

Figure 1. Reconstructed ion chromatogram (RIC) of a bonded-phase extract of cresote- and pentachlorophenol-contaminated groundwater.

solvent, the method minimizes sample exposure of the technician to possibly hazardous samples. This aspect is important, in view of the increasing demand for analysis of hazardous-waste-related samples. Using this method in the field would avoid the shipment, and possible breakage in transit, of potentially hazardous water samples. New sample preparation methods such as these complement the advanced analytical instrumentation already available today.

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RECEIVED for review May 25, 1984. Accepted August 29, 1984. The use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Synthesis and Chelation Properties of Hydrazones Derived from Isoquinoline-1-carboxaldehyde, 2-Quinoxalinecarboxaldehyde, 4-Isoquinolylhydrazine, and 2-Quinoxalylhydrazine

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The preparation and properties are described of 16 new quinoxalyi- and isoquinolyihydrazones. Several of these afford very high sensitivities for spectrophotometric determinations of transition-metai ions.

In continuation of our work on the synthesis of hydrazones capable of chelating transition-metal ions (1), we have synthesized three additional types and investigated them with regard to chelation of iron(II), cobalt(II), nickel(II), and copper(II) ions. The three types differ from previously studied hydrazones in that they are related to either 2-hydrazinoquinoxaline, quinoxaline-2-carboxaldehyde, or 4-hydrazinoisoquinoline. We have found that several of these new hydrazones provide very high sensitivities in metal ion detection and measurement. They compare very favorably in this regard with previously described hydrazones for which practical analytical applications have been reported (2-7).

EXPERIMENTAL SECTION

Preparation of the Hydrazones. A mixture of 0.004 mole each of a carbonyl compound and hydrazine in 25 mL of absolute ethanol containing 1 drop of glacial acetic acid was heated at reflux for 2 h. The solvent was then evaporated and the hydrazone crystallized from the solvent specified in Table I.

The preparation of the intermediates required for these syntheses was according to methods previously described, summarized in the following sentences. 2-Hydroxyquinoxaline (8) was converted to the 2-chloro derivative (9), which treated with hydrazine (10) yielded the desired 2-hydrazinoquinoxaline. 4-Hydroxyquinazoline (8) was converted to the chloro derivative (11) from which 4-hydrazinoquinazoline (12) was obtained. 2-Methylquinoxaline (13) was oxidized by selenium oxide (14) to obtain quinoxaline-2-carboxaldehyde. Isoquinoline-1-carboxaldehyde was prepared by selenium oxide oxidation of 1methylisoquinoline (15). 4-Aminoisoquinoline was prepared by amination of 4-bromoisoquinoline (16) which was diazotized followed by reduction with stannous chloride (17) to obtain the 4-hvdrazinoisoquinoline.

Chelation Studies. The procedures used to determine the pH ranges over which color formation occurred, wavelengths and molar absorptivities of maximum absorbance, conformance to Beer's law, and ligand/metal ion ratios have been described previously (18-20).

RESULTS AND DISCUSSION

The new compounds are identified in Table I. Except for XIV, XV, and XVI, all formed colored complexes with man-

Table I. Hydrazones and Properties



							analyses					
					orvet		calco				found	
	R_1	\mathbf{R}_2	R_3	mp, °C	solvent	formula	С	Н	N	С	Н	N
I	2-quinoxalyl	н	2-pyridyl	249	C₂H₅OH	$C_{14}H_{11}N_5^{\ a}$				•		
II	2-quinoxalyl	н	2-quinolyl	283	methylcellosolve	$C_{18}H_{13}N_5$	72.23	4.38	23.40	71.75	4.51	23.10
III	2-quinoxalyl	Н	3-isoquinolyl	268	methylcellosolve	$C_{18}H_{13}N_5$	72.23	4.38	23.40	72.14	4.47	23.53
IV	2-quinoxalyl	2-pyridyl	phenyl	222	methylcellosolve	$C_{20}H_{15}N_5$	73.83	4.65	21.52	73.52	4.81	21.17
v	2-quinoxalyl	2-pyridyl	methyl	193	C ₂ H ₅ OH	$C_{15}H_{13}N_5$	68.43	4.98	26.60	68.32	5.18	26.26
VI	2-quinoxalyl	2-pyridyl	2-pyridyl	189	C ₂ H ₅ OH	$C_{19}H_{14}N_{6}$	69.93	4.82	25.75	70.04	4.49	25.91
VII	2-quinoxalyl	н	2-quinoxalyl	325	methylcellosolve	$C_{17}H_{12}N_6$	67.99	4.03	27.99	68.14	4.08	28.18
VIII	2-quinoxalyl	н	1-isoquinolyl	233	C_2H_5OH	$C_{18}H_{13}N_5$	72.23	4.38	23.40	72.06	4.54	23.07
IX	2-pyridyl	н	2-quinoxalyl	256	methylcellosolve	$C_{14}H_{11}N_5$	67.46	4.45	28.09	67.53	4.49	28.26
х	2-quinolvl	н	2-quinoxalvl	298	methylcellosolve	$C_{18}H_{13}N_5$	72.23	4.38	23.40	71.84	4.48	23.31
XI	1-quinazolvl	н	2-quinoxalvl	255	C ₂ H ₅ OH	$C_{12}H_{14}N_6O^b$	64.14	4.43	26.40	64.06	4.50	26.59
XII	2-pyridyl	н	1-isoquinolyl	187	CH ₃ ŎH	$C_{15}H_{12}N_{4}$	72.56	4.87	22.52	72.82	5.13	22.55
XIII	2-quinolvl	н	1-isoquinolyl	209	methylcellosolve	$C_{19}H_{14}N_4$	76.49	4.73	18.78	76.59	4.97	19.03
XIV	4-isoquinolvl	н	2-pyridyl	226	C ₂ H ₅ OH	$C_{15}H_{12}N_{4}$	72.56	4.87	22.59	72.59	5.04	22.54
XV	4-isoquinolyl	н	2-quinolvl	263	methylcellosolve	CIGHIAN	76.49	4.73	18.78	76.31	4.94	18.77
XVI	4-isoquinolyl	Н	2-quinoxalyl	296	dimethylformamide	$C_{18}H_{13}N_5$	72.23	4.38	23.40	71.83	4.58	23.35
^a Prep	^a Prepared in: US Patent 3 600 165 1971. ^b Hydrate.											

Table]	II. P	roperties	of Ir	on(II).	Nickel(II).	and Cor	per(II)	Chelates
		~ ~ p ~ ~ ~ ~ ~ ~ ~ ~ ~	~ ~ ~ ~			/,			

		ir	on(II) chela	te												
		band I		ba	band II nickel(II) chelate			copper(II) chelate								
compd	color	λ	λ	λ	λ	λ	λ	£	λ	ε	color	λ	é	color	λ	e
I	green	494	16 900	625	5 900	gold	500	41 000	gold	492ª	42 000					
II	orange	531	6 000			red	532	44600	orange	521	42600					
III	green	a	а	610	7 900	orange	512	34000	gold	500^{b}	52000					
IV	green	505	17400	646	8 600	orange	509	45400	orange	484^{a}	42700					
V	green	495	12700	642	5 900	gold	487ª	38500	gold	483ª	37600					
VI	green	504	20200	642	9 300	orange	510	48 000	orange	500	48 000					
VII	c	с	с	· c	с	purple	562	42000	purple	571	22700					
VIII	brown	525	20000			orange	534	58500	orange	520	58100					
IX	green	503	28200	675	5060	pink	553	47000	pink	550	28700					
Х	c	с	с	с	с.,	brown	562	40600	brown	571	22500					
XI	orange	512	23000	690	5000	orange	512	54600	orange	497	52500					
XII	green	а	a	600	11300	orange	488	35700	orange	500	29 300					
XIII	orange	а	а	654	9 500	orange	512	52 000	orange	515 ^b	34 400					
XIV–XVI	c	с	С	с	с	c	с	с	c	c	С					

"Absorption of blank also appreciable at this wavelength. "Wavelength not of maximum absorbance but at long wavelength side of band where blank absorption falls off to near zero. "No spectral evidence of chelate formation.

ganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II) over the range in pH from 3 to 11. Visible absorption data are compiled in Tables II and III for ethanol-water (60:40 v/v) solutions of the complexes buffered at pH 7 with ammonium acetate. The metal chelates of VIII and XI are the most intensely absorbing. On comparing the data for these with data for previously reported hydrazones, in Table IV, it is evident that enhanced sensitivity is afforded by a quinoxalyl or quinazolyl in place of a 2-pyridyl in the R_3 group (derived from the aldehyde) of the hydrazone.

Compounds VIII and XI merit consideration as highly sensitive chromogenic reagents in analytical applications. These as well as compound II appear to have potential value as reagents for simultaneous spectrophotometric determination of two or more metals. For example, the spectra of the cobalt(II) and nickel(II) chelates of XII are sufficiently different to enable their simultaneous determination in the absence of copper and iron.

Failure of XIV, XV, and XVI to form colored chelates is believed to be a consequence of steric hindrance. The nitrogen atom of the 4-isoquinolyl group is improperly oriented for participation in chelation, hence only bidentate chelation is possible for these three compounds. However, coordination of three bidentate ligands to satisfy the normal hexacoordinate requirement of the metal(II) ions is sterically hindered by clashing of bulky substituents between two or more bound ligands, as can be seen by steric models of these three compounds. Similar steric effects are well documented in ferroin-type complexes (23).

It was of interest to establish the stoichiometry or the ligand-metal ratio of the complexes and hence the denticity of the ligands. This was accomplished by mole ratio measurements of the formation of the cobalt(II) chelates. As evidenced by the results given in Table III, only VIII chelates as a bidentate ligand, while the others bind in terdentate fashion to form colored chelates. The iron(II) chelate of VIII was also found to have three ligands, thus bidentate rather than terdentate ligands. A possible explanation for the uniqueness of VIII with respect to the others is that its synthesis provided exclusively the syn isomer (the heterocyclic

Table III. Properties of Cobalt(II) Chelates

compd	color	λ _{max} , nm	ε, L mol ⁻¹ cm ⁻¹	ligand/ Co, ratioª	$\log K_{\rm f}$
I	gold	489	25 600	1.93	>12
II	orange	522	38700	2	8.2
III	orange	519	33 200	1.87	>12
IV	orange	531	29 300	2	11.8
v	orange	519	26300	1.97	>12
VI	red	525	30 000	2.02	>12
VII	magenta	556	15000	1.95	8.6
VIII	orange	515	32 000	3	17.0
IX	brown	544	28 000	2	9.0
Х	brown	555	13000	1.80	8.5
XI	orange	494	38100	2	10.1
XII	red	516	36 600	1.97	>12
XIII	magenta	545	36700	2	11.0
XIV-XVI	b	Ь	ь	ь	b

^a Experimental values obtained by a conventional mole ratio plot are expressed by three significant figures; all other were deduced by the α -plot method of Chriswell and Schilt (20). ^bNo evidence of chelate formation.





hydr	azone	mo of				
R ₁	R ₃	Fe	Co	Ni	Cu	ref
2-pyridyl	1-isoquinolyl	11.3	36.6	35.7	29.3	Ь
2-pyridyl	2-quinolyl			62	58	5
pyrazinyl	3-isoquinolyl	38	34	54	58	21
2-pyridyl	3-isoquinolyl	37	44	72	63	21
2-quinolyl	2-pyridyl	10.2	18.0	19.6	22.8	22
2-quinolyl	2-quinolyl				58	4
2-quinoxalyl	2-quinoxalyl	0	15.0	42.0	22.7	b
2-quinoxalyl	1-isoquinolyl	20.0	32.0	58.5	58.1	Ь
4-quinazolyl	2-quinoxalyl	23.0	38.1	54.6	52.5	Ь

^a Expressed in units mL mol⁻¹ cm⁻¹ and at wavelengths of their respective maxima in the visible region. ^bThis work.

groups directed away from the same side of the >C=Nmoiety), which models show can only act as a bidentate (not terdentate) ligand.

The relative stabilities (formation constants) of the co-

balt(II) chelates, listed in Table IV, are of particular interest in revealing that VIII and XII form highly stable as well as intensely colored chelates, ideal for applications as metal ion chelation reagents.

Registry No. I. 16085-64-6; II. 92096-83-8; III. 92096-84-9; IV. 92096-85-0; V, 92096-86-1; VI, 92096-87-2; VII, 92096-88-3; VIII, 92096-89-4; IX, 92096-90-7; X, 92096-91-8; XI, 92096-98-5; XII, 92096-92-9; XII iron(II) chelate, 92096-75-8; XII nickel(II) chelate, 92096-77-0; XII copper(II) chelate, 92096-79-2; XII cobalt(II) chelate, 92096-81-6; XIII, 92096-93-0; XIII iron(II) chelate, 92096-76-9; XIII nickel(II) chelate, 92096-78-1; XIII copper(II) chelate, 92096-80-5; XIII cobalt(II) chelate, 92096-82-7; XIV, 92096-94-1; XV, 92096-95-2; XVI, 92096-96-3; 2-hydrazinoquinoxaline, 61645-34-9; 2-hydrazinopyridine, 4930-98-7; 2hydrazinoquinoline, 15793-77-8; 4-hydrazinoisoquinoline, 92096-97-4; 4-hydrazinoquinazoline, 36075-44-2; pyridine-2carboxaldehyde, 1121-60-4; quinoline-2-carboxaldehyde, 5470-96-2; isoquinoline-3-carboxaldehyde, 5470-80-4; 2-acetylpyridine, 1122-62-9; 2-benzoylpyridine, 91-02-1; bis(2-pyridyl)methanone, 19437-26-4; guinoxaline-2-carboxaldehyde, 1593-08-4; isoquinoline-1-carboxaldehyde, 4494-18-2.

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RECEIVED for review June 22, 1984. Accepted July 17, 1984.