aldehydesulfonate and zinc, cobaltous, nickelous and cupric ions. The sodium salts of these compounds have been isolated. The entropy of formation of bis-(5-salicylaldehydesulfonate)-copper was determined.

EVANSTON, ILLINOIS RECEIVED JANUARY 7, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

Stability of Chelate Compounds. V. The *o*-Formylnaphthoxide Chelates[1]

BY MELVIN CALVIN AND NORTEN C. MELCHIOR[2]

A previous report[3] from this Laboratory showed that the stability of cupric chelates of salicylaldehyde and its derivatives, or of β-diketones, varies, within a given group, inversely as the acid strength of the organic portion. Further, it was shown that the stability of cupric chelates is also related to the degree of "doublebondedness" in the ion of the organic portion, thus indicating a partial extension of the resonance in the negative ion to the cupric ion. A study[4] of the stability of the zinc, cobaltous, nickelous and cupric derivatives of 5-salicylaldehydesulfonate has shown that the stability of these chelates increases in the order given, and this order has been shown to be in accord with this idea.

In order to study these related effects more closely the three possible *o*-formylnaphthols were prepared, and the preparation of their metal derivatives was studied.

Experimental

1-Formyl-2-naphthol.[5]—This compound was prepared as described in "Organic Syntheses." The product was further purified by precipitating the cupric chelate by treatment with cupric acetate in alcoholic solution. The washed chelate was decomposed with a slight excess of 2 *N* sulfuric acid and the naphthol distilled with steam; very light yellow-green needles, m. p. 82.2–82.5 uncor.

3-Formyl-2-naphthol.[6]—Thirty-eight grams of purified 3-acetoxy-2-naphthoyl chloride was placed in a three-necked flask with 200 ml. of C. P. xylene, 6.0 g. of palladium on barium sulfate and 0.6 ml. of quinoline–sulfur poison. The reduction at 150–155° (bath temperature) was 91% complete in two hours, and was stopped after three hours. The catalyst was filtered from the hot solution and the cooled filtrate treated with 600 ml. of 1 *N* sodium hydroxide. A heavy orange precipitate formed immediately. The mixture was heated under reflux until all the solid had dissolved (twenty-five minutes), then indirectly steam distilled until the distillate was clear. The clear, deep red solution was cooled and the orange crystals which separated were isolated and washed with a little ice-water. A second crop was obtained by concentrating the mother liquor. The wet sodium 3-formyl-2-naphthoxide was treated with 200 ml. of water and 15 ml. of acetic acid on the steam-bath and the precipitated solid recrystallized from ethanol–water in bright yellow crystals, m. p. 97–98°; yield 20.6 g., 81%. Boehm and Prafft report 40%.

1-Hydroxy-2-naphthoic Acid.—This acid, prepared by passing carbon dioxide into a suspension of sodium 1-naphthoxide in boiling toluene,[7] was recrystallized from toluene and found to melt at 204–205° (dec.) uncor. Since the highest melting point reported for this compound is 191°,[8] a sample of the acid was titrated potentiometrically. No titratable phenolic group was found. The lower melting points reported are probably due to small amounts of impurities, since the compound decomposes rapidly as low as 180° when in the liquid phase, and thus would appear to give a sharp melting point.

1-Acetoxy-2-naphthoyl Chloride.—Preparation of this compound by usual methods was not satisfactory. A procedure modeled after Fischer[9] was successful. 1-Hydroxy-2-naphthoic acid was acetylated with acetic anhydride in acetic acid, recrystallized from acetic acid and dried *in vacuo*. The dry ester was stirred in an ice-bath with ten times its weight of acetyl chloride and treated with 1.1 equivalents of phosphorus pentachloride in small portions. The mixture was then allowed to warm to room temperature, filtered to remove a small amount of solid, and reduced to one-half volume under vacuum at room temperature. The crystals which formed when the residue was cooled to 0° were filtered off, washed with two small portions of cold petroleum ether and dried *in vacuo*. A second crop was obtained by removing everything volatile at 20° and 1.0 mm. from the mother liquor, dissolving the residue in acetyl chloride at room temperature, and cooling at 0°; yield 86% of white crystals, m. p. 112–113°.

2-Formyl-1-naphthol.—1-Acetoxy-2-naphthoyl chloride was reduced under the same conditions used in the preparation of 3-formyl-2-naphthol above, and the acetoxyaldehyde hydrolyzed as before, substituting 0.5 *N* sodium hydroxide for the 1 *N* base. Since preliminary experiments had shown that 2-formyl-1-naphthol was very easily oxidized, the calculated amount of 6 *N* sulfuric acid was added to the reaction mixture as soon as all the xylene had been removed, and the aldehyde steam distilled. The distillate was stored overnight at 0° and the aldehyde which separated was filtered off and dried over calcium chloride as very light green crystals, m. p. 59–60°; yield based on acetoxyacid chloride, 60%. Weil[10] obtained 27%, based on the hydroxy acid.

***o*-Formylnaphthoxide Chelates.**—Fifty ml. of 95% alcohol containing 1 g. of the desired formylnaphthol was heated to boiling in a round-bottom flask. Ten ml. of 1.2 *M* sodium acetate and 10 ml. of a water solution which was 0.29 *M* in the desired metal ion acetate were added in succession. A rubber stopper fitted with a stopcock was inserted and the system evacuated until the alcohol boiled vigorously. The stopcock was closed and the mixture heated on the steam-bath for from two to ten hours, cooled to room temperature and filtered. The precipitate was washed well with water and dried over calcium chloride *in vacuo*. Analyses and other data are collected in Table I.

Cupric 3-Formyl-2-naphthoxide.—Preparation by the method above gave a red precipitate upon addition of the

---

[1] Abstracted from the thesis submitted by N. C. Melchior in partial fulfillment of the requirements for the Ph.D. degree at the University of California, Berkeley, California, September, 1946.

[2] Shell Research Fellow in Chemistry, 1945–1946; present address: Northwestern University, Evanston, Illinois.

[3] M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

[4] M. Calvin and N. C. Melchior, *ibid.*, **70**, 3270 (1948).

[5] "Organic Syntheses," **22**, 63 (1942).

[6] T. Boehm and E. Prafft, *Arch. Pharm.*, **269**, 25 (1931).

[7] "Beilstein," Vol. IV, **10**, p. 331.

[8] R. T. Arnold and J. Sprung, THIS JOURNAL, **60**, 1163–1164 (1938).

[9] E. Fischer, *Ber.*, **38**, 612 (1905).

[10] H. Weil, *ibid.*, **54**, 3217 (1921).

TABLE I

METAL *o*-FORMYLNAPHTHOXIDE CHELATE COMPOUNDS

Compound	Color[a]	% H_2O[b]	Color[c]	Analyses, %		
				C	H	Residue
$\mathrm{Co(2\text{-}1)_2\cdot 2H_2O}$[d]	Orange	8.7	Yellow-brown	60.8	4.21	18.0
$\mathrm{Co(1\text{-}2)_2\cdot 2Py}$[e]				68.8	4.56	14.1
$\mathrm{Co(3\text{-}2)_2\cdot 2.5H_2O}$	Orange	10.8	Red-orange	59.8	4.31	18.3
$\mathrm{Ni(1\text{-}2)_2\cdot 2H_2O}$	Green-yellow	8.7	Red-orange	60.4	4.68	17.2
$\mathrm{Ni(2\text{-}1)_2\cdot 2H_2O}$	Green-yellow	8.9	Orange	60.6	4.29	19.4
$\mathrm{Ni(3\text{-}2)_2\cdot 3H_2O}$	Red-orange	10.8	Red	58.4	4.69	16.1
$\mathrm{Cu(1\text{-}2)_2\cdot H_2O}$[f]	Light green	4.4	Olive	65.0	3.72	19.8
$\mathrm{Cu(2\text{-}1)_2}$	Yellow-brown	0.1	Yellow-brown	65.4	3.88	19.8
$\mathrm{Cu(3\text{-}2)_2}$	Red	0.0	Red	65.2	3.72	19.8
$\mathrm{Zn(1\text{-}2)_2\cdot 2H_2O}$[f]	Light green	8.65	Light green	64.7	3.85	20.4
$\mathrm{Zn(2\text{-}1)_2\cdot 1.5H_2O}$[f]	Yellow-green	5.85	Yellow-green	64.9	3.70	19.8

[a] Color of solid dried *in vacuo* over calcium chloride at room temperature. [b] Weight lost on heating solid dried as *a* to 140° at 0.001 mm. [c] Color of sample dried at 140°. [d] $\mathrm{Co(2\text{-}1)_2\cdot 2H_2O}$ is the shorthand notation for cobaltous 2-formyl-1-naphthoxide dihydrate. [e] Recrystallized from pyridine. The compound is the dipyridinate. [f] Isolated as the hydrate indicated, but analyzed after drying at 140°.

cupric acetate solution. As the heating proceeded, the precipitate darkened and after twelve hours was dark brown. Analysis showed the material to be largely cupric oxide. Preliminary experiments indicated the red substance would be extremely difficult to purify; therefore, a method was devised to give the minimum contamination with cupric hydroxide. Three grams (0.015 mole) of sodium 3-formyl-2-naphthoxide in 500 ml. of water was added slowly to a stirred solution of 0.0072 mole of cupric nitrate in one liter of water. The bright red solid which precipitated immediately was separated, washed with two 100-ml. portions of water and two 50-ml. portions of 50% alcohol, and dried as before (analysis in Table I).

Zinc 3-Formyl-2-naphthoxide.—All attempts to prepare this compound failed. On one experiment a mixture of the free formylnaphthol and basic zinc acetate was recovered, while in another the solid recovered was largely sodium 3-formyl-2-naphthoxide.

(2,4-Diazo-1,5-hexadiene)-dinaphthoxide Chelates.—Fifty ml. of hot 95% alcohol containing 1 g. of the desired formylnaphthol was treated with 10 ml. of 1.2 *M* sodium acetate and 0.27 ml. of 68% ethylenediamine. The flasks were evacuated as before and heated on the steam-bath for two hours. They were then opened while hot and 10 ml. of 0.29 *M* metal acetate solution added. The procedure from this point was identical with that for the formyl naphthoxides. Pertinent data are collected in Table II.

TABLE II

METAL (2,4-DIAZA-1,5-HEXADIENE-)DINAPHTHOXIDE CHELATE COMPOUNDS

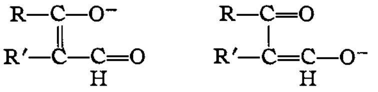
Compound	Color	% Wt. loss at 140°	Analyses, %			
			C	H	N	Residue
Co 1-2-I[a]	Red	0.8	67.8	4.52	6.5	19.0
Co 2-1-I	Purple	.5	67.5	4.39	6.7	18.7
Co 3-2-I	Red-brown	.8	67.3	4.25	6.5	18.5
Ni 1-2-I	Red-orange	.0	68.1	4.42	7.0	16.7
Ni 2-1-I	Brown-red	.2	67.8	4.15	6.9	17.0
Ni 3-2-I	Orange	.3	67.9	4.43	6.6	16.6
Cu 1-2-I	Brown	.0	67.0	4.45	6.7	18.5
Cu 2-1-I	Brown	.3	67.4	4.25	6.3	18.6
Cu 3-2-I	Gilt	.0	66.9	4.43	5.4	18.1
Zn 1-2 En[b]	Yellow	1.6	74.4	5.16	6.8	6.0
Zn 2-1 En	Yellow	2.7	70.5	5.20	...	9.9
Zn 3-2 En	Yellow	1.9	71.0	5.13	6.9	9.5

[a] "Co 1–2–I" is the shorthand notation for "Cobaltous 1-(2,4-diaza-1,5-hexadiene)-di-2-naphthoxide." [b] "Zn 1–2 En" is shorthand for the compound formed in an attempt to prepare "Zn 1–2–I"; it may be zinc di-1-[2,4-diaza-(1,5-hexadiene)-6-(2-naphthol)]-2-naphthoxide.

Titrations.—Comparison titrations were carried out as described previously.[4] One hundred ml. of 0.002 *M* 1-formyl-2-naphthol in 60% alcohol was placed in the titration vessel, followed by 10 ml. of 0.01 *M* nitric acid and 1 ml. of pure water or 0.01 *M* metal acetate, and the mixture titrated. The results are shown in Fig. 1. In every case in spite of the low concentration of metal ion, a Tyndall effect was observed at the conclusion of all titrations except the blank. Since the separation of solid prevented accurate results, the observations are of qualitative significance only and were not extended.

Discussion

If we consider the common naphthalene nucleus of the *o*-formylnaphthols, we find that the major resonance forms of this nucleus are such that the bond between carbon atoms one and two is about two-thirds of a double bond, while that between carbon atoms two and three is only one-third of a double bond. If a resonance of the type



above is important in the formation of the chelate molecule as has been indicated in previous work,[3,4,11] we would expect to find that chelates formed from 3-formyl-2-naphthol were less stable than corresponding derivatives of either 2-formyl-1-naphthol or 1-formyl-2-naphthol, since in the latter two the bond joining the functional groups is two-thirds of a double bond, and can therefore participate in this important resonance to a greater extent than can the former where the critical bond is only one-third of a double bond. Arnold and Sprung[8] have given a somewhat similar explanation of the low value they found for the ionization constant of 3-formyl-2-naphthol, $K_a = 1.2 \times 10^{-10}$ as compared to its ortho isomers: K_a 2-formyl-1-naphthol $= 1.4 \times 10^{-8}$ and K_a 1-formyl-2-naphthol $= 5.4 \times 10^{-9}$.

We interpret these results as indicating less resonance in the ion of 3-formyl-2-naphthol, as ex-

---

[11] M. Calvin and R. H. Bailes, THIS JOURNAL, 68, 949 (1946).

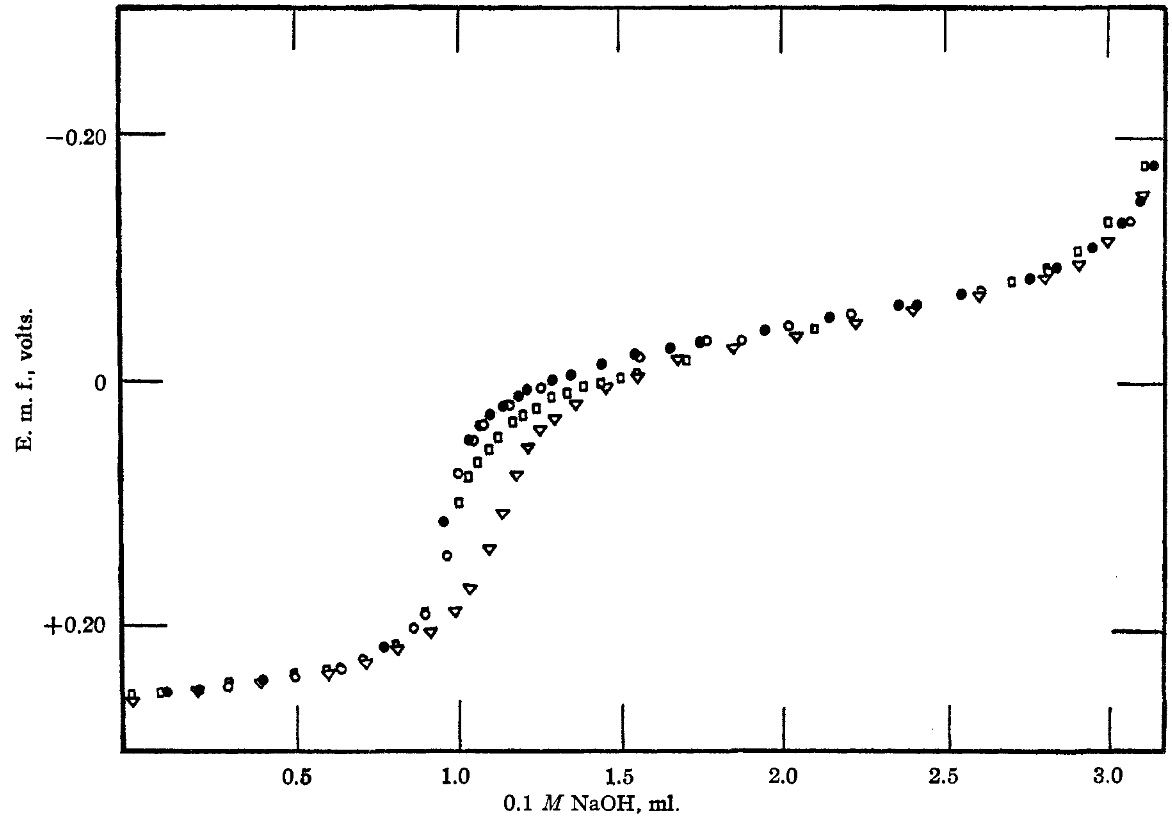


Fig. 1.—Titrations of 2-formylnaphthol: ○, ●, 0.002 M 2-formylnaphthol, 0.001 M HNO_3; □, acid and naphthol as before, 0.0001 M Ni^{++} or Co^{++} (the curves are not resolvable); ▽, acid and naphthol as before, 0.0001 M Cu^{++}.

pected. Further we expect from our previous work[4] that the stability of the chelates formed from any one formylnaphthol will be in the order $Cu^{++} \gg Ni^{++} > Co^{++} > Zn^{++}$. This stability is that defined by the equilibrium constant for the reaction

$$Me^{++} + 2Ke^- \rightleftharpoons MeKe_2$$
$$K = (MeKe_2)/(Me^{++})\,(Ke^-)^2$$

where the symbol Ke^- indicates an o-formylnaphthoxide ion.

The titrations in Fig. 1 show that cupric ion forms a more stable complex with 1-formyl-2-naphthoxide ion than do either cobaltous or nickelous ions, but the very low solubility of these chelates prevents more accurate work. Qualitatively the results are as predicted.

Further qualitative confirmation of our expectations is found in the difficulty experienced in the preparation of cupric 3-formyl-2-naphthoxide.[12] This compound, although extremely insoluble, is unstable in the preparation solution and decomposes into cupric oxide. This effect might be ascribed to the fact that this naphthol is a much weaker acid than its isomers, except that it has been shown previously[3] that weak acidity leads to more stable rather than less stable chelates. Zinc 3-formyl-2-naphthoxide is expected to be the least stable compound of this group. The failure of attempts to prepare this compound is not unequivocal, but is in the direction predicted.

The (2,4-diaza-1,5-hexadiene)-dinaphthoxides appear to form as expected except for the zinc compounds. In this case the analyses indicate that the zinc ion reacts with two molecules of the chelating agent rather than with one, as is the case with the other metals. This apparent change in the type of compound, although unexpected, agrees with our previously expressed[4] concept that the *d* orbitals of the metals are directly involved in the binding of these nitrogen compounds. Zinc, having no available *d* orbital, apparently forms a different kind of compound.

Summary

Cupric, nickelous, cobaltous and zinc derivatives of the three possible o-formylnaphthols, and of the three possible o-(2,4-diaza-1,5-hexadiene)-dinaphthols have been described. The relative stabilities of these compounds have been discussed with regard to theories of chelate binding.

BERKELEY, CALIFORNIA RECEIVED JANUARY 7, 1948

---

[12] It should be noted that this compound is a brilliant red solid in contrast to the usual green of cupric compounds of this type. The nickel compound is red-orange instead of the usual green or greenish-yellow.