PREPARATION AND THERMAL STABILITIES OF SOME METAL CHELATE POLYMERS OF NAPHTHAZARIN*†

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Abstract—Metal chelate polymers have been prepared from naphthazarin and the divalent metal ions: cobalt, nickel, zinc, copper and beryllium. The chelates are fine deliquescent powders which are insoluble in a wide variety of polar and non-polar solvents. The metal to ligand ratio is one to one for all chelates, except for the copper chelate which has a ratio of three to four. The cobalt, nickel and zinc chelates are hydrates, while the copper and beryllium chelates are not. Thermal stabilities of the chelates were determined using a manually-operated thermobalance, which was constructed from readily available equipment. The order of thermal stability of the chelates based on procedural decomposition temperatures is: B > Ni > Zn > Co > Cu. Static heating showed the beryllium and nickel chelates to be stable up to 316 °C. An attempt is made to account for the observed order of stability. Several unsuccessful attempts were made to prepare a beryllium–naphthazarin (1:2) complex and also a platinum(II)–naphthazarin complex.

NAPHTHAZARIN (5,8-dihydroxy-1,4-naphthoquinone) is a polyfunctional ligand which is capable of forming polymers by coordination with metal ions. Polymers with cobalt⁽¹⁾ and beryllium⁽²⁾ have been reported but have not been studied extensively. Their preparation has been repeated and also other polymers with nickel, zinc and copper have been prepared. The compositions, thermal stabilities and infra-red spectra of the chelates have been investigated.

EXPERIMENTAL

Chemicals. All chemicals were reagent grade. Common organic solvents, commercially available, were used without further purification. Crude naphthazarin was obtained from the Aldrich Chemical Company, Milwaukee, Wisconsin and was purified by extraction and recrystallization using skelly-solve E, b.p., 100–120°C., as a solvent.

Preparation of cobalt-, copper-, nickel-, zinc-naphthazarin complexes. Solutions containing 1.0 g of cobalt acetate dihydrate or 2.0 g of either copper sulphate pentahydrate, copper nitrate trihydrate, nickel acetate tetrahydrate, or zinc acetate dihydrate in 50 ml of warm distilled water were added to hot solutions of 0.5 g naphthazarin in 50 ml of 95 per cent ethanol. The mixtures were heated to boiling, stirred for several minutes, and then cooled to room temperature. The precipitates were collected by centrifugation and washed several times with water, then with ethanol, and finally with boiling acetone. They were transferred to fritted glass filtering crucibles with warm acetone and air dried. The yields ranged from 0.5 to 0.7 g.

Preparation of beryllium-naphthazarin (1:1) complex. The procedure was essentially that of UNDERWOOD et al.⁽²⁾ A solution containing approximately 1.0 g of beryllium sulphate tetrahydrate in 25 ml of distilled water was added to a solution of approximately 1.0 g of naphthazarin in 300 ml of 95 per cent ethanol. Sodium hydroxide solution (0.2 N) was added until the red colour of the metal ionligand mixture turned to the purple colour of the complex. The solution was diluted with distilled

⁽¹⁾ R. H. BAILES and M. CALVIN, J. Amer. Chem. Soc. 69, 1892 (1947).

⁽²⁾ A. L. UNDERWOOD, T. Y. TORIBARA, and W. F. NEUMANN, J. Amer. Chem. Soc. 72, 5597 (1950).

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water to about 425 ml and heated to $50-60^{\circ}$ C. The precipitate which formed was collected by centrifugation, washed several times with distilled water, dried, then washed several times each with ethanol and acetone and finally dried at room temperature in an Abderhalden drying apparatus. The yield was about 0.5 g.

Attempted preparation of beryllium-naphthazarin (1:2) complex. Repeated attempts to prepare this complex according to the directions of UNDERWOOD *et al.*⁽²⁾ were unsuccessful.

Attempted preparation of a platinum(II)-naphthazarin complex. Several attempts were made to prepare a complex of naphthazarin and platinum(II) by slowly adding an alcoholic solution of naphthazarin to an aqueous solution of potassium platinum(II) chloride. When heated on a steam-bath, the mixture changed from orange-red to orange-brown and became very viscous. Cooling the mixture produced a gummy material which was soluble in acetone and in benzene. Attempts to isolate a pure compound by recrystallizing the gummy material from acetone were unsuccessful.

Analyses. Carbon and hydrogen analyses were performed by the Midwest Microlab, Indianapolis, Indiana. Samples for metal analysis, except for beryllium, were prepared by digesting 0.1-0.2 g of the complex in a mixture of 5 ml of concentrated sulphuric acid and 3 ml of concentrated nitric acid. Nickel was determined gravimetrically using dimethylglyoxime. Zinc was determined gravimetrically as zinc mercuric thiocynate. Copper and cobalt were determined by electrogravimetry. Beryllium was determined by ignition of the complex to beryllium oxide.

Infra-red absorption spectra. All infra-red absorption spectra measurements were made with a Perkin-Elmer Infra-red Spectrophotometer, Model 21, equipped with sodium chloride optics. Samples were prepared using the potassium bromide disk method. Infra-red spectra were obtained on samples of complex taken before, during, and after the heating process. Ordinarily, about 0.5 mg of sample was needed to obtain a good spectrum of the particular complex. Larger weights of about 1 mg were required to get suitable spectra of samples which had undergone thermal decomposition.

Thermogravimetric measurements. For the thermogravimetric analysis of naphthazarin and the metal-naphthazarin complexes, a simple, manually-operated thermobalance was constructed from readily available apparatus and materials. The balance used was an ordinary analytical balance. The furnace, which was made from transite cylinders, had a temperature range from room temperature to about 500°C. The temperature of the furnace was controlled by a Temco input controller, model CP-515T. The overall rate of heating was nearly linear, averaging $4-5^{\circ}C$ per min. Temperature measurements of the sample chamber were made with a Leeds and Northrup double-range potentiometer, Model 8657-C, using an iron-constantan thermocouple.

The furnace was flushed with dry nitrogen for approximately 30 min before starting a run. After a sample was placed in the furnace, the rate of flow of nitrogen was adjusted so it would not disturb the equilibrium of the balance.

Small glass vials with support loops made from nichrome wire were used as sample containers. These were suspended in the sample chamber using a nichrome wire chain. Static heating tests showed that the vials could be heated to 450°C without showing any loss in weight; higher temperatures were not investigated.

A study of the effect of the furnace temperature on balance readings using two empty sample vials of known weight indicated that the balance readings were not affected up to 220° C. Above 220° C, there was an apparent continuous loss in weight amounting to 1.7 mg at 450° C. A calibration curve of weight loss versus temperature was prepared from the two determinations, and all subsequent data were corrected using this curve. After each run, as a check on the final weight loss readings on the thermobalance, the samples were cooled in a desiccator and weighed on a chainomatic balance. In every instance, the weights were within 0.2 mg of the corrected weight loss as determined by the thermobalance.

The thermograms were obtained using approximately 50 mg of the compound which had been air dried for 24 hr or longer. The copper and beryllium complexes were dried for an additional 2 hr under high vacuum at 60° C. Duplicate runs were made for each complex.

RESULTS AND DISCUSSION

Physical properties. All of the complexes prepared from naphthazarin were similar in physical form in that they were all fine powders, purple to deep-blue in colour. They were insoluble in a wide variety of polar and non-polar solvents including: water,

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acetone, methanol, ethanol, benzene, ether, dioxane, dimethylformamide and tetrahydrofuran. None of the complexes sublimed on heating. Estimation of the chain length was not possible because the insolubility of the complexes prevented the determination of molecular weights by the usual cryoscopic and viscosity measurements.

Composition. A study of the infra-red spectra and the thermal behaviour of the complexes indicated that the cobalt, nickel and zinc complexes contained water as part of the co-ordination sphere, whereas the copper and beryllium complexes did not.

All the complexes were somewhat difficult to analyse because constant weight could not easily be obtained. Samples dried in vacuum had a tendency to pick up moisture if exposed to the air, particularly the cobalt and zinc complexes. The nickel complex appeared to be the most stable in this respect. It could be exposed to the air for some time without any significant increase in weight. Samples containing water as part of the co-ordination sphere also contained some adsorbed water which was not removed by air drying. Drying in vacuum removed the adsorbed water and part of the coordinated water so that constant weight was extremely difficult to obtain. As a result, the samples were air dried and submitted for carbon and hydrogen analyses. Metal analyses were performed on portions of the same samples.

All of the data in Table 1, except for zinc, was corrected for adsorbed water. In so doing, it was assumed that the difference between the calculated value based on the formation of a 1:1 polymer of infinite length for all complexes, "except copper, for which a ratio of 3:4 was used," and the experimental value was the result of adsorbed water. This assumption was based on observations of several elemental analyses in which samples, shown by thermogravimetric data to contain more than the theoretical amount of water, gave high values for hydrogen and low values for carbon and metal. One sample, containing less than the theoretical amount of water, gave a low value for carbon and metal. In addition, several samples of the cobalt complex, dried to remove some coordinated water, gave values for cobalt in a range between the theoretical value for the dihydrate and that of the anhydrous complex.

It would appear from the compositions of the metal complexes that cobalt(II), nickel(II), and zinc(II), which show a co-ordination number of six, are octahedral in configuration, while the copper(II) and beryllium(II) complexes, which show a coordination number of four, are either planar or tetrahedral in configuration. An octahedral configuration in which naphthazarin and metal alternate to form a linear chain, with the water molecules occupying the remaining two trans positions, has been proposed for the cobalt complex.⁽¹⁾ A similar structure is proposed for the nickel complex. The zinc complex may also have the same structural arrangement. A structure in which metal and ligand alternate to form a linear polymer has been proposed for the beryllium complex.⁽²⁾ The configuration of the complex is probably tetrahedral. Of the beryllium complexes whose structures are known, the only one which is planar is beryllium phthalocyanine;⁽³⁾ all others are tetrahedral. Beryllium phthalocyanine readily forms hydrates which may be indicative of lower stability in the forced planar configuration. The addition of two molecules of water would allow octahedral co-ordination. Unlike beryllium phthalocyanine, the beryllium-naphthazarin complex was found to be only slightly hygroscopic, and it is, therefore, quite likely that its configuration is tetrahedral. The copper-naphthazarin complex is probably planar since most copper chelates are planar. The formula, three copper

⁽³⁾ R. P. LINSTFAD and J. M. ROBERTSON, J. Chem. Soc. 1736 (1936).

atoms to four naphthazarin molecules, which has been proposed on the basis of elemental analysis indicates only the simplest combination of metal and ligand possible. The polymeric nature of the complex may allow for the other formulas of much higher molecular weights.

DUBSKY *et al.*⁽⁴⁾ reported the preparation of a copper–naphthazarin salt containing 20 per cent copper. They assigned the complex a formula of $C_{10}H_4O_4Cu$. $4H_2O$, which would thus account for the analysis showing 20 per cent copper. On heating at

	Element	Calculated	Experimental	Corrected	Carbon to metal ratio
C ₁₀ H ₄ O ₄ Co.2H ₂ O	C	42.43	39.52	41.95	10.00:0.96
-	Со	20.79	20.20	21.41	
	Н	2.83	3.47	2.83	•
$C_{10}H_4O_4Ni.2H_2O$	С	42.46	43.55	42.46	10.00:1.12
10	Ni	20.71	22.53	21.90	
	Ni*	23.77	23.98		
	Н	2.82	2.49	2.82	
$C_{10}H_4O_4Zn.2H_2O$	С	41.48	41.02		10.00:1.02
	Zn	22.57	22.00		
	Н	2.76	3.06		
$C_{10}H_4O_4Be$	С	60.91	56.59	60.28	10.00:0.90
**	Be	4.56	4.05	4.31	
	н	2.03	2.71	2.03	
$(C_{10}H_4O_4)_4Cu_3^{\dagger}$	С	50 ·89	48.90	50.56	40.00:3.11
	Cu	20.16	20.20	20.44	
	Н	1.90	2.27	1.90	

TABLE 1.—COMPOSITION OF METAL-NAPHTHAZARIN CHELATES

* Values are for $C_{10}H_4O_4Ni$. Sample was dried to constant weight in thermobalance furnace at 260°C; at this temperature all of the water is lost.

 \dagger Composition was the same whether an excess of copper or naphthazarin was used in the preparation of the complex.

 150° C, however, they reported a loss in weight of only 10.75 per cent as compared to the calculated value of 22.26 per cent for four molecules of water. This investigation has shown that the copper complexes studied contain 20 per cent copper and no water. The absence of water in these complexes was shown not only from the thermogravimetric data, but also, from the infrared spectrum which showed no absorption due to free OH stretching vibrations which was present in the spectra of the other complexes which contained water.

If the assumed spatial arrangements of the cobalt, nickel and zinc complexes are correct, it would be easy to understand why the anhydrous zinc and cobalt complexes are quite deliquescent while the nickel complex is not. Loss of water would leave the tetraco-ordinated metals in a planar configuration. Since nickel is quite stable in a planar configuration, it does not readily absorb moisture. Tetraco-ordinated zinc and cobalt, however, usually have a tetrahedral structure, and would have a much lower stability than nickel in the proposed planar configuration. They, therefore, absorb moisture to restore the more stable octahedral configuration.

Thermal properties. The thermograms for naphthazarin and the metal-naphthazarin

(4) J. V. DUBSKY, A. LANGER and E. WAGNER, Mikrochemie, 22, 114 (1937).

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complexes are shown in Fig. 1. From curve A, it can be seen that naphthazarin decomposes in the region of 194°C. Actually considerable sublimation also occurs at this temperature as evidenced by the evolution of red vapours characteristic of naphthazarin when it sublimes. Curves B-F show that the copper and beryllium complexes are not hydrates, while the cobalt, zinc and nickel complexes are. The loss



in weight of the latter complexes due to the removal of water was: 15.5 per cent at 272° C for the cobalt complex, 12.3 per cent at 232° for the zinc complex, and 17.1 per cent at 234° for the nickel complex. The theoretical loss in weight for two molecules of water is: 12.7 per cent for the cobalt complex, 12.4 per cent for the zinc complex and 12.7 per cent for the nickel complex. The high experimental values for the cobalt and nickel complexes are due to adsorbed water.

Static decomposition temperatures obtained by heating a dried sample of complex

at a series of fixed temperatures are given in Table 2. Only the beryllium and nickel complexes were stable above 316° C. Decomposition of the complex involved the slow decomposition of the organic portion of the polymer and the formation of metal oxide. A sample of copper complex heated to constant weight at 316° C gave the calculated amount of copper oxide.

Temperature	Time heated (hr)	Per cent weight loss				
(°C)		Be	Cu	Ni	Zn	Co
225	1.0		1.6	0	0.5	0.4
260	1.0		1.9	0.4	1.6	1.9
316	2.0	1.0	d*	0	d	d

TABLE	2.—Static	DECOMPOSITION	TEMPERATURES	OF
	METAL-NAI	PHTHAZARIN COM	IPLEXES	

* d denotes decomposition

Procedural decomposition temperatures for the anhydrous complexes are listed in Table 3. The order of decreasing thermal stability is:

TABLE 3.—PROCEDURAL DECOMPOSITION TEMPERATURES

Substance	Procedural decomposition Temperature (°C)†		
Naphthazarin	194		
Cobalt complex	272		
Copper complex	260		
Zinc complex	318		
Nickel complex	327		
Beryllium complex	350		

† NEWKIRK⁽⁵⁾ has recently pointed out that the temperatures will be approximately correct; they will, however, have shifted upward by the effect of the rate of heating.

Be > Ni > Zn > Co > Cu. The relative stabilities of the zinc, cobalt, and coppercomplexes seems reasonable since zinc has a fixed oxidation state of two while cobalt and copper can exhibit variable oxidation states. The variable oxidation states of cobalt and copper could give rise to catalytic effects in the decomposition of the complexes in which they are found. MARTIN⁽⁶⁾ has proposed this explanation to account for the unusual thermal stability of several bis- α -thiopicolinamido chelate polymers of zinc as compared with those of copper and nickel. Although nickel can also show variable oxidation states, its complex with naphthazarin was found to be more stable than that of zinc. The greater stability found for the nickel complex may be due to the spatial arrangement of the polymers in which nickel would appear to be more stable in a planar configuration than zinc, if the assumed structures are correct. The small size of the beryllium ion and its fixed oxidation state of two would account for its position in this series.

⁽⁵⁾ A. E. NEWKIRK, Analyt Chem. 32, 1558 (1960).

⁽⁶⁾ K. V. MARTIN, J. Amer. Chem. Soc. 80, 233 (1958).

Infra-red spectra. Infra-red absorption spectra did not give conclusive evidence with regard to the nature of the end-groups present in the complexes; slight absorption peaks, however, appearing as shoulders in the 6 μ region, where the free carbonyl stretching frequency of naphthazarin appears, in the spectra of the cobalt and zinc complexes may possibly be an indication that the ligand molecule was present as an end-group in these complexes. It is possible, however, that such absorption could also be the result of traces of unreacted naphthazarin in the sample. No evidence of free carbonyl absorption was found in the spectra of the other complexes. The fact that little, if any, absorbance due to free carbonyl was present in the spectra of the complexes indicated that both carbonyl groups of the naphthazarin molecule functioned as co-ordinating groups. The carbonyl absorption frequencies for naphthazarin and the metal-naphthazarin complexes are listed in Table 4. The differences between the carbonyl frequency in naphthazarin and in the various metal complexes are also given.

Compound	Carbonyl frequency (cm ⁻¹)	Frequency shift (cm ⁻¹)	
Naphthazarin	1621		
Cobalt complex	1547	74 ·	
Copper complex	1545	76	
Zinc complex	1551	70	
Nickel complex	1552	69	
Beryllium complex	1541	80	

INICKEI COMPIEX	1552	09	
Beryllium complex	1541	80	
			-
The naphthazarin molecule has no s	harp absorpt	tion peak due t	o OH stretching
ie 3 μ region because of strong intra-	nolecular hy	drogen bondin	g, so that little u
ould be made of this region in deter	miming the	function of the	e phenolic group
otentiometric and spectrophotometric	work reporte	ed for the beryl	lium–naphthazai
stem ⁽²⁾ has, however, confirmed the ex	kistence of a d	one to one, meta	al to ligand, spec
nd has shown that both phenolic hyd	lrogens were	released in the	formation of th
becies. The absence of pronounced	absorption	bands at 3μ	for the free C
retching vibration in the spectra of the	copper and b	peryllium compl	lexes indicated th
ater was not present in these compl	aves The L	and of an and in	stad

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th use cc ps. Р rin sy ies aı his sŗ ЭН st nat water was not present in these complexes. The loss of co-ordinated water during heating from the cobalt, nickel and zinc complexes was shown by the gradual disappearance of this same absorption band.