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

Spectrophotometric, Polarographic and Solubility Behavior of the Chelate Compounds of the Group IVB Metals with Aromatic N-Nitrosohydroxylamines

BY PHILIP J. ELVING AND EDWARD C. OLSON

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Those properties of the Group IVB metal chelates of three aromatic N-nitrosohydroxylamines (cupferron, and the α-naphthyl and *p*-xenyl analogs) which might be useful in the application of the standard techniques of analytical chemistry to the determination of the metals have been studied. The solubilities of the compounds are about 10^{-7} mole per liter in water, are somewhat greater in 2 *M* sulfuric acid, and increase with atomic weight with the thorium salts being very soluble in the acid solution. Only small differences in polarographic and spectrophotometric behavior exist between similar chelates of the different metals. The chelates absorb at 7.5 and 8.2 μ, where the acids do not. The extent of the shift to longer wave lengths on chelation for bands in the acids increases with atomic weight of the metal. Similar shifts occur in the ultraviolet region, where zirconium has the minimum molar absorptivity in each group of chelates. Values of pK_a for the three acids were determined from their ultraviolet spectra. In 4 *M* perchloric acid solution titanium, zirconium and hafnium form a series of soluble dichelates, MA_2^{+2}, with each of the three cupferrons. The half-wave potential of the aromatic N-nitrosohydroxylamine is shifted 400 mv. on chelation; in all cases the shift follows the same order, *i.e.*, the titanium chelate is the weakest (least stable) and hafnium the strongest (most stable).

The voluminous literature on the chemistry of metal ions and so-called organic reagents, in particular, chelating agents, is generally lacking in systematic investigations of those properties of the reaction products of a related group of metal ions with a homologous or otherwise related group of organic compounds which would be useful from the viewpoint of analytical method development.

The present investigation is a study of the effects of varying the secondary organic structure and the central metallic atom on the spectrophotometric, polarographic and solubility properties of a related group of chelate compounds, formed by the metals of one group of the Periodic Table (Group IVB: titanium, zirconium, hafnium and thorium) with a series of organic molecules possessing the same functional grouping in reference to chelation, *i.e.*, three aromatic N-nitrosohydroxylamines. Such an investigation has also provided information on the effect of metal ions on the polarographic and spectrophotometric behavior of the organic compounds, which is the reverse of the usual situation, in which the effect of the organic ligand on the properties of the metal atom is studied.

The terms, cupferron, neocupferron and *p*-phenylcupferron, are generally used in the present study to refer to the ammonium salts of the N-nitrosohydroxylamines (phenyl, α-naphthyl and *p*-xenyl, respectively) while the term cupferrate is used to indicate the compound formed with a Group IVB metal. The *p*-xenyl derivative is a new compound and has not heretofore been investigated as an organic reagent.

Generally, a Group IVB metal ion will react in acid solution with a chelating agent such as cupferron in the molar ratio of 1:4

$$M(IV) + 4HCupf \longrightarrow M(Cupf)_4 + 4H^+ \qquad (1)$$

In sulfate solution the metal ion is probably originally present largely as the trisulfate anion. In the present study, the existence of dichelate species in which the metal:cupferron ratio is 1:2 has been established.

Absorption Spectra. Ultraviolet.—Study of the solubility of the metal chelates of cupferron in organic solvents[1] indicated chloroform as generally the best solvent. Therefore, the titanium, zirconium, hafnium and thorium compounds of cupferron, neocupferron and *p*-phenylcupferron were precipitated, dried, weighed and dissolved in chloroform, and the ultraviolet absorption spectra recorded together with the spectra of the corresponding ammonium salts and free acids. The wave lengths of maximum absorption and the corresponding molar absorptivities are tabulated in Table I. Attempts to study the spectra of the metal chelates in methanol, ethanol and ethyl ether failed because of the low solubility of these compounds in solvents other than chloroform.

TABLE I

REGIONS OF MAXIMUM ABSORPTION AND CORRESPONDING ABSORPTIVITIES FOR THE ACIDS, AMMONIUM SALTS AND GROUP IVB METAL CHELATES OF AROMATIC N-NITROSOHYDROXYLAMINES IN CHLOROFORM

		Absorptivities	
Compound[a]	Wave length λ_{max}, mμ	Specific $a_s \times 10^{-4}$	Molar $a_M \times 10^{-7}$
HCup	260	1.28	0.198
NH_4Cup	260	1.32	0.222
$TiCup_4$	261	5.52	3.29
$ZrCup_4$	277	3.54	2.26
$HfCup_4$	273	5.59	4.06
$ThCup_4$	287	8.18	6.38
HNcup	292	0.488	0.091
NH_4Ncup	292	0.478	0.095
$TiNcup_4$	293	5.84	4.64
$ZrNcup_4$	297	3.52	2.96
$HfNcup_4$	297	5.21	4.83
$ThNcup_4$	292	6.17	6.05
HPcup	290	1.59	0.34
NH_4Pcup	290	1.51	0.34
$TiPcup_4$	298	12.0	10.9
$ZrPcup_4$	308	7.19	6.78
$HfPcup_4$	308	9.15	9.43
$ThPcup_4$	307	17.9	19.5

[a] Cup, Ncup and Pcup represent the anions of cupferron, neocupferron and phenylcupferron, respectively.

Only minor shifts occur in the wave length of maximum absorption of the aromatic N-nitrosohydroxylamines on forming chelate compounds with the Group IVB metals; the smallest shifts occur with titanium while the heavier metals all produce approximately the same shift. However,

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(1) N. H. Furman, W. B. Mason and J. S. Pekola, *Anal. Chem.*, **21**, 1325 (1944).

there is a marked change in the molar absorptivity of the chelates as the metallic ion is changed; within each series a minimum value occurs for the zirconium species. The phenyl and α-naphthyl chelates have approximately equal molar absorptivities; those of the *p*-xenyl compounds are much higher. In these respects, the behavior of these Group IVB metal chelates is analogous to that of many other chelate compounds.[2] In the case of the free acids and the ammonium salts, the α-naphthyl derivative shows markedly less absorption than the other two.

The spectra of the N-nitrosohydroxylamines vary pronouncedly with *p*H (Table II) in aqueous solution. Since the compounds are weak acids, the spectra in strongly acid solution may be attributed to the undissociated acid, and those in alkaline solutions to the anion. Plots of absorbance at the wave length of maximum absorption of each form lead to the usual S-shaped curves, from which the *pK* values were determined (Table III). The three acids vary only slightly in strength with neocupferron being the strongest and cupferron the weakest.

TABLE II

EFFECT OF *p*H ON THE ULTRAVIOLET ABSORPTION OF AROMATIC N-NITROSOHYDROXYLAMINES[a]

Cupferron			Neocupferron			*p*-Phenylcupferron		
*p*H	A_{253}	A_{284}	*p*H	A_{260}	A_{282}	*p*H	A_{252}	A_{300}
2.06	0.957	0.275	2.30	0.372	0.465	2.39	0.375	0.256
2.78	.870	.290	3.40	.455	.507	3.22	.386	.260
3.93	.715	.560	3.62	.504	.540	3.80	.395	.272
4.46	.568	.780	4.12	.610	.604	4.10	.700	.451
5.62	.430	1.04	4.73	.705	.660	5.78	.885	.550
11.33	.420	1.06	5.62	.750	.695	11.20	.900	.580
			11.10	.755	.700			

[a] Lower wave length in the case of each compound is that of characteristic absorption of the acid: upper wave length is that of the anion. The concentrations are 8.9×10^{-5} *M* for cupferron, 2.6×10^{-4} *M* for neocupferron and 6.3×10^{-5} *M* for *p*-phenylcupferron.

TABLE III

pK_a VALUES OF AROMATIC N-NITROSOHYDROXYLAMINES AS DETERMINED SPECTROPHOTOMETRICALLY

Cupferron		Neocupferron		*p*-Phenylcupferron	
λ, mμ	pK_a	λ, mμ	pK_a	λ, mμ	pK_a
253	4.10	260	3.91	252	4.00
284	4.13	282	3.90	300	3.94

Infrared.—It was hoped that appreciable differences in the behavior of zirconium and hafnium compounds might be found in a property such as infrared absorption, which might be expected to depend on the large difference in mass which exists between these two metals.

The infrared spectra in Nujol mull of the Group IVB metal salts of *p*-phenylcupferron and of the free acid were studied; the absorption bands together with those of the zirconium and hafnium chelates of cupferron and neocupferron are summarized in Table IV. Attempts to obtain infrared spectra of these compounds in chloroform solution failed due to the rapid decomposition of the sample at the relatively high concentrations required.

Only minor shifts occur in the wave length of maximum absorption as the metal atom is changed while the anion is kept constant, although there are some marked changes from the spectrum of the free acid. All of the chelates absorb in seven wave length regions; two of these regions of common absorption (7.38–7.50 and 8.20–8.28 μ) are not present in the free acid, three at 9.35–9.35, 10.72–10.88 and 13.14–13.20 μ are shifted in wave length in going from the acid to the chelate, and two at 7.6–7.75 and 9.80–9.96 μ are not appreciably shifted when chelation occurs. It therefore seems probable that the absorption in the regions of 7.4 and 8.2 μ results from chelation of the metal by the aromatic N-nitrosohydroxylamine.

The failure of the infrared spectra to show any marked changes as the metal is varied could possibly result from the formation of a symmetrical molecule, which is easily postulated. The three absorption bands that shift as the metal atom is changed, all shift in the same direction. For the absorption at 7.4 μ which appears on chelation, the titanium species absorbs at 7.40, zirconium at 7.45, hafnium at 7.44 and thorium at 7.50. Thus, zirconium and hafnium appear to be intermediate between titanium and thorium but equal to each other in effect. Similar shifts are observed for the bands that occur at 8.66 and 10.90 μ in the spectrum of the free acid. Since zirconium and hafnium introduce the same shift in all cases, which is midway between those due to titanium and thorium, it seems reasonable to assume that it is the size of the ion which is influencing the frequency shift rather than its mass. If this is the case, these frequencies would appear to arise from the chelate ring since this is where the size of the metallic ion would exert the greatest influence. In each case the absorption band of the hafnium compound occurs at slightly shorter wave length than the corresponding band in the zirconium chelate; the difference is, however, much too small to be considered significant.

Polarographic Behavior.—The polarographic studies were carried out in 1:1 methanol–benzene solution saturated with chelate. N,N-Dimethylformamide, dioxane, various Cellosolves and polyalcohols, acetone, ethyl ether, methyl ethyl ketone, acetonitrile, methanol, ethanol, pyridine and glacial acetic acid were ineffective as polarographic solvents; chloroform, in which the chelates are soluble, could not be used inasmuch as it is itself polarographically active.

Since it was necessary to use saturated solutions of the metal chelates to obtain reasonable wave heights, only the half-wave potentials, $E_{1/2}$ are given (Table V). In most cases, $E_{1/2}$ in acidic solution is approximately that of the free N-nitrosohydroxylamine, which indicates that the dissolved chelate is probably destroyed in the acidic solution; in neutral solution, however, $E_{1/2}$ values for the chelates are all considerably more positive than those of the parent compounds.

In acid solution, $E_{1/2}$ for titanium cupferrate is apparently that of Ti(IV); there is also a poorly defined wave starting more positive to −0.8 v. and running into the hydrogen discharge wave, which may be the cupferron wave. The ratio of the wave heights in the case of titanium neocup-

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(2) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952.

TABLE IV

INFRARED ABSORPTION BANDS OF VARIOUS ACID FORMS AND CHELATES OF AROMATIC N-NITROSOHYDROXYLAMINES IN NUJOL MULL (WAVE LENGTH IN μ)

ZrCup$_4$[a]	HfCup$_4$	ZrNcup$_4$[a]	HfNcup$_4$	HPcup[a]	TiPcup$_4$	ZrPcup$_4$	HfPcup$_4$	ThPcup$_4$
				5.24				
5.90	5.92							
				6.26	6.25	6.27	6.26	6.25
				6.36				
		6.62	6.62					
		6.69	6.68	6.74	6.72	6.74	6.72	6.72
		7.16	7.16	7.06	7.06	7.08	7.07	7.07
7.38	7.40	7.50	7.48		7.40	7.45	7.44	7.50
7.73	7.75	7.68	7.66	7.69	7.68	7.70	7.68	7.70
		7.97	7.96					
8.26	8.28	8.20	8.20		8.25	8.25	8.25	8.26
8.45	8.44	8.35	8.34		8.50	8.56	8.55	8.60
8.62	8.62			8.66				
		8.85	8.85					
					9.05	9.05	9.04	9.05
				9.15				
					9.36	9.36	9.34	9.35
9.35	9.41	9.45	9.43	9.45				
9.85	9.86	9.85	9.80	9.96	9.96	9.96	9.95	9.95
		10.10	10.10	10.35				
10.74	10.74	10.88	10.84		10.60	10.72	10.70	10.82
				10.90				
		11.77	11.77	11.94	11.90	11.90	11.92	11.91
12.20	12.20	12.35	12.35					
		12.63	12.61					
13.14	13.14	13.18	13.18	13.12	13.16	13.20	13.20	13.20
13.25	13.25							
13.33	13.32							
				14.02				
14.50	14.58			14.45	14.45	14.45	14.45	14.45
14.92	14.92							

[a] Cup, Ncup and Pcup represent the anions of cupferron, neocupferron and phenylcupferron, respectively.

TABLE V

HALF-WAVE POTENTIALS, VOLTS, OF THE GROUP IVB METAL CHELATES OF AROMATIC N-NTIROSOHYDROXYLAMINES IN 1:1 BENZENE-METHANOL SOLUTION AT 25°

Cation	Cupferron	Neocupferron	p-Phenylcupferron
	Supporting electrolyte, 0.2 N H_2SO_4		
NH_4	−0.796	−0.748	−0.698
Ti	− .31	− .28, −0.74	− .76
Zr	− .82		− .68
Hf	− .83		− .66
Th		− .74, −1.02	− .94
	Supporting electrolyte, 0.3 M LiCl		
NH_4	−1.6	−1.6	−1.6
Ti	−0.90, −1.09 −1.40	−0.88, −1.05 −1.36	−1.02, −1.50
Zr	−1.23, −1.50	−1.26, −1.57	−0.38, −1.54
Hf	−1.28, −1.48	−1.26, −1.52	− .40, −1.56
Th		−1.32, −1.58	

ferrate is 1:23, which is about that expected for the reduction of one Ti (1e) and four cupferrons (24e).

The wave heights for the neutral solutions containing zirconium, hafnium and thorium compounds are about 1:2 and the waves probably represent the two-stage (2e and 4e) reduction of the cupferrons. The wave height ratio for titanium solutions is 0.5:1:2 which corresponds to Ti(IV) reduction (1e) and the two-stage cupferron reduction. All waves of the p-phenylcupferrates are small due to the low solubility of the chelates; the more positive $E_{1/2}$ values for the zirconium and hafnium compounds possibly indicate a stronger complex with the intermediate reduction compound of the p-phenylcupferron.

Solubility.—The chelates of the Group IVB metals with the three cupferrons are extremely insoluble in water and in 10% sulfuric acid with the exception that the thorium salts are very soluble in the latter (Table VI). The solubilities were determined by polarographic measurement on the saturated solution and are probably not more accurate than about one order of magnitude, due to the small height of the polarographic waves obtained. The magnitudes of these solubilities indicate why the addition of a reasonable excess of an aromatic N-nitrosohydroxylamine will cause quantitative precipitation of the Group IVB metals even in the presence of a high concentration of a complexing anion such as fluoride.[3]

Dichelate Formation.—Early in the present investigation it was noticed that amperometric titration curves for titanium, zirconium and hafnium in 10% sulfuric acid solution showed a slight gradual increase in current as cupferron was added until approximately one-half of the volume re-

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(3) (a) E. C. Olson and P. J. Elving, *Anal. Chem.*, **26**, 1747 (1954); (b) **27**, 1817 (1955).

TABLE VI

SOLUBILITIES OF THE GROUP IVB METAL CHELATES OF AROMATIC N-NITROSOHYDROXYLAMINES IN 1.8 *M* SULFURIC ACID AND IN WATER AT 25°

Cation	Solubility of indicated compound in moles/l. Cupferron	Neocupferron	*p*-Phenylcupferron
	Solvent, 1.8 *M* H_2SO_4		
Ti	1.1×10^{-6} 9.2×10^{-7}	9.6×10^{-7}	2.5×10^{-8}
Zr	$(2.3, 3.1, 2.8, 2.5$ $2.5, 1.1) \times 10^{-6}$ $(6.4, 3.1) \times 10^{-7}$	1.7×10^{-8}	2.8×10^{-8}
Hf	1.4×10^{-6} $(4.7, 9.2) \times 10^{-7}$	1.7×10^{-8}	2.0×10^{-8}
	Solvent, water		
Ti	2.3×10^{-7}	3.2×10^{-7}	2.5×10^{-8}
Zr	2.3×10^{-8}	1.1×10^{-7}	2.5×10^{-8}
Hf	3.3×10^{-8}	3.3×10^{-8}	8.8×10^{-9}
Th	1.6×10^{-7}	7.6×10^{-8}	8.8×10^{-9}

quired to reach the equivalence point had been added. The current then decreased gradually until the equivalence point was reached. This behavior was initially attributed to the fact that these metals form fairly stable sulfate complexes. To test this postulate, titrations were carried out in 4 *M* perchloric acid. Surprisingly, it was found that there was a much greater increase in current in the latter solution.

Figure 1 shows the titration curves for the same amount of zirconium in both sulfuric and perchloric acid solutions. It was further noticed that, at the beginning of the titration, the precipitate formed when the cupferron was initially added to the solution dissolved slowly and after a few minutes had disappeared completely. No permanent precipitate was formed until the amount of cupferron added was slightly in excess of that calculated on the basis of two cupferron molecules per zirconium atom. Similar results were obtained in the titration of titanium and hafnium.

This phenomenon was studied polarographically. The data (Table VII) indicate a shift of nearly 400 mv. in $E_{1/2}$ of the aromatic N-nitrosohydroxylamine on chelation; the shift always follows the same order, *i.e.*, the greatest shift in $E_{1/2}$ of the chelating agent occurs with hafnium and the smallest with titanium, indicating the titanium chelate to be less stable than the zirconium compound, while that of hafnium is most stable. Unfortunately, the irreversibility of the reduction processes involved invalidates quantitative calculations from these shifts.

TABLE VII

HALF-WAVE POTENTIALS, VOLTS, OF THE GROUP IVB METAL DICHELATES (MA_2^{+2} SPECIES) OF AROMATIC N-NITROSOHYDROXYLAMINES IN 4 *M* PERCHLORIC ACID AT 25°

Cation	Cupferron	Neocupferron	*p*-Phenylcupferron
H	−0.49	−0.46	−0.39
Ti	− .80	− .70	− .72
Zr	− .83	− .79	− .70
Hf	− .90	− .81	− .71

Other qualitative studies confirm the stability of the dichelates formed by titanium, zirconium and hafnium with the three cupferrons. When an aromatic N-nitrosohydroxylamine is added to 4 *M* perchloric acid, the solution begins to turn brown within a few minutes due to the formation of decomposition products. However, if the N-nitrosohydroxylamine is added to a solution of 4 *M* perchloric acid containing titanium, zirconium or hafnium, and the first permanent precipitate formed is removed by filtration, the resultant solution will remain stable, at room temperature, for several days.

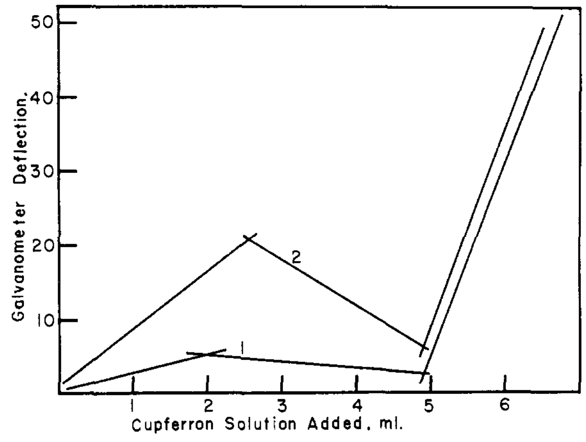

Fig. 1.—Amperometric titration of zirconium with cupferron in (1) 1.8 *M* sulfuric acid and in (2) 4 *M* perchloric acid.

The ultraviolet absorption spectra of the dichelates in 4 *M* perchloric acid were compared with the spectra of the free acids. The shifts in the wave lengths of maximum absorption (Table VIII) and the changes in shape of the absorption spectra again indicate the formation of chelate compounds, although the order of magnitude of the shifts is too small to permit the development of an analytical method for the simultaneous individual determination of zirconium and hafnium.

TABLE VIII

WAVE LENGTHS OF MAXIMUM ABSORPTION, mμ, OF THE GROUP IVB METAL DICHELATES[a] OF AROMATIC N-NITROSOHYDROXYLAMINES IN 4 *M* PERCHLORIC ACID

Cation	Cupferron	Neocupferron	*p*-Phenylcupferron
H	218, 292, 304	254, 269s,[b] 277s, 353	236, 353
Ti	219, 279, 300	241s, 252, 264s, 340	245, 350
Zr	216, 280	218, 244	229, 310
Hf	217, 278	218, 246	230, 307
Th	287	295	250, 307

[a] MA_2^{+2} species. [b] s refers to a shoulder on the absorption curve.

Analytical Application.—The information obtained in the present investigation has been applied to the development of gravimetric and amperometric titrimetric methods for the determination of zirconium, hafnium and titanium under conditions where other analytical methods are less satisfactory.[3,4]

Experimental

Apparatus.—Polarograms were taken at 25°, using a Sargent Model XXI Polarograph (potentials checked poten-

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(4) P. J. Elving and E. C. Olson, *Anal. Chem.*, **28**, 251, 338 (1956).

tiometrically) and a jacketed H-cell[5] containing a reference saturated calomel electrode. Ultraviolet spectra were recorded with a Cary Model 11 spectrophotometer equipped with 1-cm. glass-stoppered quartz cells, and infrared spectra with two Perkin-Elmer Model 21 spectrophotometers and sodium chloride cells.

Chemicals.—Standard metal solutions were prepared by dissolving (a) National Bureau of Standards titanium dioxide, Sample No. 154, according to directions supplied with the sample, (b) pure zirconium metal in boiling concentrated sulfuric acid, (c) purified hafnium dioxide[3b] in a mixture of sulfuric and hydrofluoric acids followed by removal of the fluoride by fuming, and (d) Baker and Adamson reagent grade thorium nitrate.

Perchloric acid solutions of titanium, zirconium and hafnium were prepared by precipitating the metals with cupferron and extracting the cupferrates with chloroform. After washing the chloroform layer several times with water, it was extracted with 1:1 nitric acid; the resulting aqueous layer was evaporated nearly to dryness after the addition of hydrochloric acid. The residue was diluted with nitric and perchloric acids; this solution was repeatedly evaporated to strong fumes of perchloric acid until colorless.

G. F. Smith Chemical Co. reagent grade cupferron (ammonium salt of N-nitrosophenylhydroxylamine, m.p. 162.5–163.5°) was recrystallized.[3a] The neocupferron (ammonium salt of N-nitroso-α-naphthylhydroxylamine, m.p. 124–126°) was prepared essentially by the method of Smith.[6] *p*-Phenylcupferron (ammonium salt of N-nitroso-*p*-xenylhydroxylamine, m.p. 177–179°) was prepared by nitrosation of *p*-xenylhydroxylamine[7] in an ether solution saturated with ammonia.

The nitrogen used to purge solutions of oxygen was passed through a chromous sulfate bath to remove any residual oxygen, then through a sulfuric acid trap to remove spray and finally through a portion of the background solution to obtain vapor pressure equilibration. All other chemicals were of reagent or C.P. grade and were used without further purification.

Photometric Procedures.—In all ultraviolet absorption experiments oxygen was removed from the solvent with purified nitrogen to minimize the effects of air oxidation of the sample. The aromatic N-nitrosohydroxylamine chelates of the Group IVB metals were precipitated in the oxygen-free solution, filtered by centrifugation, followed by suction, and dried *in vacuo*. Their spectra were run as soon as possible after preparation to prevent decomposition. In a few cases the sample was prepared by extracting the organic chelate from aqueous solution with chloroform; the chloroform layer was dried over anhydrous sodium sulfate before being placed in the cell.

The solutions used to observe the dichelate absorption were prepared by adding dilute cupferron compound solution to a solution of the metal in 4 M $HClO_4$ until a permanent precipitate was formed. The solution was then filtered and diluted to give an absorbance of about 1.

The infrared spectra of the Group IVB metal chelates of the aromatic N-nitrosohydroxylamines were run in Nujol mull as soon as possible after the isolation of each of the prepared salts. The samples were prepared in oxygen-free solution, dried and stored in a desiccator under nitrogen until examined.

In the photometric nomenclature used, log $(I_0/I) = A$ (absorbance) $= a_M bc$, where a_M is the molar absorptivity, b is the radiant energy path through the sample in cm., and c is the molar concentration of absorbing species; a_s is the specific absorptivity in grams per liter.

Polarographic Procedures.—A rapid nitrogen stream was passed through the background solution to remove oxygen; a weighed portion of the compound was then dissolved to form the test solution. The polarographic cell was rinsed once or twice with the test solution and then filled with it. The capillary was introduced and a rapid nitrogen stream passed through the cell for 2 to 3 min., during which time the initial potential of the polarograph was set. Nitrogen was then passed over the solution as the polarogram was run. The aqueous test solutions contained 0.01 to 0.02% gelatin as a maximum suppressor.

The solutions of dichelates were prepared as described in the preceding section on photometric procedures.

The amperometric titration procedure has been described.[3]

Solubility Determination Procedures.—The aromatic N-nitrosohydroxylamine salts of the Group IVB metals were prepared and washed with distilled water *via* centrifugation until free from foreign ions. The freshly prepared moist salts were then suspended in either water or 10% sulfuric acid (oxygen-free) and maintained at 25.0 ± 0.05° for a period of 3 hr. with occasional shaking; it had previously been determined that saturation was complete in about 2 hr. In the case of the sulfuric acid suspensions, the polarographic cell was rinsed several times with the suspension; after filling the cell, a rapid nitrogen stream was passed through the cell for 10 min.; the polarogram was then run and the diffusion current measured. By means of standard series curves, the concentration of the particular N-nitrosohydroxylamine in question was determined and the solubility obtained by dividing this concentration by four since each mole of salt that goes into solution produces four moles of N-nitrosohydroxylamine. The aqueous suspensions were filtered and diluted exactly 1:1 with an oxygen-free solution of 20% sulfuric acid. From this point, the procedure was the same as with the sulfuric acid suspensions except that the result obtained was multiplied by 2 to correct for dilution.

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ANN ARBOR, MICHIGAN

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[5] J. C. Komyathy, F. Malloy and P. J. Elving, *Anal. Chem.*, **24**, 431 (1952).

[6] G. F. Smith, "Cupferron and Neocupferron," G. F. Smith Chemical Co., Columbus, Ohio, 1938.

[7] H. Gilman and J. E. Kirby, THIS JOURNAL, **48**, 2190 (1926).