centrated hydrochloric acid. The white crystalline product had a melting point of 202-203.5 °C (decomp) (lit. mp 200 °C) (*5*).

***N*-(2,4,6-Tribromophenyl)glycinamide (*V*).** IV (7.5 g, 0.018 mol) and absolute ethanol (300 mL) were placed in a flask and warmed slightly to dissolve all of the crystals. Then the solution was saturated with anhydrous ammonia while the flask was cooled in ice water. White needles separated after the clear solution stood at room temperature for 3 days. The mixture was cooled in ice water, and the crystals were filtered and washed with a small amount of cold ethanol. A second crop of crystals (1.1 g) was obtained by evaporating the filtrate to a volume of 35 mL and cooling in ice water. The total yield was 6.1 g (89%), mp 185-185.5 °C. The IR spectrum showed absorption bands at 3450 (s, NH), 3300 (s, NH), 1674 (s, C=O), 670 (m, CBr), 603 (w, CBr), and 560 (s, CBr) cm^{-1}.

2,4-Diamino-6-(2′,4′,6′-tribromoanilinomethyl)-1,3,5-triazine (Id). Freshly prepared biguanide (6.1 g, 0.06 mol) in methanol (700 mL) was placed in a flask equipped with a stirrer and a soda lime trap to exclude CO_2. IV (25.0 g, 0.06 mol) was added all at once through a powder funnel. After the solution was stirred for 10 min at room temperature, a white precipitate began to form. After being stirred for 7.5 h, the mixture was allowed to stand overnight. The crystals were filtered and washed with fresh methanol. They were then slurried with water (250 mL), filtered again, and washed with methanol. A crude yield of 21.9 g (81%) was obtained. It was recrystallized by dissolving 21.8 g in 80 mL of hot DMF (125 °C) and then adding 9 mL of water dropwise. When the solution cooled, white crystals separated. A second crop of crystals was obtained from the filtrate. The total recovery was 15.5 g, a yield of 57% based on the theoretical yield of 27.2 g. An analytical sample with a melting point of 250-251 °C was obtained by recrystallizing again from hot DMF and finally washing with cold methanol. The IR spectrum showed absorption bands at 3470 and 3450 (s, doublet, NH), 3320 and 3300 (m, doublet, NH), 1655 and 1633 (s, doublet, NH), 605 (w, CBr), 582 (w, CBr), and 535 (s, CBr) cm^{-1}.

2,4-Bis[bis(hydroxymethyl)amino]-6-(2′,4′,6′-tribromoanilinomethyl)-1,3,5-triazine (VI). Id (25.0 g, 0.055 mol) and 37% aqueous formaldehyde (250 mL) were placed in a 500-mL flask and adjusted to pH 9.2 by the addition of 10 drops of 25% NaOH. It was refluxed for 10 min with stirring. During the reflux period, 4 drops more of 25% NaOH were added. After the solution was cooled to room temperature, the pH was readjusted to 9.1 by adding 4 drops more of 25% NaOH. A white precipitate formed as the mixture cooled. After several hours the mixture was cooled in ice water and diluted with ice water to a volume of ~600 mL to complete precipitation. It was filtered, and the precipitate was slurried with cold water, filtered again, and washed on the filter with more cold water. After being thoroughly air dried, the white crystals weighed 30.3 g (96% yield, mp 137-138 °C (decomp). The IR spectrum showed a broad absorption band at 3320 (s, OH), and bands at 665 (w, CBr), 640 (w, CBr), and 620 (w, CBr) cm^{-1}. All of the bands attributed to NH for Id disappeared for methylolated Id.

Acknowledgment

I thank Nancy M. Morris for the IR spectra.

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Received for review June 13, 1980. Accepted July 30, 1980.

Preparation and Chromogenic Properties of Semicarbazones Containing the Ferroin Group

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The syntheses of a series of semicarbazones containing the ferroin group and their chromogenic reactions with iron, copper, cobalt, and nickel ions are described.

In search of new reagents for spectrophotometric determinations of trace metal ions, eleven semicarbazones, all containing the ferroin group $-N{=}\overset{|}{C}-\overset{|}{C}{=}N-$, were prepared and tested for chromogenic properties in reactions with iron(II), copper(I), cobalt(II), and nickel(II). Four of these (*1*-*4*) have already been synthesized, but none has been evaluated previously as a chromogenic reagent. The semicarbazones are identified in Table I.

Experimental Section

A mixture of 0.006 mol each of semicarbazide hydrochloride and aldehyde or ketone was treated with 7 mL of 1 M sodium acetate. After heating 30 min on the steam bath, the mixture was cooled, and the precipitate removed by filtration and crystallized from the solvent indicated in Table I.

To test for chromogenic properties as a function of pH, we prepared 0.01 M solutions of the semicarbazones in ethanol and added them to 0.002 M test metal ion solutions, adjusted to known pH values with appropriate buffers. The iron(II) and copper(I) oxidation states were attained by addition of ascorbic acid as reductant. All other reagents, standard solutions, and

Table I. Semicarbazones Containing the Ferroin Group $R_1R_2C{=}NNHCONH_2$

compd	R_1	R_2	mp, °C	cryst solvent	formula
I	2-pyridinyl (*1*)	H	206	C_2H_5OH	$C_7H_8N_4O$
II	2-quinolyl (*2*)	H	239	methyl cellosolve	$C_{11}H_{10}N_4O$
III	3-isoquinolyl	H	227	C_2H_5OH	$C_{11}H_{10}N_4O$
IV	2-pyridinyl (*3*)	methyl	204	CH_3OH	$C_8H_{10}N_4O$
V	2-quinolyl	methyl	243	methyl cellosolve	$C_{12}H_{12}N_4O$
VI	pyrazinyl	methyl	227	C_2H_5OH	$C_7H_9N_5O$
VII	2-pyridinyl	phenyl	184	CH_3OH	$C_{13}H_{12}N_4O$
VIII	pyrazinyl	phenyl	210	C_2H_5OH	$C_{12}H_{13}N_5O_2{}^a$
IX	2-pyridinyl (*4*)	2-pyridinyl	223	CH_3OH	$C_{12}H_{11}N_5O$
X	pyrazinyl methyl	2-pyridinyl	203	CH_3OH	$C_{12}H_{12}N_6O$
XI	2-pyridinyl methyl	2-pyridinyl	158	CH_3OH	$C_{13}H_{13}N_5O$

[a] Monohydrate. Satisfactory analyses were obtained for all compounds.

Table II. Chromogenic Properties of Iron(II) and Copper(I) Complexes

	iron(II) complex				copper(I) complex			
compd	color	pH	λ^a	absorpt[b]	color	pH	λ^a	absorpt[b]
I	red	5	490	100				
	blue	9	*c*	*c*				
II	colorless				orange	5	491	2500
III	yellow	5	425[d]	200				
	purple	9	450[d]	900				
IV	red	5	482	500				
	magenta	9	569	769				
V	colorless				purple	5	500	3900
VI	violet	5	550	140				
	green	9	606	460				
VII	colorless							
VIII	violet	5	575	100				
	magenta	9	538	800				
IX	red	5	513	300	gold	5	450[d]	1700
	blue	9	587	3600				
X	red	5	494	320				
	blue	9	579	4900				
XI	orange	5	491	400				
	purple	9	578	5000				

[a] Wavelength (nm) of maximum absorbance in visible region. [b] Approximate absorptivity (L mol^{-1} cm^{-1}) based on assumption that complex is completely formed. [c] Color fades rapidly, preventing measurement. [d] Shoulder.

spectrophotometric procedures were as described elsewhere (*5*).

Results and Discussion

With the exception of II, V, and VII, all the compounds yielded colored iron(II) complexes, consistent with the behavior expected of compounds with ferroin groups. Semicarbazones II and V formed colored copper(I) complexes, indicating that their ferroin groups are similar to that of cuproine, i.e., sterically hindered for octahedral coordination of iron(II) but not for tetrahedral coordination of copper(I) (*6*). Apparently the ferroin group in VII is completely blocked, because it failed to yield colored products with any metal ion tested. None of the compounds yielded colored products with cobalt or nickel ion that were significantly different in color from that of the semicarbazone tested.

In comparison to ferroin-type complexes in general (*6*), the most remarkable property of the iron(II) chelates of the semicarbazones is their decidedly low stability. Modest dilution of strongly absorbing, concentrated solutions of the iron(II) chelates led to pronounced decreases in absorbance. Studies by the mole ratio method (*7*) revealed that the iron(II) chelates were too weak to determine their ligand-to-iron ratios. Deviations from Beer's law were so serious as to preclude reliable measurement of the molar absorptivities of the chelates. The absorptivity values listed in Table II are therefore only approximate and at best only lower limits for the true values.

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Received for review May 16, 1980. Accepted July 25, 1980.