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

Some Metal Derivatives of Azo and Azomethine Dyes[1]

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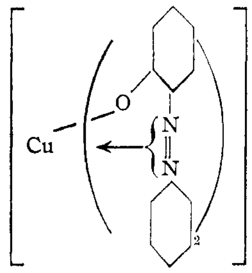
Cobalt and nickel lakes of one azomethine and three azo dyes have been prepared and studied, and are formulated as Werner complexes. The tendency for the metal to completely utilize both the primary and secondary valences is very strong, and determines the composition of the complex, even to the extent of determining the oxidation state of the metal. Magnetic measurements indicate that the nickel lakes may be either planar or tetrahedral, depending upon the nature of the dye. The azo and azomethine groups each occupy one coördination position.

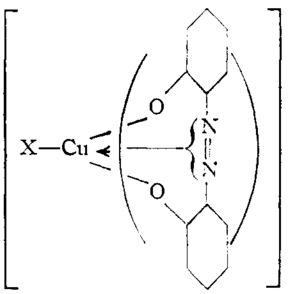
It has long been known that the azo group has some ability to form a coördinate link with metal ions, and addition compounds of azobenzene with platinic chloride and similar compounds have been described.[2]

While the exact nature of this link is unknown, its formation is of great practical importance. If the azobenzene contains hydroxy, carboxy, amino or other donor groups ortho to the azo group, a chelate ring can be formed; this greatly enhances the stability of the metal–dye bonds, as well as the stability of the organic molecule itself. Dye lakes, containing functional groups ortho to the azo linkage, show a greater fastness toward light and washing than do the unmetallized dyes. The stability is further increased by the presence of substituents in ortho positions of both rings, the lakes assuming fused ring forms. Substituents in the meta and para positions have little or no effect.

Drew and his co-workers[3] clearly demonstrated that these lakes fit into the Werner scheme, that both the coördination number of the metal ion and its valence must be satisfied, and that the azo group occupies one coördination position. It cannot be stated with certainty which of the nitrogen atoms of the azo group is implicated in the formation of the chelate ring. The linkages may be stabilized by resonance involving the entire group; indeed, there is some possibility that the double bond is involved. This uncertainty is indicated by a bracket enclosing the entire azo group. Drew, *et al.*, found that *o*-hydroxyazobenzene reacts with cupric ion to give the inner complex lake



The dihydroxy dye, on the other hand, gives lakes which may be formulated as



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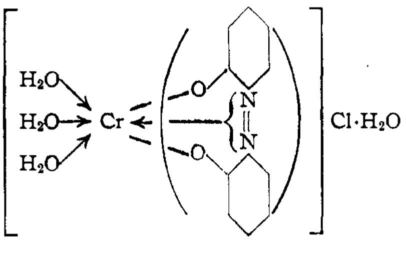

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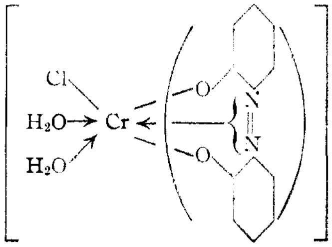
[1] Correspondence concerning this article should be addressed to John C. Bailar, Jr., at the University of Illinois.

[2] M. S. Kharasch and T. A. Ashford, THIS JOURNAL, **58**, 1736 (1936).

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

where X represents a molecule of water, pyridine or quinoline. The chromium lake is soluble in warm water, and was shown to contain ionic chlorine. On drying in the oven, two molecules of water escape, and the chlorine loses its ionic character



Lakes of other metals were shown to fit into this pattern, also.

The work described in the present paper was undertaken to test these suggestions, and to extend them in several directions. Lakes of nickel and cobalt with three azo dyes and one azomethine dye have been studied. Each of the dyes contains a hydroxy group ortho to the chromophore group; three of the four also contain a functional group in the ortho position in the other ring. In one case this group is hydroxyl, in one it is carboxyl, and in one it is amino.

The results show that the number and nature of functional groups in the dye determine the composition and stereochemistry of the lake, as well as the oxidation state of the metal in it. Magnetic measurements indicate that some of the nickel lakes are planar, while others are tetrahedral. They also show that cobalt in some lakes assumes the +2 oxidation state, while in others it becomes +3, depending upon the structure of the dye. This is apparently the first report of stabilization of an oxidation state of a metallic ion brought about by the stereochemical demands of the coördinating group.

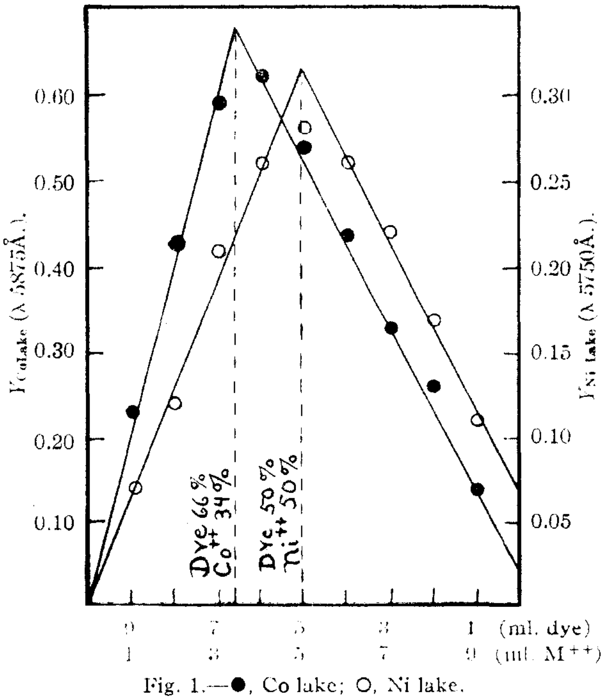


Fig. 1.—●, Co lake; O, Ni lake.

The lakes were prepared by modifications of three different methods: (1) An excess of a suitable metal salt was dissolved in 80% alcohol in the flask of a soxhlet extractor, and the dye was placed in the extraction shell. Upon refluxing, the materials were mixed, the inorganic salt remaining in excess at all times. The lake which formed was filtered and washed, and dried at 110°. When possible, the lakes were recrystallized from alcohol. (2) Solutions of the salt and dye in alcohol or mixtures of alcohol and water were mixed. (3) The same as method (2), but hydrogen peroxide was added to ensure oxidation of the cobalt to the +3 state.[4]

The lakes were recrystallized from alcohol, or other suitable solvent, before analysis. Those of 5-chloro-2-hydroxybenzeneazo-3-naphthylamine tend to decompose in boiling solvents, and it proved to be impossible to obtain them in highly pure form. The method of continuous variations was therefore used to establish their compositions.[5] Spectrophotometric measurements were made on a Cary automatic recording spectrophotometer using 2×10^{-4} *M* solutions of the dye, $Ni(NO_2)_2 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$. Examination of the spectra in the range from 3000–8000 Å. indicated that the complexes had characteristic peaks at 5750 Å. for the nickel lake and 5875 Å. for the cobalt lake. Table I indicates the variation in Y, the difference in the measured optical density for mixtures of metal salt and dye solutions and the theoretical optical density calculated for the concentration of dye in each solution. At the wave lengths used, the measured optical density of the pure dye solution did not exceed 0.07.

TABLE I

Solution no.	Ml. dye/ml. M^{++}	Y(Ni lake) 5750 Å.	Y(Co lake) 5875 Å.
1	10/0	0	0
2	9/1	0.07	0.23
3	8/2	.12	.43
4	7/3	.21	.59
5	6/4	.26	.62
6	5/5	.28	.54
7	4/6	.26	.44
8	3/7	.22	.33
9	2/8	.17	.26
10	1/9	.11	.14
11	0/10	.08	.04

These data, as plotted in Fig. 1, indicate the composition of the lakes. The failure of the optical density to attain the ideal maximum is probably due to the instability of the complex which forms.

Data on the properties and composition of the lakes are given in Table II.

Lakes of Benzene-azo-β-naphthol.—Elkins and Hunter[4] reported that the cobalt lake of this dye contains the metal in the +3 state, while Ernsberger and Brode[6] believed it to be in the +2 state. Magnetic measurements support the former view, for the compound was found to be diamagnetic, even when prepared in the absence of an oxidizing agent. This is the stable arrangement because the coördination number of the metal and its ionic charge are balanced by three molecules of dye.

The nickel derivative contains only two dye residues for each nickel ion. Since each dye residue is attached to the nickel through only two atoms, the covalences of the nickel are free to assume any configuration: the lake was found to be diamagnetic and is therefore assumed to be planar.

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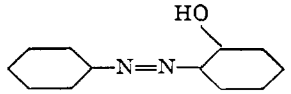
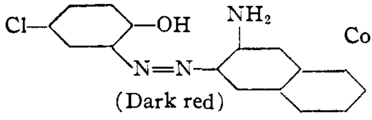
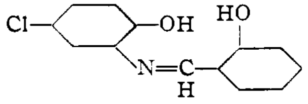
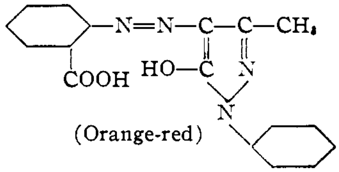
(4) M. Elkins and L. Hunter, *J. Chem. Soc.*, 1598 (1935).

(5) P. Job, *Ann. chim.*, [10] **9**, 113 (1928); W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

(6) M. L. Ernsberger and W. R. Brode, *J. Org. Chem.*, **6**, 331 (1941).

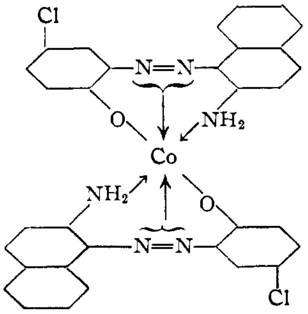
TABLE II

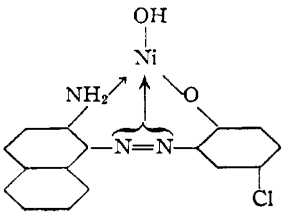
	Dye	Metal salt	Method of prepn.	Color of lake	Solubility of lake	Yield, %	Composition lake
1	 (Cherry-red)	$Co(OAc)_2 \cdot 4H_2O$	3	Dark red-brown	Insol. H_2O Sl. sol. EtOH	23	$Co(dye)_3$ Co^{+3}
		$Co(OAc)_2 \cdot 4H_2O$	2	Dark red-brown	Insol. H_2O Sl. sol. EtOH	21	$Co(dye)_3$ Co^{+3}
		$Ni(OAc)_2 \cdot 4H_2O$	2	Green-black	Insol. H_2O	..	$Ni(dye)_2$
2	 (Dark red)	$CoCl_2 \cdot 6H_2O$	1	Dark purple	Insol. H_2O Sol. hot EtOH	21	$Co(dye)_2$ Co^{+2}
		$Ni(OAc)_2 \cdot 4H_2O$	2	Dark red-brown	Insol. H_2O	..	$Ni(dye)OH$ $Ni(dye)OH \cdot H_2O$
3	 (Yellow-brown)	$CoCl_2 \cdot 6H_2O$	1	Yellow-brown	Insol. H_2O Insol. EtOH	10	$Co(dye) \cdot 2H_2O$ Co^{+2}
		$NiCl_2 \cdot 6H_2O$	1	Yellow	Insol. H_2O Insol. EtOH	67	$Ni(dye) \cdot H_2O$
4	 (Orange-red)	$Co(OAc)_2 \cdot 4H_2O$	2	Brown	Insol. H_2O Decomposed by acid	80	$Co(dye) \cdot H_2O$ Co^{+2}
		$Ni(OAc)_2 \cdot 4H_2O$	2	Yellow-brown	Insol. H_2O Sl. sol. acetone	80	$Ni(dye) \cdot H_2O$

		Magnetic susc. (Bohr magnetons)	Configuration of lake		Analyses, %				
					Carbon	Hydrogen	Nitrogen	Chlorine	Metal
1	Cobalt lake	Diamagnetic		Requires	71.99	4.13	10.50		7.40
				Found	71.96	4.29	10.56		7.27
	Cobalt lake	Diamagnetic		Requires	71.99	4.13	10.50		7.40
				Found	71.96	4.42	10.69		7.30[a]
	Nickel lake	Diamagnetic	Planar	Requires	69.47	3.98	10.13		10.66
				Found	69.40	4.16	10.08		10.79[a]
2	Cobalt lake	5.26		Requires				10.87	9.03
		5.28		Found				10.46	9.11
	Nickel lake	2.77	Tetrahedral	Requires	(Anhydrous or monohydrate)			9.53–9.07	15.76–15.05
				Found				9.12	15.42
3	Cobalt lake	5.97		Requires				10.36	17.23
				Found				10.3	17.59
	Nickel lake	3.65	Tetrahedral	Requires				10.97	18.2
				Found				10.95	17.96
4	Cobalt lake	4.69		Requires	51.39	3.54	14.10		
				Found	51.60	3.60	13.87		
	Nickel lake	3.96	Tetrahedral	Requires	49.19	3.88	13.50		
				Found	48.24	3.67	13.18		

[a] Calculated from C-H residue.

Lakes of 5-Chloro-2-hydroxybenzeneazo-β-naphthylamine.—This dye, while satisfying one "primary" valence of the metal, fills three coördination positions. It is not surprising, therefore, that the cobalt was stabilized in the divalent condition. A true covalent complex of divalent cobalt would show a magnetic moment of 1.73 Bohr magnetons; the much higher value given by this lake indicates that the compound is largely ionic. Two molecules of dye balance the charge on the cobaltous ion and fill its coördination sphere. In the case of nickel, which shows a coördination number of four, only one molecule of dye is accommodated, the remaining coördination position being filled by a hydroxyl group. The complex is evidently tetrahedral, for it is paramagnetic.



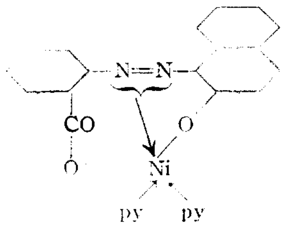


Lakes of 2'-Hydroxybenzal-2-hydroxy-5-chloroaniline.—In the cobalt lake, the metal remained in the cobaltous state, but the yield of lake was very small. Later work indicated that some cobaltic lake may have been formed, also, but that it escaped detection because of its solubility. The lake would be expected to contain either one or three molecules of water, giving the cobalt a coördination number of four or six; it is probable that some coördinated water was lost on drying.

Nickel shows a coördination number of only four in the lake with this dihydroxy compound, as it does in many coördination compounds. As might be expected from the structure of the dye, magnetic measurements indicated the lake to be tetrahedral.

Lakes of 2′-Carboxybenzene-4-azo-1-phenyl-3-methylpyrazol-5-one.—This dye resembles the previous one in having two replaceable hydrogen atoms in groups ortho to the chromophore group. Again, the cobalt was found to be in the cobaltous condition.

Drew and Fairbairn[3b] isolated the nickel complex of *o*-carboxybenzeneazo-*β*-naphthol as the dihydrate, and postulated that the nickel and the carboxyl group are not joined. This suggestion was supported by the fact that solution of the dihydrate in pyridine gave a dipyridino compound.



In the nickel and cobalt lakes of 2′-carboxybenzene-4-azo-1-phenyl-3-methylpyrazol-5-one, which has a similar structure, the carboxyl group evidently takes part in lake formation, for these lakes are monohydrates rather than dihydrates.

The authors take pleasure in acknowledging their indebtedness to the General Aniline and Film Corporation for grants which made this work possible, and for generous gifts of the dyes used.

Urbana, Illinois

[Contribution from the Research Laboratories, K-25 Plant, Carbide and Carbon Chemicals Company, Union Carbide and Carbon Corporation]

Preparation and Physical Properties of Niobium Pentafluoride[1]

By J. H. Junkins, R. L. Farrar, Jr., E. J. Barber and H. A. Bernhardt

Received January 18, 1952

Niobium pentafluoride was prepared by fluorinating the metal with elemental fluorine at 300°. The melting point was found to be 78.9 ± 0.2°, the boiling point 233.3 ± 0.5°, and the heat of fusion was estimated to be 8600 cal./mole. A sample of the compound was distilled in a 20-plate column. The vapor pressure of the middle fraction was measured and may be expressed by equation (1). Using the value of the heat of fusion given above, the vapor pressure over the solid may be expressed by equation (3). The liquid density was measured in the range of 86 to 125° and may be expressed by equation (4). The following thermodynamic quantities for the vaporization process were calculated from the vapor pressure data and corrected for deviation from ideality by the density measurements: $\Delta C_p = -8.5$ cal. deg.$^{-1}$ mole^{-1}; $\Delta H_v = 16{,}800 - 8.5\ T$; $\Delta S_v = (16{,}800/T) - 8.5$. The compound was found to be more stable toward hydrolysis than either ruthenium pentafluoride or uranium hexafluoride. There was no evidence of decomposition of niobium pentafluoride at temperatures up to 255°.

Introduction

The chemistry of inorganic fluorides has been a subject of increased interest in recent years partially as a result of the unusual character of many of these compounds but to a greater extent on account of the possible application to new chemical processes. Among the many compounds first studied but incompletely characterized by Ruff and his co-workers[2,3] was niobium pentafluoride. In view of the reactive nature of this compound, especially with glass, one can well appreciate the difficulties encountered by the early workers; and since the data in the literature were somewhat inconsistent, measurements of the vapor pressure, melting point, liquid density and the calculation of associated thermodynamic properties were undertaken.

Experimental and Results

Preparation and Purification.—Niobium pentafluoride was prepared by direct fluorination of niobium metal in a nickel reactor at 300°. The powdered metal was placed in one leg of the L shaped reactor tube before the segments of the L were welded together. After fabrication the system was warmed and pumped to remove air and traces of moisture; then, with the outlet of the reactor connected to a vacuum pump and the inlet to a source of fluorine, the leg of the reactor which contained the niobium metal was placed in an electric tube furnace and the other leg was suspended in Dry Ice slush. The temperature of the furnace was increased to 300° and fluorine was admitted into the static system forming the pentafluoride which deposited in the cool leg of the preparation tube.

Since this crystalline white solid niobium fluoride reacts with traces of moisture in the air, transfers of material from the preparation tube to other apparatus were made in an atmosphere which had a dew point of −40° or lower. The composition of the preparation is shown in Table I. The purity is limited by the presence of the order of 0.5 mole % of tantalum in the niobium metal, according to spectrographic analysis.

Table I

Analysis of Niobium Pentafluoride

	Found	Theoretical (NbF_5)
Niobium, %	49.7 ± 1.0	49.5
Fluorine, %	50.2 ± 0.6	50.5

A sample of niobium pentafluoride prepared in the manner just described was used without further purification for the determination of the melting point and estimation of the heat of fusion. Material employed in the determination of the vapor pressure was purified by distillation in a nickel fractionating column whose efficiency had been found by the

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[1] (a) This document is based on work performed for the Atomic Energy commission by Carbide and Carbon Chemicals Company, Union Carbide and Carbon Corporation, Oak Ridge, Tennessee. (b) The information in this document was presented at the Fluorine Chemistry Symposium, American Chemical Society, New York Meeting, September 4, 1951.

(2) Otto Ruff and Emil Schiller, *Z. anorg. Chem.*, **72**, 329 (1911).

(3) Otto Ruff and Julian Zedner, *Ber.*, **42**, 492 (1909).