationships observed among the corresponding phthiocol complexes. From 470–580 $m\mu$ the absorption characteristics of the cobalt(II), copper(II), and nickel(II) complexes are again similar to the phthiocol compounds. The color of the inner complexes is caused more by the formation of the chelate ring than by the presence of a particular metal. This latter fact has been observed in all of the studies on the absorption spectra of *o*-quinone monoxime, *o*-hydroxyazo dye, and *o*-hydroxyquinone inner complexes prepared in this Laboratory.^{10,11}

The absorption spectra curves for 2-acetylalizarin and 3-nitroalizarin, with those for their

(7) Crossley, *THIS JOURNAL*, **41**, 2081 (1919).

(8) Perkin, *J. Chem. Soc.*, **75**, 447 (1899).

(9) Hilbert, Wulf, Hendricks and Liddel, *THIS JOURNAL*, **58**, 548 (1936).

(10) Geyer with Smith, *ibid.*, **63**, 3071 (1941).

(11) Haendler with Smith, *ibid.*, **62**, 1669 (1940).

copper(II) complexes, are similar in gross detail to the corresponding hydroxyanthraquinone curves.

Experimental

The experimental procedure for absorption spectra measurements¹² was the same as that described in our earlier publication.¹⁰ The concentrations of the *n*-butanol solutions ranged from 0.00003 to 0.0002 *M*. Values of the extinction coefficients were calculated by Beer's law.

Catalytic Behavior of the Inner Complex¹⁰

It was found that certain of the inner complexes prepared could catalyze the chemiluminescent oxidation of luminol (3-amino-phthalhydrazide) by hydrogen peroxide. The cobalt(II) and copper(II) complexes of 1-hydroxyanthraquinone and the copper(II) complexes of 2-acetylalazarin and 3-nitroalazarin all exhibit decreasing degrees of catalytic activity, in that order. The free quinones are inactive.

The 1-hydroxyanthraquinone-cobalt(II) complex produces a bluish violet-white luminescence, lasting over three hours, but not as intense as the light produced with the cobalt(II) complex of

(12) With H. M. Haendler.

phthiocol. The copper(II) complex produces a blue-white light of three-hour duration, but of lower intensity than either the 1-hydroxyanthraquinone cobalt(II) complex or the phthiocol copper(II) complex. Solubility and stability of the complex appear to be the governing factors in the catalysis of chemiluminescent oxidation.

Summary

1. The preparation and properties of the cobalt(II), copper(II), magnesium, manganese(II), nickel(II), diaquonickel(II), and uranyl inner complexes of 1-hydroxyanthraquinone, as well as the copper(II) inner complexes of 2-acetylalazarin and 3-nitroalazarin have been described.

2. The absorption spectra of these inner complexes in *n*-butanol solution have been determined in the visual region.

3. The color of the complex is due to the chelation of the quinone with the metal.

4. The cobalt(II) and copper(II) inner complexes of 1-hydroxyanthraquinone and the copper(II) inner complexes of 2-acetylalazarin and 3-nitroalazarin catalyze the chemiluminescent oxidation of luminol by hydrogen peroxide.

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The Molecular Weights of the Schardinger Alpha and Beta Dextrins¹

BY DEXTER FRENCH AND R. E. RUNDLE

The work of Freudenberg² and others³ indicates that the Schardinger dextrans are composed solely of glucose residues bonded by α -1,4-glucosidic linkages as in starch. Though these dextrans are of much lower molecular weight than starch, they are completely non-reducing. The only structure which appears to be consistent with these chemical properties is a cyclic structure.⁴

Several molecular species with the chemical properties given above are known to occur in the dextrin mixture obtained by the *B. macerans* enzymolysis of starch. The main components of the mixture have been separated and characterized

by Freudenberg and Jacobi.⁵ The molecular weights which these authors suggest for these species were determined by cryoscopic methods, but since these dextrans are of comparatively high molecular weight and are very difficult to free from low molecular weight impurities (solvent of crystallization and inorganic ash), the cryoscopic molecular weights can be expected to be but rough approximations.

A method better adapted to the determination of the molecular weights of high molecular weight crystalline compounds is X-ray diffraction combined with crystal density measurement. In this method low molecular weight impurities are of minor importance, and their contribution to the crystal density can be determined and corrected for with satisfactory accuracy.

By this method we have found Schardinger's

(5) K. Freudenberg and R. Jacobi, *Ann.*, **518**, 102 (1935).

(1) Journal Paper No. J-979 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project No. 639. Supported in part by a grant from the Corn Industries Research Foundation.

(2) K. Freudenberg, G. Blomquist, L. Ewald and K. Soff, *Ber.*, **69**, 1258 (1936).

(3) J. C. Irvine, H. Pringsheim and J. MacDonald, *J. Chem. Soc.*, **125**, 942 (1924).

(4) K. Freudenberg, *Ann. Rev. Biochem.*, **8**, 81 (1939).