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Chelating Polymers.
III. Chelating Monomers and Polymers from s-Triazinyl Substituted Hydrazinoacetic Acids*

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SUMMARY

The model chelating compounds β-[2,4-bis(dimethylamino)-s-triazin-6-yl] hydrazinoacetic acid, β-[2,4-bis(dimethylamino)-s-triazin-6-yl] hydrazino-N, N-diacetic acid, 2,4-bis(dimethylamino)-s-triazin-6-yl-aminoacetic acid, and 2,4-bis(dimethylamino)-s-triazin-6-yl-iminodiacetic acid have been synthesized and characterized by composition analysis, infrared spectroscopy, and potentiometric titration data. The copper(II), nickel(II), cobalt(II), zinc(II), magnesium(II), and palladium(II) complexes of the first two model compounds, and the copper, nickel, cobalt, and zinc complexes of the third and fourth model compounds have been prepared. The infrared absorption spectra of the model compounds and their complexes were recorded for the range 3800 to 600 cm^{-1}, and the assignment of pertinent bands was made by comparison with reported infrared correlations. In those cases where applicable, shifts in the NH stretching vibration and carboxylate stretching vibration frequencies of the metal complexes were compared to those of the proper references and used as an indication of possible chelation effects in the metal complexes.

The aldehyde-reactable β-[2,4-diamino-s-triazin-6-yl] hydrazinoacetic acid

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*Taken in part from the Ph.D. Dissertation of T. R. Dehner.

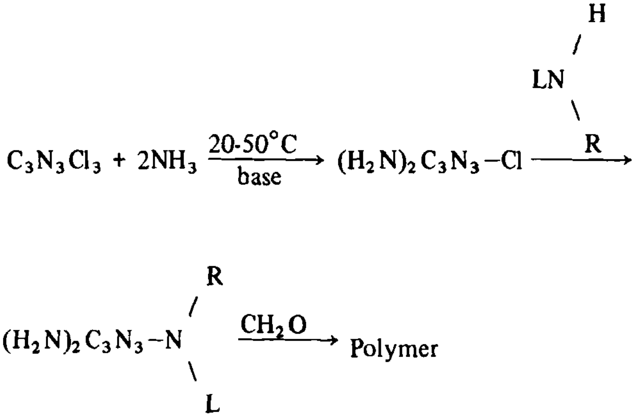
was also prepared and characterized; its polymers were prepared by the reaction of both the free ligand and its copper(II) complex with formaldehyde. Qualitative studies on the reaction of these polymers with metal ions and on the ease of metal ion elution from the polymers indicate that this is a promising chelating polymer system.

INTRODUCTION

Although the use of substituted 1,3,5-triazines to form anion exchange resins has been reported [1, 2], the synthesis of a successful chelating polymer with a triazine matrix has not yet been reported. The condensation polymerization of polyaminotriazines with formaldehyde to form polymers has been studied extensively [3, 4]. The polycondensation reaction proceeds through methylol intermediates, and can be highly controlled by variation of pH, temperature, ratio to reactants, length of reaction time, and method of isolation, to give fusible dimeric, trimeric, etc., oligomers, as well as insoluble, infusible, high-molecular-weight polymers.

It is well known that a chloro group attached to a carbon in the s-triazine ring is reactive toward nucleophilic substitution, behaving chemically in much the same manner as the chloro group in an acid chloride [5-8]. Therefore, amino acids or aminopolycarboxylic acids containing a replaceable amino hydrogen can be attached as potential ligands to the triazine ring by reaction with a chloro-s-triazine in the presence of base.

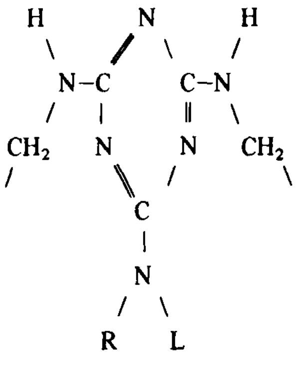
The above facts suggest that selective chelating polymers could be prepared by reacting aminocarboxylic acids with 2,4-diamino-6-chloro-s-triazine, thereby attaching the chelating group to the triazine ring, and then reacting the resulting model compound with formaldehyde under appropriate conditions to give the polymer:



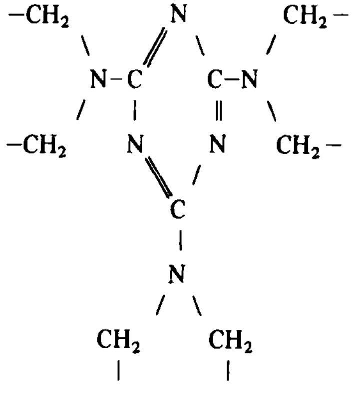
$$C_3N_3Cl_3 + 2NH_3 \xrightarrow[\text{base}]{20\text{-}50^{\circ}C} (H_2N)_2C_3N_3{-}Cl \xrightarrow[R]{\begin{smallmatrix} & H \\ & / \\ LN & \\ & \backslash \end{smallmatrix}}$$

$$(H_2N)_2C_3N_3{-}N\begin{smallmatrix} R \\ / \\ \\ \backslash \\ L \end{smallmatrix} \xrightarrow{CH_2O} \text{Polymer} \tag{1}$$

The symbol LNHR represents any ligand molecule containing an amino or imino moiety and an active hydrogen such as NH_2CH_2COOH, $NH(CH_2COOH)_2$, NH_2NHCH_2COOH, $NH_2N(CH_2COOH)_2$, or $NH_2C_2H_4NHCH_2COOH$. The triazinyl repeating unit of the polymer of Eq. (1) would be expected to have the Structures I and II

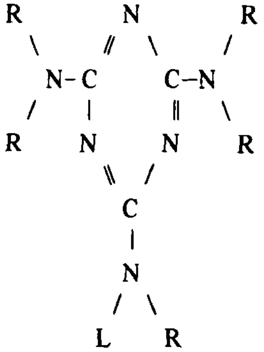


I



II

for which the analogous prototype model compound is Structure III.



III

The literature on the chelating characteristics of compounds of Structure III appears to be nonexistent. Therefore, we decided to follow our previous approaches [9, 10] of first preparing and evaluating those model compounds related in structure to the repeating unit of the polymer as reference points for the polymer studies. Thus, the objectives of this investigation were:

(1) To prepare several model chelating compounds based on amino-triazine-substituted amino acids.

(2) To prepare some transition metal complexes of these model compounds and to characterize these complexes particularly by means of infrared spectroscopy because profile changes and band shifts in the NH stretching vibration region and in the carboxylate stretching vibration regions of the spectra offer evidence for metal-nitrogen and metal-oxygen interactions, respectively.

(3) On evidence of chelating in any of the model compounds, to prepare at least one structurally related polymer and to determine its chelating capabilities.

EXPERIMENTAL

Physical Measurements

All melting points were determined with a Thiele melting point bath and are uncorrected. Decomposition points are recorded as the temperature at which decomposition was initially observed.

Infrared spectra were obtained on a Perkin-Elmer 421 Grating Spectrophotometer for the range 3800 to 600 cm^{-1}.Wave number calibration was made by comparison with polystyrene standard peaks. The potassium bromide disk technique was used to obtain the spectra [11]. Concentrations ranged from 0.8 to 1.2 mg of sample per 300 mg of potassium bromide.

A Beckman Model 76 Expanded Scale pH Meter with glass and saturated calomel electrodes was used for potentiometric titrations.

Thermogravimetric data were obtained on a Dupont 950 Thermogravimetric Analyzer.

Syntheses

Model Compound I: β-[2,4-Bis(dimethylamino)-s-triazin-6-yl]hydrazinoacetic Acid. This compound was prepared by the reaction of hydrazino-N-ethylacetate hydrochloride with 2,4-bis(dimethylamino)-6-chloro-s-triazine.

Preparation of Hydrazino-N-ethylacetate Hydrochloride, $NH_2NHCH_2COOC_2H_5 \cdot HCl$. This compound was prepared by three different methods, all involving the reaction of chloroacetic acid with aqueous hydrazine. All three methods gave the desired product, but the method of Swirska [12] proved the most efficient, giving 30-40% of theoretical yields, and is described here in detail. Hydrazine hydrate (93.7 g of 85% $N_2H_4 \cdot H_2O$, 1.6 mole; Matheson, Coleman, and Bell Co.) and 150 ml of ethyl alcohol were mixed in a 500-ml three-necked flask equipped with stirrer, condenser, and thermometer. Chloracetic acid (45 g, 0.48 mole) was dissolved in 75 ml of ethyl alcohol and added to the hydrazine solution with rapid stirring. The solution was then refluxed for 5 hr. An alcoholic hydrochloric acid solution was prepared by bubbling dry HCl gas through 400 ml of ethyl alcohol until a weight increase of 117 g was observed. As this acid solution was added to the refluxing solution in the flask, a thick white precipitate was formed. After complete addition of the acid solution, the mixture was refluxed one more hour and then filtered while hot. Approximately 125 g of hydrazine dihydrochloride were obtained. Shiny white platelets precipitated from the filtrate as it cooled. The product was collected by filtration and recrystallized from absolute ethyl alcohol. The recrystallized product (26.2 g, 35.5% of theoretical) melted at 148-149°, lit. 148° [12].

Analysis calculated for $C_4H_{11}N_2O_2Cl$: C, 31.00%; H, 7.14%; N, 18.10%. Found: C, 31.04%; H, 7.24%; N, 18.06%.

Preparation of 2,4-Bis(dimethylamino)-6-chloro-s-triazine, $[N(CH_3)_2]_2$-C_3N_3-Cl. Dimethylamine (72 g of 25% aqueous solution, 0.40 mole) was added to 400 g of crushed ice in a 1-liter beaker, and several grams of sodium chloride were added to give a slurry temperature of -7°. Cyanuric chloride (18.5 g, 0.10 mole) was dissolved in 100 ml of hot acetone and filtered into the ice slurry with rapid stirring. The milky white mixture was stirred for 1 hr while the temperature was kept below 15°. The product was collected by filtration and recrystallized from hexane. The white needles (18 g, 90% of theoretical) melted sharply at 69.5-70°, lit, 66-68° [7].

Analysis calculated for $C_7H_{12}N_6Cl$: C, 41.74%; H, 6.00%; N, 34.71%. Found: C, 42.60%; H, 6.21%; N, 34.62%.

Preparation of β-[2,4-Bis(dimethylamino)-s-triazin-6-yl]hydrazinoacetic Acid, $[N(CH_3)_2]_2$-C_3N_3-$NHNHCH_2COOH$. 2,4-Bis(dimethylamino)-6-chloro-s-triazine (8.1 g, 0.04 mole) was dissolved in 60 ml of p-dioxane. Hydrazino-N-ethylacetate hydrochloride (6.5 g, 0.042 mole) was dissolved in 50 ml of 3.0 M aqueous sodium hydroxide solution. The two solutions were mixed in a three-necked flask equipped with stirrer, condenser, and thermometer, and refluxed for 12 hr. A small amount of white solid was then removed by filtration, and concentrated hydrochloric acid solution

(12M) was added to the filtrate until no further precipitation was observed. The final pH of the filtrate was approximately 4-5. The white product was separated by filtration, washed with warm water, and dried in vacuo for 24 hr. Additional product was obtained by partial evaporation of the filtrate. The crude white powder (8.6 g, 84% of theoretical) sublimed at 200-205°. The solid was dissolved in a minimum volume of 3 M hydrochloric acid solution, and then sodium hydroxide solution (6 M) was added dropwise, effecting the recrystallization of the product. The pure material sublimed at 214°.

Analysis calculated for $C_9H_{17}N_7O_2$; C, 42.36%; H, 6.72%; N, 38.40%. Found: C, 42.65%; H, 6.77%; N, 38.32%.

The sodium salt of this compound was isolated by evaporation of a concentrated aqueous solution of the compound at pH 9.

Metal Complexes of β-[2,4-Bis(dimethylamino)-s-triazin-6-yl]-hydrazinoacetic Acid. The general procedure previously published [9] was followed in the preparation of the metal complexes. In this method 0.0055 mole of ligand was dissolved in 5.0 ml of 1.0 M sodium hydroxide solution. The solution was warmed and filtered into 2.5 ml of 1.0 M metal nitrate solution with vigorous stirring. For the Pd complex, K_2PdCl_4 was used as the source of metal ions. A precipitate formed immediately. A few milliliters of deionized water were added and the mixture was stirred periodically over a period of 2 hr and then filtered under reduced pressure. The solid recovered was washed with several portions of hot, deionized water and then dried for 24 hr in vacuo over P_2O_5. The results are summarized in Table 1.

Model Compound II: β-2,4-Bis(dimethylamino)-s-triazin-6-yl-hydrazino-N,N-diacetic Acid. This model compound was prepared by two methods. In the first method, Model Compound I was reacted with chloroacetic acid in the presence of excess base at reflux temperature. In the second method, which gave the best yield, 2,4-bis(dimethylamino)-6-hydrazino-s-triazine was reacted with an excess of chloroacetic acid at reflux temperature.

Preparation of 2,4-Bis(dimethylamino)-6-hydrazino-s-triazine, $(N(CH_3)_2)_2$-C_3N_3-$NHNH_2$. Aqueous hydrazine solution (5.87 g of 85% $N_2H_4 \cdot H_2O$, 0.10 mole) and sodium bicarbonate (8.4 g, 0.10 mole) were mixed with 80 ml of p-dioxane in a 500-ml three-necked flask equipped with condenser, stirrer, and thermometer. 2,4-Bis(dimethylamino)-6-chloro-s-triazine (20.16 g, 0.10 mole) was dissolved in 150 ml of dioxane and added to the mixture in the flask. The mixture was then refluxed for 6 hr while being stirred.

Table 1. Metal Complexes of β-[2,4-Bis(dimethylamino)-s-triazin-6-yl] hydrazinoacetic Acid

Formula	Color	Analysis, % C	H	N	
$Cu(C_9H_{16}N_7O_2)_2 \cdot H_2O$	Green	36.64	5.81	33.23	Calc.
		36.78	5.80	31.80	Found
$Ni(C_9H_{16}N_7O_2)_2 \cdot 2H_2O$	Light blue	35.83	6.01	32.51	Calc.
		35.78	6.25	32.56	Found
$Co(C_9H_{16}N_7O_2)_2 \cdot H_2O$	Pink; lavender when dry	35.82	6.01	32.49	Calc.
		35.66	6.21	32.79	Found
$Zn(C_9H_{16}N_7O_2)_2$	White	37.67	5.62	34.17	Calc.
		37.60	5.74	34.18	Found
$Mg(C_9H_{16}N_7O_2)_2 \cdot 4H_2O$	White	35.74	6.67	32.42	Calc.
		35.58	6.78	32.41	Found
$Pd(C_9H_{16}N_7O_2)_2 \cdot H_2O$	Bright yellow	33.64	5.33	30.54	Calc.
		33.41	5.37	27.54	Found

During this time most of the solid dissolved, and a small amount of sodium bicarbonate was added to keep the pH of the solution between 7 and 8. After 6 hr, the solution was cooled and then evaporated to dryness under reduced pressure. The while solid (30 g) was extracted with four 50-ml portions of dioxane, leaving 10.5 g of white powder. The dioxane solution was evaporated under reduced pressure to a final volume of 25 ml and then cooled. The white solid which precipitated from the cooled solution was collected by filtration and dried in vacuo for 10 hr. The white crystalline solid (12.0 g, 61% of theoretical) melted at 144-145°. The infrared spectrum of the product exhibited two sharp bands in the N-H stretching vibration region.

Analysis calculated for $C_7H_{15}N_7$: C, 42.62%; H, 7.67%; N, 49.71%. Found: C, 42.75%; H, 7.94%; N, 49.68%.

Preparation of β-[2,4-Bis(dimethylamino)-s-triazin-6-yl]hydrazino-N, N-diacetic Acid, $[N(CH_3)_2]_2$-C_3N_3-$NHN(CH_2COOH)_2$· 2,4-Bis(dimethylamino)-6-hydrazino-s-triazine (7.80 g, 0.04 mole) was weighed into a three-necked 100-ml flask equipped with stirrer, condenser, and thermometer. Chloroacetic acid (11.34 g, 0.12 mole) was neutralized with 20 ml of 6 M sodium hydroxide solution and added to the solid in the flask. The mixture was stirred and heated for 1 hr. A clear solution with a pH of approximately 5 resulted. The reaction solution was then stirred and refluxed for 9 hr. During this time the pH of the solution was maintained between 8 and 10 with sodium hydroxide solution. A total of 20 ml of 6 M sodium hydroxide solution was used. Hydrochloric acid solution (approximately 10 ml, 6 M) was added to the cooled mixture to bring the pH to 3. The white precipitate which formed in this process was collected by filtration and dried. The dry product (5.4 g) turned dark at about 200° and decomposed at 220-225°. The product was recrystallized from boiling water. The recrystallized product decomposed sharply at 232° with evolution of gas. Final yields of pure product by this method varied between 50 and 60% of theoretical. The infrared spectrum of the product exhibited a strong carbonyl absorption band at 1740 cm^{-1}.

Analysis calculated for $C_{11}H_{19}N_7O_4$: C, 42.16%; H, 6.11%; N, 31.29%. Found: C, 42.21%; H, 6.21%; N, 30.69%.

Metal Complexes of β-[2,4-Bis(Dimethylamino)-s-triazin-6-yl]hydrazino-N, N-diacetic Acid. The general procedure previously published [9] was followed in the preparation of these complexes. 0.0025 mole of ligand was dissolved in 5.0 ml of 1.0 M sodium hydroxide solution. The solution was filtered into 2.5 ml of 1.0 M metal nitrate solution. The solid formed was washed with hot, deionized water until the washings were clear, and then dried at room temperature in vacuo for 24 hr. The results are summarized in Table 2.

Model Compound III: 2,4-Bis(dimethylamino)-s-triazinyl-6-yl-aminoacetic acid. Preparation of 2,4-Bis(dimethylamino-s-triazin-6-yl-aminoacetic Acid, $[N(CH_3)_2]_2$-C_3N_3-$NHCH_2COOH$. This model compound was prepared by two different methods.

Method A. 2,4-Bis(dimethylamino)-6-chloro-s-triazine (4.03 g, 0.02 mole) was dissolved in 50 ml of dioxane. Glycine (1.65 g, 0.022 mole) was neutralized with 30 ml of 1.0 M sodium hydroxide solution. The two solutions were mixed in a three-necked flask equipped with stirrer, condenser, and thermometer, and refluxed with stirring for 14 hr. During this time the pH of the reaction mixture was maintained between 8 and 10 by addition of sodium hydroxide solution. Hydrochloric acid solution (6 M) was then added to the mixture with stirring, and a white solid precipitated. The solid was separated by filtration, washed with water, and dried in vacuo for 12 hr. The dry product decomposed at 238-243°. The white solid was dissolved in 6 M hydrochloric acid solution and then precipitated by the dropwise addition of 6 M sodium hydroxide solution. The dry, recrystallized produce (2.45 g, 51% of theoretical) decomposed at 244-246°.

Analysis calculated for $C_9H_{16}N_6O_2 \cdot HCl$: C, 39.06%; H, 6.19%; N, 30.37%. Found: C, 39.58%; H, 6.43%; N, 29.66%.

Method B. Glycine (3.75 g, 0.05 mole) was neutralized with 50 ml of 1.0 M sodium hydroxide solution in a 500-ml beaker. Ice was added to the glycine solution to give a slurry with a temperature of -2°. Cyanuric chloride (9.25 g, 0.05 mole) was dissolved in 60 ml of hot acetone and filtered into the stirred slurry over a period of 0.5 hr. The temperature was maintained in the range of -2 to +5° throughout by the addition of ice to the mixture. As the acetone solution mixed with the ice-water slurry, a fine white precipitate was formed. After a few minutes, much of this solid dissolved to form a bright yellow solution. Dimethylamine (40 ml, 25% aqueous) was then added, and the mixture was heated on a steam bath to 60° for 0.5 hr. The solution was kept basic by addition of dimethylamine while the acetone was removed under reduced pressure. The pale yellow mixture was then transferred to a three-necked flask equipped with stirrer, condenser, and thermometer. Dimethylamine (20 ml) was added to the mixture, and the clear yellow solution was refluxed for 4 hr and then stirred overnight. Hydrochloric acid (10 ml, 6 M solution) was added to the re-

Table 2. Metal Complexes of β-[2,4-Bis(dimethylamino)-s-triazin-6-yl]-hydrazino-N,N-diacetic Acid

Formula	Color	Analysis, % C	H	N	
$Cu(C_{11}H_{17}N_7O_4)\cdot 3H_2O$	Blue-green	30.80	5.40	22.86	Calc.
		31.18	5.40	22.96	Found
$Ni(C_{11}H_{17}N_7O_4)\cdot 2H_2O^a$	Pale blue-	32.54	5.21	24.15	Calc.
	green	32.61	5.69	23.75	Found
$Co(C_{11}H_{17}N_7O_4)\cdot H_2O$	Pink	34.03	4.93	25.25	Calc.
	(when dry)	34.24	5.00	24.48	Found
$Zn(C_{11}H_{17}N_7O_4)\cdot 1.6H_2O^b$	White	32.64	5.03	24.21	Calc.
		33.09	5.51	24.20	Found
$Mg(C_{11}H_{17}N_7O_4)\cdot 1.3H_2O^{a,b}$	White	36.81	5.50	27.31	Calc.
		36.45	5.55	26.59	Found

[a] Required heating before precipitate formed.

[b] Thermogravimetric analysis showed 7.1% H_2O for Zn complex and 6.5% H_2O for Mg complex.

action solution, and a white solid precipitated. The solid was collected by filtration, washed with water, and dried in vacuo for 24 hr. Partial evaporation of the filtrate gave another portion of white solid. The crude product (11.7 g, 85% of theoretical) decomposed at 225-235°. The product was dissolved in 6 M hydrochloric acid and precipitated by the addition of 6 M sodium hydroxide solution. The recrystallized solid decomposed at 240-243°. The infrared spectrum of this material was identical to the spectrum of the product from Method A.

Metal Complexes of 2,4-Bis(dimethylamino)-s-triazin-6-yl-amino-acetic Acid. The general procedure previously published [9] was followed in the preparation of these complexes. 0.002 mole of the ligand was added to 15 ml of hot, deionized water. Sodium hydroxide solution (1.0 ml of 1.0 M) was pipetted into the stirred mixture to give a pale yellow solution. Metal nitrate solution (1.0 ml of 1.0 M) was then added, and the mixture which resulted was stirred periodically for 0.5 hr and then filtered. The solid was washed with several portions of warm water and dried in vacuo at 60° for 10 hr. The results are summarized in Table 3.

Model Compound IV: 2,4-Bis(dimethylamino)-s-triazin-6-yl-iminodiacetic Acid. Preparation of 2,4-Bis(dimethylamino)-s-triazin-6-yl-iminodiacetic Acid, $[N(CH_3)_2]_2$-C_3N_3-$N(CH_2COOH)_2$. Disodium iminodiacetate monohydrate (10.0 g, 0.05 mole) was added to approximately 100 ml of an ice-water slurry in a large beaker. Cyanuric chloride (10.0 g, 0.05 mole) was dissolved in 100 ml of hot acetone and filtered into the stirred slurry. A milky white mixture resulted. During this process the temperature of the slurry was maintained between -5 and 0° by the addition of ice. Dimethylamine (20 g of 25% aqueous solution, 0.11 mole) was added to the mixture. The reaction mixture was transferred to a 500-ml three-necked flask equipped with stirrer, condenser, and thermometer, and heated to 50° over a period of 0.5 hr. A clear solution was formed, and the pH dropped to approximately 4. The solution was kept basic by the addition of dimethylamine, as necessary, and was heated to 80° to remove the acetone. The condenser was then attached, and the solution was refluxed and stirred for 7 hr. During this process, dimethylamine was added, as necessary, to keep the pH of the reaction solution between 8 and 10. The solution was then cooled and filtered, and hydrochloric acid solution (10 ml of 6 M) was added to the filtrate to bring the pH to 3. Stepwise evaporation of the solvent under reduced pressure yielded two portions of white solid which, when dry, melted between 190 and 200°. This product was dissolved in a

Table 3. Metal Complexes of 2,4-Bis(dimethylamino)-s-triazinyl-6-yl-aminoacetic Acid

Formula	Color	Analysis, % C	H	N	
$Cu(C_9H_{15}N_6O_2)_2 \cdot H_2O$	Deep blue	38.60	5.76	30.01	Calc.
		37.67	5.77	29.56	Found
$Ni(C_9H_{15}N_6O_2)_2 \cdot 3H_2O$	Pale green	36.56	6.14	28.42	Calc.
		36.62	6.16	27.67	Found
$Co(C_9H_{15}N_6O_2)_2 \cdot H_2O$	Pink	38.92	5.80	30.25	Calc.
		38.95	5.86	27.90	Found
$Zn(C_9H_{15}N_6O_2)_2 \cdot H_2O$	White	38.48	5.74	29.91	Calc.
		38.86	6.16	28.67	Found

minimum amount of 1 M sodium hydroxide solution, and then precipitated by the dropwise addition of 6 M hydrochloric acid solution. The white solid was collected by filtration, washed with water, and dried in vacuo at 60° for 12 hr. The recrystallized product (6.8 g, 45% of theoretical) melted at 208-209°, and decomposed with evolution of gas by 225°.

Analysis calculated for $C_{11}H_{18}N_6O_4$: C, 44.35%; H, 6.07%; N, 28.15%. Found: C, 44.36%; H, 6.82%; N, 27.69%.

Metal Complexes of 2,4-Bis(dimethylamino)-s-triazin-6-yl-iminoacetic Acid. 2,4-Bis(dimethylamino)-s-triazin-6-yl iminodiacetic acid (0.60 g, 0.002 mole) was mixed with 10 ml of deionized water. The pH of this mixture was between 3 and 4. Sodium hydroxide solution (2.0 ml of 1.0 M) was added to the stirred mixture to give a clear solution with a pH between 6 and 7. Metal (II) nitrate solution (1.0 ml of 1.0 M) was added to the ligand solution, and a precipitate began to form after the solution was stirred vigorously for approximately 15 sec. The mixture was stirred periodically for 0.5 hr and then filtered. The solid was washed with cold water and then dried in vacuo at 50° for 20 hr. The results are summarized in Table 4.

β-[2,4-Diamino-s-triazin-6-yl]hydrazinoacetic Acid. Polymers were prepared by the direct condensation of β-[2,4-diamino-s-triazin-6-yl]hydrazinoacetic acid or its copper complex with formaldehyde. The β-[2,4-diamino-s-triazin-6-yl]hydrazinoacetic acid was prepared by the reaction of hydrazinoethylacetate and 2,4-diamino-6-chloro-s-triazine in the presence of excess base by the same procedure used to prepare Model Compound I. The recrystallized product turned yellow at 250°C and dark brown at 260-262°C.

Analysis calculated for $C_5H_9N_7O_2 \cdot HCl$: C, 25.48%; H, 4.24%; N, 41.60%. Found: C, 26.62%; H, 4.24%; N, 43.05%.

The 2,4-diamino-6-chloro-s-triazine was prepared according to the method of Thurston [5] in which cyanuric chloride is reacted with aqueous ammonia at 40-50°. The product did not melt by 320°C.

Analysis calculated for $C_3H_4N_5Cl$: C, 24.74%; H, 2.75%; N, 48.09%. Found: C, 24.61%; H, 2.56%; N, 48.00%.

Preparation and Properties of Polymers

(A) Polymerization of β-[2,4-Diamino-s-triazin-6-yl]hydrazinoacetic Acid with Formaldehyde. Formaldehyde solution (3 ml) was acidified to a pH of approximately 4 by the addition of 15 drops of 0.10 M hydrochloric acid. β-[2,4-Diamino-s-triazinyl]hydrazinoacetic acid (0.20 g, 0.001 mole) was

Table 4. Metal Complexes of 2,4-Bis(dimethylamino)-s-triazin-6-yl-iminodiacetic Acid

Formula	Color	Analysis, %			
		C	H	N	
$Cu(C_{11}H_{16}N_6O_4)$	Blue-green,	36.52	4.71	23.22	Calc.
	blue when dry	36.82	4.82	23.10	Found
$Ni(C_{11}H_{17}N_6O_4)_2 \cdot H_2O$	Pale green	39.37	5.39	25.03	Calc.
		39.28	5.53	25.06	Found
$Co(C_{11}H_{17}N_6O_4)_2$	Pink	40.44	5.23	25.72	Calc.
		40.31	5.31	25.22	Found
$Zn(C_{11}H_{17}N_6O_4)_2 \cdot H_2O$	White	38.98	5.34	24.79	Calc.
		39.36	5.46	24.98	Found

weighed into a 6-ml flask and covered with the formaldehyde solution. A condenser was attached to the flask, and the mixture was refluxed for 1.5 hr. During this time a clear, viscous solution was formed. The solution was cooled, filtered, and transferred to a 5-ml beaker. The beaker was then placed in an oven at 100° for 10 hr. The pale yellow, glassy pellet formed was ground with a mortar and pestle, washed with several portions of deionized water, and then dried in an oven at 110° for 24 hr. The yellow powder (0.30 g, 135% of theoretical for completely crosslinked polymer) turned glassy at 280°.

This reaction was repeated with some modification of the curing procedure. After refluxing for 1 hr, the solution was filtered and adjusted to pH 6 by the addition of sodium hydroxide solution. It was then transferred to a 5-ml beaker and cured in an oven at 60° for 12 hr, and then at 80° for 4 hr. The glassy white pellet formed (0.54 g) was ground into a powder, washed with several portions of water, and then dried in an oven at 110° for 6 hr. The weight of the dry powder was 0.27 g (120% of theoretical for the completely cross-linked polymer).

Analysis calculated for $(C_7H_9N_7O_2)_n$: C, 37.67%; H, 4.06%; N, 43.92%. Found: C, 37.45%; H, 4.32%; N, 39.89%.

(1) Treatment of the Polymer with Metal Ions. A portion of this polymer was stirred in 1 M sodium hydroxide solution for 0.5 hr, and then washed thoroughly with water. Samples of this material were then placed on watch glasses, and metal nitrate solutions (1.0 M) were added dropwise to the white samples. Immediately the solid turned deep green in the copper(II) nitrate solution, leaving a colorless liquid. Nickel(II) nitrate solution caused the solid to turn light green immediately. Cobalt(II) nitrate solution imparted a pink color to the solid. The pink color became more intense as the polymer was stirred in the cobalt solution.

The colored samples were washed with several portions of water, but they retained their respective colors. The samples were then stirred for 0.5 hr in 1 M sodium chloride solution. No fading of the colors was observed during this treatment.

A few drops of 1 M hydrochloric acid solution were then added to the colored samples. In each case, the solid became nearly white, and a colored solution was formed. As the mixtures were stirred some of the solid appeared to dissolve.

Copper(II) nitrate solution was added to a sample of the polymer which had not been treated with sodium hydroxide solution. The solid turned green very slowly.

(2) Impregnation of Filter Paper and Cloth with the Chelating Polymer. β-[2,4-Diamino-s-triazin-6-yl] hydrazinoacetic acid was refluxed with acidic formaldehyde solution in a 5-ml flask for 1 hr. Pieces of white filter paper and cotton cloth were then dipped into the clear, viscous solution. The paper and cloth were then placed in an oven at 100° for 1 hr. The dry paper and cloth had increased in weight by approximately 80%. The remaining solution was diluted with an equal volume of water. Additional pieces of filter paper and cloth were dipped in this solution and then cured in an oven at 100°. The dry paper and cloth showed a weight increase of from 5 to 7%. The dry materials were then soaked in 0.1 M sodium hydroxide solution, dried at 100°, and, finally, washed thoroughly with water and dried at 110°.

(3) Treatment of the Paper and Cloth with Metal Ion Solutions. Solutions of metal nitrates (1 M) were added dropwise to the impregnated paper and cloth. In all cases immediate coloration of the paper and cloth was noted [green with copper(II), pink with cobalt(II), pale green with nickel(II), and brownish-yellow with iron(II)]. The paper and cloth were then soaked in water but the colors remained, although the colors from nickel and cobalt faded noticeably. A plain piece of filter paper was treated with the metal ion solutions in the same manner, but the colors were almost completely washed out by water.

A piece of cloth which had been impregnated with the polymer and then treated with copper(II) nitrate solution was soaked for 6 hr in 1 M sodium cheloride solution. No fading of the green color was observed. The same piece of cloth was then stirred in 0.1 M hydrochloric acid solution for 5 min, and the green color faded considerably. When the cloth was stirred in 1 M hydrochloric acid solution for 1 min, nearly all of the remaining color was washed out. After 0.5 hr in the acid solution the cloth was completely white.

This piece of white cloth was then stirred in 1 M sodium hydroxide solution for 15 min, washed with water until the washings were neutral, and then stirred in 1 M copper(II) nitrate solution for 10 min. The cloth again became light green. This green color, which was much less intense then the original green color before treatment with acid, remained after several washings with water.

(B) Copolymerization of β-[2,4-Diamino-s-triazin-6-yl] hydrazinoacetic acid and 2,4,6-Triamino-s-triazine with Formaldehyde. Formaldehyde solution (3 ml) was acidified by the addition of 10 drops of 1.0 M hydrochloric acid solution to a pH of approximately 3. 2,4-Diamino-6-hydrazinoacetic acid-s-triazine (0.20 g, 0.001 mole) and 2,4,6-triamino-s-triazine

(0.084 g, 0.0067 mole) were weighed into a 6-ml flask and covered with the formaldehyde solution. A condenser was attached, and the mixture was refluxed for 1 hr. A clear, viscous solution resulted. The solution was filtered and brought to pH 6 by the addition of sodium hydroxide solution. The solution was then transferred to a 5-ml beaker and cured in an oven for 2 hr at 60° and then for 8 hr at 90°. The clear white pellet (0.63 g) formed was ground to a powder, washed with water, and then dried at 110° for 12 hr.

Analysis calculated for completely cross-linked polymer: C, 40.47%; H, 3.93%; N, 47.08%. Found: C, 38.38%; H, 4.55%; N, 39.19%.

Treatment of the Copolymer with Copper(II) Nitrate Solution. A sample of the ground copolymer was stirred in 1 M sodium hydroxide solution and heated to 80° for 1 hr. The mixture was then filtered, and the solid was washed with water until the washings were neutral. When this solid was stirred with 1 M copper(II) nitrate solution, it became bright green. The green color did not fade when the solid was thoroughly washed with water.

A portion of this green solid was stirred in 1 M sodium chloride solution for 1 hr. No fading of the green color was noticed, and the addition of concentrated ammonia solution to the filtrate failed to produce any blue coloration.

The green solid was then stirred in 0.1 M hydrochloric acid solution for 15 min. Again, there was no detectable fading of the green color. However, a very pale blue solution resulted when concentrated ammonia solution was added to the filtrate.

The sample was then stirred in 1 M hydrochloric acid solution for 10 min. During this time the green color became progressively lighter. A deep blue solution resulted when concentrated ammonia solution was added to the filtrate. After being stirred in 2.5 M nitric acid solution for 5 min, the polymer was still pale green. None of the solid appeared to dissolve.

This sample was then stirred in 1 M sodium hydroxide solution for 5 min, and then washed thoroughly. A few drops of 1 M copper(II) nitrate solution were added to this sample, and the solid again turned bright green.

(C) Preparation of Polymer from Copper Complex of β-[2,4-Diamino-s-triazin-6-yl]hydrazinoacetic Acid. *Preparation of Bis-[β-(2,4-diamino-s-triazin-6-yl)hydrazinoacetato]copper(II),* $Cu\ (C_5H_8N_7O_2)_2$. Sodium hydroxide solution (3.0 ml of 1.0M) was pipetted into a beaker containing β-[2,4-diamino-s-triazin-6-yl]hydrazinoacetic acid (0.60 g, 0.003 mole). The clear solution was filtered into 1.5 ml of 1.0 M copper(II) nitrate solution.

A green-blue precipitate was formed immediately. The mixture was stirred periodically for 1 hr and then filtered. The solid was washed with water until the washings were clear, and then dried for 10 hr in vacuo. The dry green-blue powder weighed 0.71 g (99% of theoretical).

Polymerization of Copper Complex with Formaldehyde. Bis-[β-(2,4-diamino-s-triazin-6-yl)hydrazinoacetato]-copper(II) (0.23 g) was placed in a 5-ml flask and covered with 3 ml of 37% formaldehyde solution. The mixture was adjusted to pH 8 by the addition of sodium hydroxide solution, and a condenser was attached to the flask. The mixture was then refluxed for 2 hr. The deep green solution which resulted was transferred to a 5-ml beaker and cured in an oven at 80° for 4 hr, and then at 110° for 20 hr. The dark green, glassy pellet formed was ground into a powder. The green powder was then covered with water, adjusted to pH 5, and placed in an oven at 110° for 10 hr. The solid was then stirred in hot water, separated by filtration, and washed until the washings were clear. The initial washings were pale blue. The green solid was dried at 110°; it weighed 0.31 g.

A sample of the polymer was treated successively with 1 M sodium chloride solution, 1 M hydrochloric acid solution, 1 M sulfuric acid solution, and 2.5 M nitric acid solution. No noticeable change in color occurred when the solid was stirred in the sodium chloride solution, and the addition of concentrated ammonia solution to the washings failed to give the characteristic deep blue color of the copper-ammonia complex. Much of the green color was washed out with the hydrochloric acid solution, and the solid became pale blue when it was stirred in the sulfuric acid solution. Addition of concentrated ammonia solution to the washings resulted in a deep blue solution. The green color completely disappeared from the solid when it was washed with the nitric acid solution. A white solid and a pale blue solution resulted.

Experiments with Amberlite Ion Exchange Resin

A few grams of Amberlite IRC-50 Cation Exchange Resin (acid form) were stirred in 1 M sodium hydroxide solution for 2 hr. A small column (0.25 in. diameter) was packed with the resin to a height of 3 in. The resin column was washed thoroughly with deionized, distilled water, and then saturated with 1 M copper(II) nitrate solution. The saturated resin was washed with water until no blue color was detected when concentrated ammonia solution was added to the washings.

Sodium chloride solution (1 M) was then passed through the column at a rate of approximately 30 drops/min. The eluent was tested (5 ml portions) for copper(II) ion by addition of concentrated ammonia solution. The first two portions gave a very deep blue color when ammonia solution was added; the next two a light blue; the fifth a very pale blue. The sixth and seventh 5-ml portions of eluent were colorless when treated with concentrated ammonia solution.

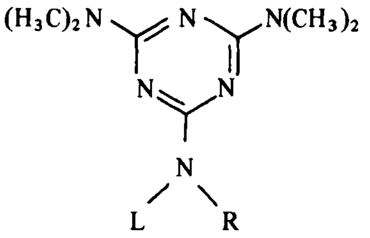
The column was then washed with 1 M sulfuric acid at the same rate. The first two 5-ml portions of eluent were light blue when treated with ammonia solution; the third was very pale blue; the fourth was colorless.

DISCUSSION

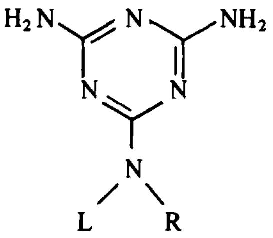
All of the model compounds in this study contain the 2,4-bis(dimethylamino)-s-triazine moiety (IV), instead of the 2,4-diamino-s-triazine moiety (V), even though actual polymerization with formaldehyde requires a replaceable hydrogen on the amino function of the substituted triazine. The dimethylamino derivative was used for the following reasons:

(1) The structure of the dimethylamino-s-triazine (IV) is more closely related to the structures in polymers I and II than is the aminotriazine (V).

(2) The aminotriazines exhibit several absorption bands in the N-H stretching vibration region of the infrared spectrum. Since this region was used to determine possible chelation effects in the metal complexes of the model compounds, it was desirable to have this region as free as possible from interfering absorption bands.



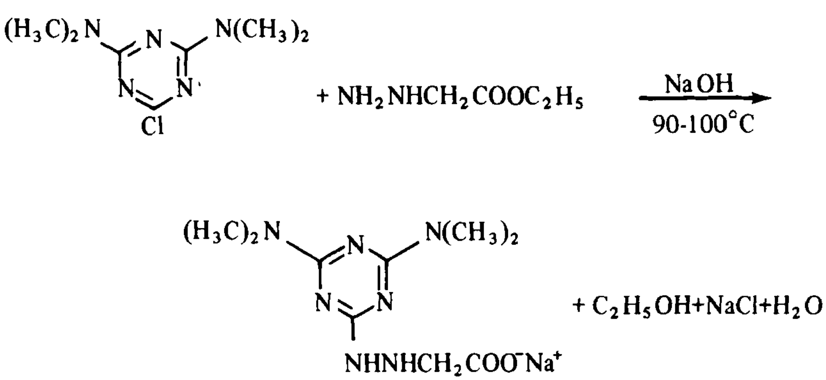
IV



V

Model Compound I: β-[2,4-Bis(dimethylamino)-s-triazin-6-yl]-hydrazinoacetic Acid and Its Metal Complexes

The reaction of 2,4-bis(dimethylamino)-6-chloro-s-triazine with hydrazinoethylacetate hydrochloride in 1:1 dioxane-water solution at reflux temperature and in the presence of excess base gave the free acid, β-[2,4-bis(dimethylamino)-s-triazin-6-yl]hydrazinoacetic acid, in good yield. The reaction conditions allowed not only the attachment of the hydrazino function to the triazin ring, but also the hydrolysis of the ester. The analysis of the product obtained from this reaction is in good agreement with the empirical formula for β-[2,4-bis(dimethylamino)-s-triazin-6-yl]-hydrazinoacetic acid. The product exhibited amphoteric properties typical of amino acids and related compounds. The potentiometric titration curve indicates pH 4.3 as the approximate isoionic point, and 6.3 as the apparent pK_a.



(2)

The metal complexes of β-[2,4-bis(dimethylamino)-s-triazin-6-yl]hydrazinoacetic acid all precipitated immediately when the ligand and metal ion solutions were mixed. The analyses of the complexes are in good agreement with the empirical formulas for a 1:2 ratio of metal-to-ligand and indicate that all of the complexes except zinc are hydrated. Hydration is supported by thermogravimetric curves, which show gradual weight loss between 60 and 200°C, followed by decomposition, for all but the zinc complex, which shows no measureable weight loss up to 200°C.

Although many infrared spectra of triazine derivatives have been published, the detailed correlation of absorption bands with specific molecular vibrations has received comparatively little attention. s-Triazine exhibits two strong absorption bands at 1560 and 1410 cm^{-1} which have been attributed to ring vibrations [13]. Similar bands have been found in the same region in the spectra of many triazine derivatives [14]. The exact positions and number of these bands appear to be highly dependent upon the nature of the ring substituents. In the spectrum of cyanuric chloride two strong bands are found at 1475 and 1450 cm^{-1}, while in the spectra of 2,4,6-triamino-s-triazine and 2,4,6-trihydroxy-s-triazine a series of four or five bands are found between 1400 and 1700 cm^{-1} [14]. In addition, the spectra of most triazine derivatives exhibit one or more strong absorption bands around 800 cm^{-1} [14]. Table 5 shows the positions of the major bands of several triazine derivatives of interest for comparison. The similarity of the spectra of 2,4-bis(dimethylamino)-s-chloro-s-triazine and 2,4-bis(butylamino)-6-chloro-s-triazine should be noted. The bands between 2800 and 3100 cm^{-1} are attributed to C-H stretching vibrations. Table 5 illustrates the many spectral changes that result from changing the substituents on the triazine ring. The strong and broad absorptions of the 2,4-bis(dimethylamino)-s-triazine nucleus between 1300 and 1600 cm^{-1} and the shifting of these bands upon further substitution caused difficulties in the interpretation of the spectra of the model compounds and their complexes.

The infrared spectrum of the ligand has a broad band at 3025 cm^{-1} and another band at 3000 cm^{-1}. These are attributed to NH and NH_2 + stretching vibrations. A series of weak shoulders is also evident in the 3000-2000 cm^{-1} region, which is also characteristic of a protonated amine group. The spectrum of the sodium salt of the ligand has absorption bands at 3290 and 3280 cm^{-1} which are attributed to NH stretching vibrations. The hydrochloride salt of the ligand exhibits a very broad profile absorption in the 3400-2000 cm^{-1} region of the spectrum. The fact that both NH stretching absorption bands are shifted in going from the sodium salt to the ligand and from the ligand to the acid salt indicates that both of the hydrazino hydrogens are involved in hydrogen bonding in the ligand and in the acid salt. This would also account for the low intensity and the broadness of the NH absorptions. Investigation of molecular models predicts extensive intramolecular hydrogen bonding.

In the spectra of both the ligand and the sodium salt there is a very broad absorption profile between 1700 and 1460 cm^{-1} which prohibits any definite assignment of the carboxylate antisymmetric vibration frequency that is expected around 1560-1600 cm^{-1}. This broad absorption is probably due to a combination of ring vibration absorptions, carboxylate stretching vibration absorption, and NH_2^+ deformation absorption, all of which are expected in this region. A definite profile change is evident in

Table 5. Major Infrared Bands for Some Triazine Derivatives

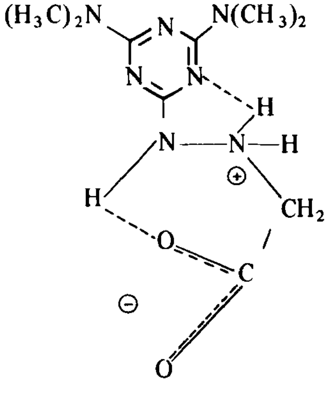
$C_3N_3H_3$	$C_3N_3Cl_3$	$C_3N_3(NH_2)_3$	$C_3N_3(OH)_3$	$[(CH_3)_2N]_2C_3N_3Cl$	$[(C_4H_9)_2N]_2C_3N_3Cl$	$[(CH_3)_2N]_2C_3N_3NHNH_2$
		3320	3400	3005	3250	3360
		3140			3120	3320m
						3205m
			2980s,b	2940	2940	2940
			2770	2875		2870
				2800		2800
			1720s,b			
		1660	1640sh	1597sh	1640	1500-1650v.b.,s
		1630				1630sh
1560	1550sh	1565		1560	1560s	1560sh
				1520	1520sh	1520s
	1475s,b	1470	1470	1482		1490sh
	1450	1440			1405	1460sh

	1360		1390	1392	1360	1385s
1410	1315			1300	1312	1295
	1275s,b					1235
						1214
1170				1192		1190
					1095	
			1050	1040		1050
			980b	980	985	980
	877					
	847					
		810		828		
	794		770s,b	787	795	803
735			750		740b	
673						

this region when the spectra of the ligand and its sodium salt are compared. The maximum of this broad band is at a lower frequency (1520 cm^{-1}) for the sodium salt than for the ligand (1560 cm^{-1}). In the spectrum of the hydrochloride salt of the ligand there are several absorption peaks in this region, at 1720, 1650, 1625, 1585, 1560, 1528, and 1470 cm^{-1}. The band at 1720 cm^{-1} is attributed to the carboxyl stretching vibration.

The carboxylate symmetric stretching vibration absorption is expected at about 1400 cm^{-1} in the spectra of the ligand and its sodium salt [15, 16]. The band at 1390 cm^{-1} is too strong for this absorption, and also appears in the spectrum of 2,4-bis(dimethylamino)-6-chloro-s-triazine. This band, in the spectra of the ligand and its sodium salt, is possibly a combination of absorptions from CH_3 symmetric deformation vibrations, carboxylate symmetric stretching vibrations, and ring vibrations.

The NH_2^+ absorption, the broadening in the 1600 cm^{-1} region, and the absence of the carboxyl absorption in the spectrum of the ligand all indicate the zwitterion structure (VI) for the ligand.



VI

Several other differences are evident when the spectra of the ligand and its sodium salt are compared with each other and with the spectrum of 2,4-bis(dimethylamino)-6-chloro-s-triazine, but no definite correlations can be stated. It should be noted that three strong absorption bands present in the spectrum of 2,4-bis(dimethylamino)-6-chloro-s-triazine (1482, 980, and 828 cm^{-1}) are not found in the spectrum of β-[2,4-bis(dimethylamino)-s-triazin-6-yl]hydrazinoacetic acid. Profile differences between those spectra in the 1500-1600 cm^{-1} region are also evident.

The NH stretching vibration frequencies for the complexes in this series are:

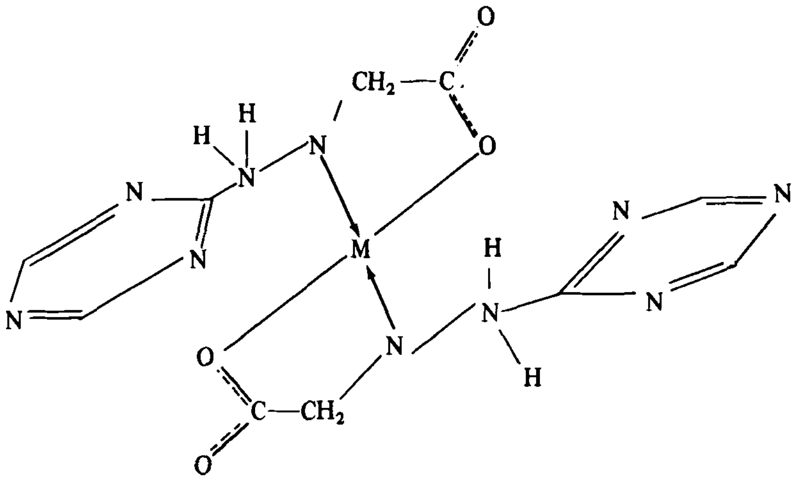
Palladium(II) complex	3140 cm^{-1}
Copper(II) complex	3170 cm^{-1}
Zinc(II) complex	3220 cm^{-1}
Nickel(II) complex	3240 cm^{-1}
Cobalt(II) complex	3250 cm^{-1}
Magnesium(II) complex	3260 cm^{-1}

The shift toward a lower frequency when compared to the uncoordinated sodium salt at 3290 cm^{-1} is, in each case, an indication of nitrogen-to-metal bonding of some covalent character. The metal nitrogen interaction appears to be considerably stronger for palladium and copper than for the other metal ions. From the infrared spectral evidence, the relative strengths of the M–N bonds appear to be: Pd > Cu > Zn > Ni > Co > Mg. This is essentially the same order as reported in studies of amino acid complexes with these metal ions [15-18]. The low intensities of the N–H stretching absorption bands are quite surprising, but may be due to strong hydrogen bonding of the amino hydrogen to the nitrogen of the triazine ring. Investigation of molecular models of the complexes indicates that this type of hydrogen bonding is expected.

Again, the broad absorption in the 1500-1600 cm^{-1} region prohibits any definite assignments for the carboxylate antisymmetric stretching vibration frequencies in the spectra of the metal complexes. However, there is a definite broadening on the high-frequency side of the absorption profile in this region in the spectra of all of the complexes compared to the same region in the spectrum of the soidum salt. This profile change suggests definite metal-oxygen interaction in the metal complexes. The relative shapes of the absorption profiles suggest that this interaction is strongest in the palladium and copper complexes.

The remaining portions of the spectra of the metal complexes are very similar to each other and to the spectrum of the sodium salt. Some variations in relative peak intensities are evident, but no correlations have been attempted. The carboxylate symmetric stretching vibration frequency, expected around 1370-1450 cm^{-1}, is apparently hidden by the strong absorption band at 1390 cm^{-1}.

The spectra of these complexes were also obtained from mineral oil



VII

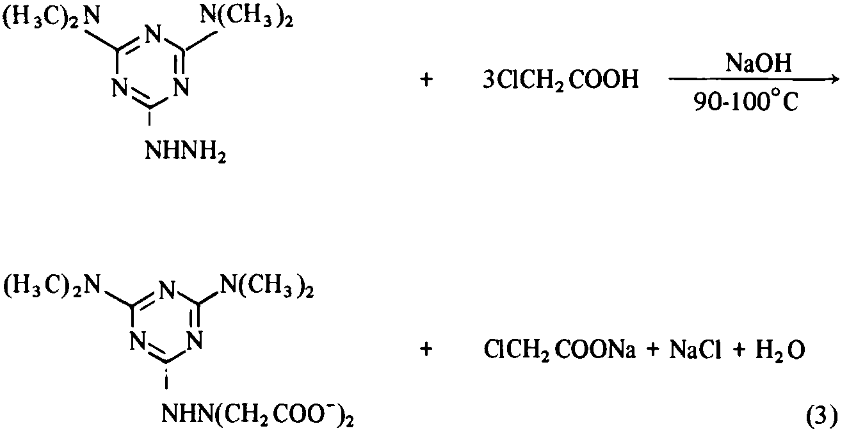
mulls. No significant differences were noted between these spectra and those obtained from potassium bromide pellets.

The spectra of the metal complexes, as compared to the spectra of the ligand and its sodium salt, indicate chelation of the metal ion to the nitrogen and oxygen of the hydrazinoacetic acid moiety. The structure of the complexes is probably similar to that found for glycine chelates with the same metal ions [19, 20], in which the two ligands are arranged in a trans-planar form about the central metal ion (VII). Similar structures have been proposed for transition metal complexes of N-phenylglycines and N-arylglycines [9, 21]. The trans-octehedral positions are probably occupied by water molecules or the carbonyl oxygen of adjacent complexes in the crystal lattice, as found in the cadium and zinc complexes of glycine [20].

Model Compound II: β-[2,4-Bis(dimethylamino)-s-triazin-6-yl]-hydrazino-N,N-diacetic Acid and Its Metal Complexes

2.4-Bis(dimethylamino)-6-hydrazino-s-triazine was prepared in good yield by the reaction of 2,4-bis(dimethylamino)-6-chloro-s-triazine in dioxane solution with aqueous hydrazine at reflux temperature. The infrared spectrum of this product exhibits three bands in the NH stretching vibration region (3360, 3320, and 3205 cm^{-1}), as well as extensive broadening in the 1600 cm^{-1} region compared to the spectrum 2,4-bis(dimethylamino)-

6-chloro-s-triazine. This broadening is probably due to NH_2 bending vibration absorption. In addition, there appears to be some shifting of the triazine ring absorption bands in this region of the spectrum. The potentiometric titration curve for the product indicates an apparent pK_a of 5.6 for this compound.



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The analysis of the product obtained from the reaction of 2,4-bis(dimethylamino)-6-hydrazino-s-triazine with chloroacetic acid is in good agreement with the empirical formula for β-[2,4-bis(dimethylamino)-s-triazin-6-yl]hydrazino-N,N-diacetic acid. The product exhibited amphoteric properties typical of amino acids and related compounds. The potentiometric titration curve indicates apparent pK_a's of 3.9 and 7.8 for the product.

The copper, cobalt, and zinc complexes of β-[2,4-bis(dimethylamino)-s-triazin-6-yl]hydrazino-N,N-diacetic acid all precipitated immediately when the ligand and metal ion solutions were mixed. The nickel and magnesium complexes required heating before precipitation occurred. The analyses of all of the metal complexes are in agreement with the empirical formula for a 1:1 ratio of metal-to-ligand. This is true even of the copper complex which was prepared from a 1:2 metal ion-ligand reactant ratio.

Elemental analyses also indicate that all of the complexes are hydrated. This is supported by the infrared spectra of the complexes and by thermogravimetric data. In the thermogravimetric determinations, the complexes were heated under nitrogen at a rate of 15°min. The data for these complexes are given in Table 6. All of the complexes showed gradual weight loss between 50 and 225°, followed by decomposition between 250 and 325°C.

Table 6. Thermogravimetric Data for Metal Complexes of 2,4-Bis(dimethylamino)-s-triazin-6-yl—hydrazino-N,N-diacetic Acid

Complex	Temperature (°C)	Initial weight (mg)	Weight loss (mg)	% Loss	#H_2O	Initial decomposition temperature (°C)
Cu	225	9.4	1.2	12.7	3.0	210
Ni	225	9.6	0.8	8.3	0.9	250
Co	225	2.06	0.07	6.8	1.5	250
Zn	200	9.9	0.7	7.1	1.6	250
Mg	225	10.8	0.7	6.5	1.3	275

The infrared spectrum of the ligand exhibits a very broad profile absorption from approximately 3400 to 2400 cm^{-1}, which is attributed to OH, NH, and NH^+ stretching vibrations. The broadness of this absorption indicates extensive hydrogen bonding in the ligand. The shoulders at 3180 and 3060 cm^{-1} are probably NH stretching vibration absorptions, while the broader peak at 2800 cm^{-1} is probably due to the NH^+ group. Comparison of this spectrum with those of the first model compound and the hydrazinotriazine intermediate shows the very marked change in the 3400-2400 cm^{-1} region.

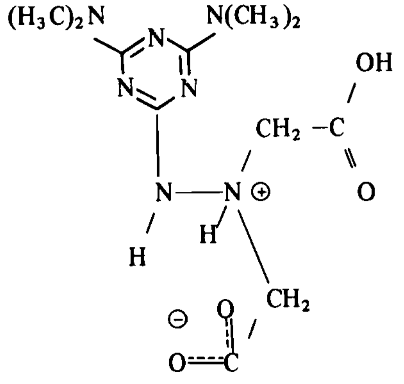
In the spectrum of the disodium salt of the ligand this very broad profile absorption is replaced by a weak band at 3400 cm^{-1} which is probably due to the NH stretching vibration.

The strong band at 1735 cm^{-1}in the spectrum of the ligand is attributed to the carboxyl group, and disappears in the spectrum of the disodium salt. The very broad and strong absorption profile in the 1500-1650 cm^{-1}region in the spectrum of the ligand is probably a composit of ring vibration absorption and carboxylate stretching vibration absorption. In the spectrum of the disodium salt of the ligand, this broad absorption is replaced by two sharp, strong bands at 1592 and 1555 cm^{-1}. The band at 1592 cm^{-1} is probably the carboxylate antisymmetric stretching vibration absorption, whereas that at 1555 cm^{-1} may be a ring vibration absorption.

Several other spectral changes are noticeable when the spectra of the ligand and its disodium salt are compared with each other and with the spectrum of 2,4-bis(dimethylamino)-6-hydrazino-s-triazine, but no definite correlations can be made. The carboxylate symmetric stretching vibration absorption is expected in the 1350-1450 cm^{-1} region in the spectra of the ligand and its sodium salt, but this region is too complex to make any definite assignment. However, changes in the profile of the strong band at 1390 cm^{-1} are noticeable.

The profile NH^+ absorption, the carbonyl absorption, and the broad absorption in the 1600 cm^{-1} region in the spectrum of the ligand, together with the potentiometric titration data, suggest the zwitterion structure (VIII) for the ligand.

The infrared spectra of the copper, nickel, cobalt, and zinc complexes of β-[2,4-bis(dimethylamino)-s-triazin-6-yl]hydrazino-N,N-diacetic acid are nearly identical. All exhibit a shoulder near 3400 cm^{-1} which is attributed to water of hydration, and a broad band at 3200 cm^{-1} which is attributed to NH stretching vibrations. This band is strongest in the nickel complex. In addition to the broad band at 3200 cm^{-1}, the spectrum of the magnesium complex has a strong and sharp absorption band at 3390 cm^{-1}. This is the



VIII

OH stretching vibration region of the spectrum, and the band is probably due to water of hydration. If so, the water is apparently bound differently in this complex than in the other complexes.

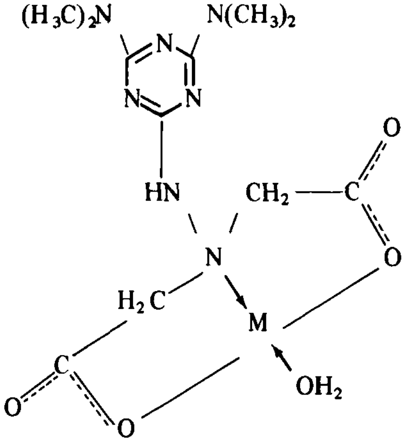
Since the nitrogen which is expected to be involved in chelation is a tertiary nitrogen in this ligand, the NH stretching vibration region of the infrared spectrum can offer no direct evidence either supporting or contradicting nitrogen-to-metal bonding in the metal complexes. However, it should be noted that the broad profile absorption attributed to NH^+ in the spectrum of the ligand is not found in the spectra of the complexes.

The carboxyl absorption band at 1735 cm^{-1} in the spectrum of the ligand is not found in the spectra of the metal complexes.

The spectra of the copper, nickel, cobalt, and zinc complexes appear to be identical in the 1500-1650 cm^{-1} region. The absorption band at 1592 cm^{-1} is attributed to the carboxylate antisymmetric stretching vibration. The fact that this absorption is at the same frequency for all four of the complexes as well as for the disodium salt indicates that the metal-carboxylate interaction is essentially electrostatic in these complexes. The shoulder near 1620 cm^{-1} in the spectra of these complexes is probably due to water of hydration, while the strong band at 1515 cm^{-1} is probably a ring vibration absorption. The strong band at 1555 cm^{-1} in the spectrum of the disodium salt of the ligand is not found in the spectra of these complexes.

The spectrum of the magnesium complex is quite different from the spectra of the other complexes, expecially in the 1500-1650 cm^{-1} region. Strong bands are found at 1535, 1575, and 1630 cm^{-1}, and an apparent shoulder is present at 1590 cm^{-1}. The band at 1630 cm^{-1} may be due to water. In this connection it should be remembered that there is a strong absorption peak in the OH stretching vibration region in the spectrum of this complex. The bands at 1575 and 1590 cm^{-1} may be due to carboxylate groups in different environments in the structure of the complex. It should also be noted that doublets appear at 1330 and 1295 cm^{-1}, 1245 and 1225 cm^{-1}, 1150 and 1118 cm^{-1}, and 812 and 792 cm^{-1} in the spectrum of this complex. In the spectra of the complexes, only one band is found in each of these regions, at 1325, 1225, 1140, and 800 cm^{-1}, respectively. These data suggest that the bonding of the metal ion to the ligand is different in the magnesium complex than in the other complexes of this ligand.

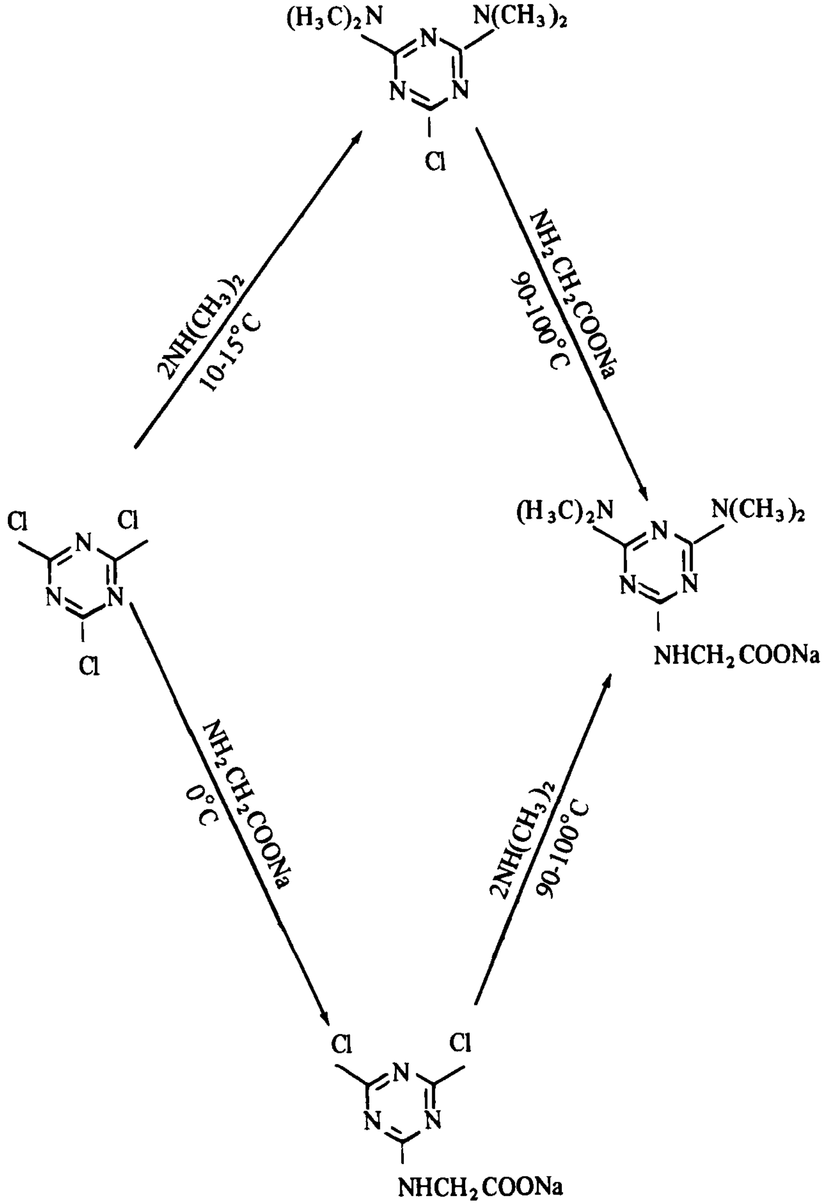
A suggested structure (IX) for the copper, nickel, cobalt, and zinc complexes is given below. In this structure three coordination positions of the metal are filled by the nitrogen and the two carboxylate oxygens, while the fourth position in the plane is occupied by a water molecule. The trans-octehedral positions may be occupied either by water molecules or by the carboxyl oxygens of adjacent complexes in the crystal structure.



IX

Model Compound III: 2,4-Bis(dimethylamino)-s-triazin-6-yl-aminoacetic Acid and Its Metal Complexes

Two methods were used in the preparation of this compound, differing only in the order of attachment of the amine function to the triazine ring. In the first method, the dimethylamino groups were attached first, and the aminoacetic acid group was attached last. In the second method, the aminoacetic acid group was attached first followed by the attachment of the


(H3C)2N
N(CH3)2
Cl
2NH(CH3)2
10-15°C
NH2CH2COONa
90-100°C
NHCH2COONa
NH2CH2COONa
0°C
2NH(CH3)2
90-100°C

(4)

dimethylamino groups. The second method gave the highest yield of the model compound. The product was isolated from acid solution, and the analysis is in agreement with the empirical formula for the hydrochloride salt of 2,4-bis(dimethylamino)-s-triazin-6-yl-aminoacetic acid. The product exhibited amphoteric properties typical of amino acids and related compounds. The potentiometric titration curve indicates pH 5.0 as the approximate isoionic point and 6.3 as the apparent pK_a. All of the metal complexes of 2,4-bis(dimethylamino)-s-triazin-6-yl-aminoacetic acid except the nickel complex precipitated immediately when the ligand and metal ion solutions were mixed. The analyses of all of the complexes except palladium are in agreement with the empirical formulas for a 1:2 ratio of metal ion-to-ligand, and indicate that the complexes are hydrated. Hydration is supported by thermogravimetric curves, which show gradual weight losses to 2 to 6% of the original weight for the complexes between 50 and 175°, followed by decomposition above 200°.

The infrared spectrum of the ligand has a strong absorption band at 3270 cm^{-1} which is attributed to NH stretching vibration. In addition, there is a very broad profile absorption between 3400 and 2000 cm^{-1} with an apparent peak at 2680 cm^{-1}. This is attributed to an NH^+ group. In the spectrum of the sodium salt of the ligand this profile absorption disappears, and the NH stretching vibration absorption appears as a strong band at 3420 cm^{-1}. In addition, there appears to be a fairly broad absorption band centered at about 3330 cm^{-1}, which may be due to water.

The strength of the NH stretching band at 3270 cm^{-1} in the spectrum of the ligand is surprising. Also, no explanation can be offered at present for the shift in this band to lower frequency in the spectrum of the ligand as compared to the spectrum of the sodium salt.

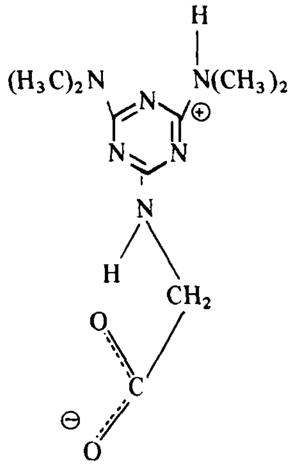
In the spectrum of the ligand there is no carboxyl absorption between 1700 and 1750 cm^{-1}, but several strong bands appear between 1500 and 1700 cm^{-1}. The bands at 1665 and 1640 cm^{-1} are at higher frequencies than those usually found for carboxylate antisymmetric stretching vibrations, and are probably due to ring vibrations or some interaction of the substituents with the ring. These bands disappear in the spectrum of the sodium salt.

The absorption maximum centered around 1590 cm^{-1} in the spectrum of the ligand is probably a composite of the carboxylate antisymmetric stretching vibration absorption and ring vibration absorption. In the spectrum of the sodium salt of the ligand this broad absorption appears to be shifted to a slightly lower frequency.

Other differences are evident when the spectra of the ligand and its sodium salt are compared, but no correlations can be stated. In particular, it should be noted that the spectrum of the ligand has two strong absorption bands at 1392 and 1364 cm^{-1}, respectively. The spectrum of the sodium salt has only one strong band in this region, at 1390 cm^{-1}, which appears to be broader than either of the bands in the spectrum of the ligand. Both are carboxylate symmetric stretching vibration and the CH_3 deformation are expected to absorb in this region.

The presence of the NH^+ profile absorption and the absence of a carbonyl absorption in the spectrum of the ligand would seem to suggest a zwitterion structure. However, the presence of the strong NH stretching band is evidence that the aminoacetic acid nitrogen is not protonated. Therefore, the proton must be attached to one of the dimethylamino substituents of the triazine ring. This is not surprising, since one would expect the dimethylamino nitrogens to be more basic than the aminoacetic acid nitrogen.

The infrared spectral evidence, then, suggests Structure X for 2,4-bis-(dimethylamino)-s-triazin-6-yl-aminoacetic acid.



X

The OH and NH stretching vibration regions of the spectra of the complexes are difficult to interpret. All of the complexes show a fairly broad absorption band centered at 3420 cm^{-1} which is attributed to water of hydration. The intensity and broadness of this band varies among the complexes. In the spectra of the nickel, cobalt, and zinc complexes there is a band centered at 3320, 3300, and 3280 cm^{-1}, respectively, which is attributed to the NH stretching vibration. This band is much stronger and sharper in the spectrum of the zinc complex than in the spectra of the cobalt and nickel complexes. The fact that the NH stretching vibration is shifted to lower frequencies in the spectra of these complexes, as compared to the sodium salt (3420 cm^{-1}), suggests some type of metal-to-nitrogen interaction in the complexes. However, it should be remembered that the NH stretching vibration is also shifted to a lower frequency (3270 cm^{-1}) in the spectrum of the ligand. No explanation can be offered at the present time for this shift.

The spectrum of the copper complex shows only an extremely weak absorption in the NH stretching vibration region of the spectrum, centered around 3250 cm^{-1}. In addition, there seems to be a broad profile absorption centered between 2900 and 3000 cm^{-1}. Since the NH stretching vibration frequency cannot be definitely assigned, no definite conclusions can be reached concerning metal-nitrogen interaction. However, the very marked profile effect, compared to the spectra of the sodium salt and of the other complexes in this series, seems to suggest some type of metal-nitrogen interaction which is apparently stronger in the copper complex than in the nickel, cobalt, and zinc complexes.

In the spectra of the cobalt, nickel, and zinc complexes there is a very broad and strong absorption band between 1500 and 1650 cm^{-1} similar to that found in the metal complexes of the other model compounds. Again, this broad band is probably due to a composite of water vibrations, carboxylate antisymmetric stretching vibrations, and ring vibrations. The high frequency side of this band is broader in the spectra of these complexes than in the spectrum of the sodium salt. This broadness is especially marked in the spectrum of the zinc complex.

While the spectra of the cobalt and nickel complexes are very similar to each other and to that of the sodium salt in the 1800-600 cm^{-1} region, the spectrum of the zinc complex is strikingly similar to that of the ligand, in both peak positions and intensities.

The spectrum of the copper is quite different from the spectra of the other complexes and of the sodium salt of this ligand. The copper complex shows three strong bands in the 1500-1700 cm^{-1} region of the spectrum. These bands are at 1670, 1610, and 1560 cm^{-1}, respectively. The carboxylate antisymmetric stretching vibration frequency is most probably at 1610 cm^{-1}. Because of the broadness of the absorption in this region in the spectra of the cobalt, nickel, and zinc complexes, no valid comparison can be made between these two sets. However, the spectral changes in this region, compared to the sodium salt, indicate some type of metal-oxygen interaction in the copper complex.

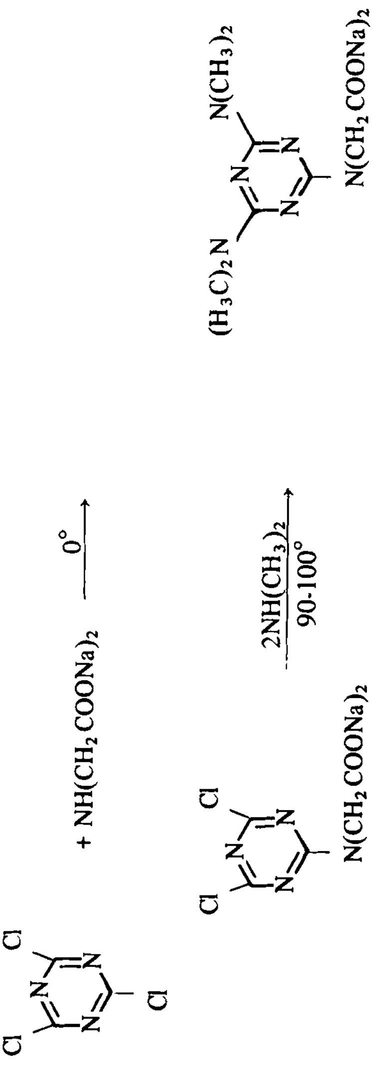
Because of the complexity of the spectral changes of 2,4-bis(dimethylamino)-s-triazin-6-yl-aminoacetic acid, its sodium salt, and its metal complexes, the above correlations must remain tentative. If metal-nitrogen bonding is present in these complexes, as the spectra seem to indicate, then their structures are most probably analogous to that proposed for the complexes of β-[2,4-bis(dimethylamino)-s-triazin-6-yl]hydrazinoacetic acid, in which the two ligands are arranged in a trans-planar square configuration about the metal ion.

Model Compound IV: 2,4-Bis(dimethylamino)-s-triazin-6-yl-iminodiacetic Acid and Its Metal Complexes.

The procedure used in the preparation of this compound was identical to that used in Method B for the preparation of 2,4-bis(dimethylamino)-s-triazin-6-yl aminoacetic acid. The product exhibited amphoteric properties typical of amino acids and related compounds. The potentiometric titration curve for a sample of the compound indicates apparent pK_a's of 3.9 and 5.9. The analytical result for C, H, and N are in agreement with an empirical formula of $C_{11}H_{20}N_6$. The molecular formula for 2,4-bis(dimethylamino)-s-triazin-6-yl-iminodiacetic acid is $C_{11}H_{18}N_6O_4$. Consideration of the chemistry of the reaction suggests that the only reasonable explanation for the two extra hydrogens would be water of hydration.

The metal complexes of 2,4-bis(dimethylamino)-s-triazin-6-yl-iminodiacetic acid were prepared by reacting the diacid ligand with sodium hydroxide solution in a 2:2 millimole ratio, followed by the addition of 1 mmole of metal ion solution. Precipitation of the complex occurred in all cases within a few seconds after the ligand and metal ion solutions were mixed.

The analytical results are in good agreement with the empirical formula for a 2:1 ratio of ligand-to-metal ion for the cobalt, nickel, and zinc complexes, and indicate that only one of the two acidic protons on each ligand has been removed. The analytical results also indicate that the nickel and zinc complexes are hydrated, whereas the cobalt complex is anhydrous. It should be mentioned that a special drying procedure was used for the analytical sample of the cobalt complex, and that the dry complex was extremely hygroscopic. All of the samples of the complexes that were used to obtain infrared spectra were dried by an identical procedure, and the spectra indicate that the cobalt complex, as well as the nickel and zinc complexes, is also hydrated.


Cl
Cl
Cl
N
N
N
+ NH(CH₂COONa)₂
0°
Cl
Cl
N(CH₂COONa)₂
2NH(CH₃)₂
90-100°
(H₃C)₂N
N(CH₃)₂
N(CH₂COONa)₂

(5)

The infrared spectrum of the ligand has a broad shoulder centered at 3300 cm^{-1} which is probably due to the OH of the carbonyl group. In addition, there is a very broad profile absorption between 3400 and 2200 cm^{-1} which is attributed to a combination of OH and NH$^+$ absorptions. The NH$^+$ band appears to be centered around 2500 cm^{-1}. It is impossible to tell from the infrared spectrum in this region which of the nitrogens in the compound is protonated. It should be remembered that the infrared spectrum of 2,4-bis(dimethylamino)-s-triazin-6-yl-aminoacetic acid indicated that one of the dimethylamino nitrogens was protonated in the zwitterion rather than the amino acid nitrogen. This may also be the case in this compound.

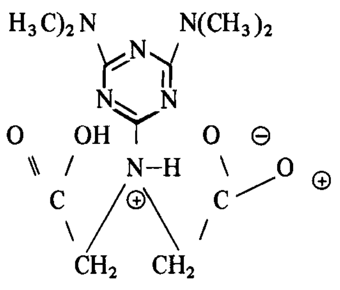
In the spectrum of the sodium salt of the ligand the broad profile absorption disappears. The weak band at 3420 cm^{-1} is probably due to water of hydration.

In the spectrum of the ligand there is a strong doublet at 1740 and 1725 cm^{-1} which is attributed to the carboxyl group. These bands are not present in the spectrum of the sodium salt. In addition, the spectrum of the ligand has a shoulder at 1660 cm^{-1}, a strong band at 1630 cm^{-1}, and a strong and broad absorption between 1500 and 1600 cm^{-1}. Two bands were also present between 1600 and 1700 cm^{-1} in the spectrum of 2,4-bis(dimethylamino)-s-triazin-6-yl-aminoacetic acid, and were attributed to ring vibrations or interaction of the substituents with the ring. The same is probably the case for the bands at 1660 and 1630 cm^{-1} in the spectrum of this model compound. The broad band between 1500 and 1600 cm^{-1} is attributed to a combination of carboxylate antisymmetric stretching vibration and absorption and ring vibration absorption.

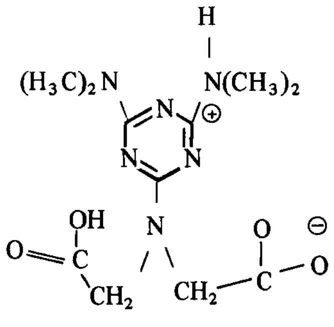
The spectrum of the sodium salt also has a sharp band at 1620 cm^{-1}, and a broad absorption between 1500 and 1550 cm^{-1}, with a shoulder at 1580 cm^{-1}. Again, because of the complexity of the spectrum in this region, it is impossible to assign a definite frequency to the carboxylate antisymmetric stretching vibration.

The presence of the OH and NH$^+$ profile absorption, the presence of the carbonyl absorption, and the broad band in the carboxylate stretching vibration region in the spectrum of the ligand all suggest either zwitterion Structures XI or XII for 2,4-bis(dimethylamino)-s-triazin-6-yl-iminodiacetic acid.

Several other differences are noticeable when the spectra of the ligand and its sodium salt are compared, but no definite correlations can be stated. In particular, the spectrum of the ligand has a strong and complex absorption pattern in the 1200 cm^{-1} region which is not present in the spectra of either the sodium salt or the metal complexes.



XI



XII

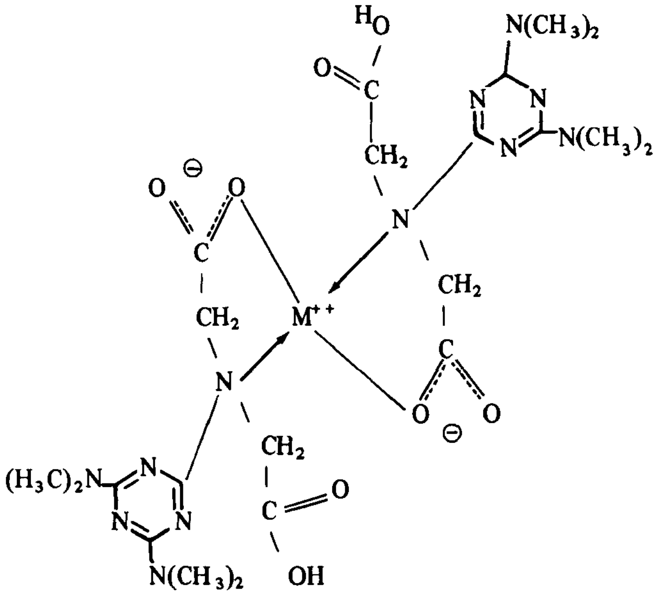
The infrared spectra of the cobalt and nickel complexes are identical throughout. A relatively sharp band appears at 3510 cm^{-1}, which is attributed to the OH of the carboxyl group. In addition, there appears to be two fairly broad absorption bands centered at 3320 and 3220 cm^{-1}. These could both be due to water of hydration. It is also possible that one of these bands is due to hydrogen bonded OH groups of one of the carboxyl groups of the complex. It should also be noted that the broad profile absorption found in the 2200-2800 cm^{-1} region in the spectrum of the ligand is not present in the spectra of the cobalt and nickel complexes.

The sharp band which appears at 1710 cm^{-1} in the spectra of both the cobalt and nickel complexes indicates the presence of a carboxyl group.

Again, the broad absorption in the 1500-1650 cm^{-1} region prohibits the assignment of a definite frequency for the carboxylate antisymmetric stretching vibration. However, the broadening and profile change of this absorption band in the spectra of the cobalt and nickel complexes as compared to the spectrum of the sodium salt indicate definite metal-carboxylate interaction.

The spectrum of the zinc complex, although not as sharp, appears to be essentially the same as the spectra of the cobalt and nickel complexes. The OH stretching vibration absorption and the carboxyl absorption are weaker and broader in the zinc complex, and the band between 1500 and 1650 cm^{-1} is considerably broader on the high frequency side. These changes could all be due to a different crystal structure in the zinc complex than in the nickel and cobalt complexes.

Since the nitrogens in this ligand are all tertiary nitrogens, the infrared spectra of the complexes in the 3800-600 cm^{-1} region can provide no direct evidence either supporting or contradicting metal-nitrogen bonding. Both the analytical results and the infrared spectra of the cobalt, nickel, and zinc complexes indicate that only one of the carboxyl groups of each ligand is ionized. If metal-nitrogen bonding does take place, it seems that Structure XIII is reasonable for the cobalt, nickel, and zinc complexes of 2,4-bis(dimethylamino)-s-triazin-6-yl-iminodiacetic acid. The trans-octehedral positions may be occupied by either the un-ionized carboxyl groups of the ligand or by water molecules.

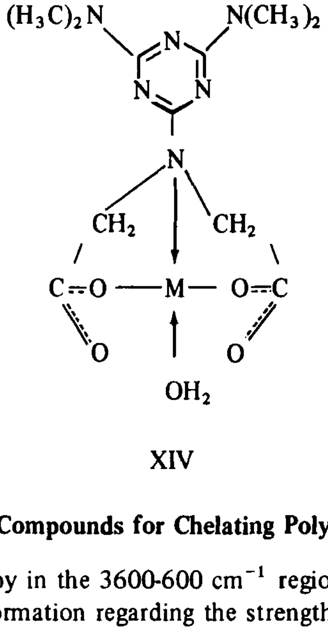


XIII

The analysis for the copper complex is in agreement with the empirical formula for a 1:1 metal ion-to-ligand ratio. The analytical sample was dried by the same procedure as used in the cobalt complex, and the dry sample was extremely hygroscopic.

The infrared spectrum of the copper complex has a broad band centered at 3420 cm^{-1} which is probably due to water of hydration. The broad profile absorption between 3400 and 3000 cm^{-1} may also be due to strongly hydrogen bonded water. No carboxyl absorption in the 1750-1700 cm^{-1} region is found in the spectrum of this complex, but the band between 1500 and 1650 cm^{-1} is very broad, and is probably a composite of absorption bands due to the two carboxylate groups, water, and ring vibrations. The profile shift of this band toward higher frequencies, as compared to the spectrum of the sodium salt, is much more pronounced in the copper complex than in the cobalt, nickel, and zinc complexes. This may be due, in part, to the fact that there are two ionized carboxylate groups in the copper complex on the same ligand molecule.

Again, no definite information regarding metal-nitrogen interaction can be obtained from the infrared spectrum of the copper complex. If metal-nitrogen bonding does take place, then Structure XIV seems reasonable for the copper complex.



XIV

Comparison of Model Compounds for Chelating Polymer Formation

Infrared spectroscopy in the 3600-600 cm^{-1} region can give only a limited amount of information regarding the strength of metal-nitrogen and metal-oxygen bonds. Because of the complexity of the spectra and spectral changes in this study, only general inferences concerning actual chelate structure can be made in most cases. The spectra, however, should prove valuable for comparison with the spectra of the model compounds and polymers and their complexes in future studies of these systems for chelating polymer formation.

Only in the case of the first model compound, β-[2,4-bis(dimethylamino)-s-triazin-6-yl]hydrazinoacetic acid, and its metal complexes, could definite assignments be made for the NH stretching vibration frequencies in all of the complexes. The observed shifts in these frequencies (20 to 140 cm^{-1})

in the spectra of the metal complexes as compared to the spectrum of the sodium salt are comparable to those found for transition metal complexes of glycine [22, 23], and indicate that palladium and copper are bound much more strongly to the nitrogen than are cobalt, nickel, zinc, and magnesium.

The infrared spectra also indicate that, at least in the case of the third model compound, 2,4-bis(dimethylamino)-s-triazin-6-yl-aminoacetic acid, and possibly also in the case of the fourth model compound, 2,4-bis(dimethylamino)-s-triazin-6-yl-iminodiacetic acid, the dimethylamino nitrogen receives the proton in the zwitterion form. It is expected in these latter compounds that this phenomenon might greatly reduce the selectivity of these ligands, since much of the selectivity of amino acid type ligands is based on the competition between the metal ion and hydrogen ion for the coordinating nitrogen.

Since the basicity of the donor nitrogen is one of the main factors determining the stability of the metal complexes with this type of ligand, some information can be gained from the potentiometric titration curves of the ligands. Table 7 lists the apparent pK_a's for the four model compounds for the reaction:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

where HA is the zwitterion form of the ligand. The pK values were obtained from the half-neutralization points of the potentiometric titration curves, and are uncorrected. However, since the titrations were all carried out under essentially the same conditions, the values should be acceptable

Table 7. Apparent pK_a Values for Model Compounds

Compound	Apparent pK_a
2,4-Bis(dimethylamino)-s-triazin-6-yl-aminoacetic acid	6.3
2,4-Bis(dimethylamino)-s-triazin-6-yl-iminodiacetic acid	5.9
2,4-Bis(dimethylamino)-6-hydrazino-s-triazine	5.6
β-[2,4-Bis(dimethylamino)-s-triazin-6-yl]hydrazinoacetic acid	6.3
β-[2,4-Bis(dimethylamino)-s-triazin-6-yl] hydrazino-N,N-diacetic acid	7.8
β-[2,4-Diamino-s-triazin-6-yl]hydrazinoacetic acid	6.1

for comparison within the series. It appears that the first three model compounds in Table 7 have essentially the same pK's, while the pK of the hydrazinodiacetic acid model compound is substantially higher, indicating a more basic nitrogen. The reason for the comparatively large difference between the pK's of the hydrazinoacetic acid and the hydrazinodiacetic acid model compounds is not immediately apparent.

Table 8. Literature pK_a Values for Some Substituted Amines and Amino Acids

Compound	pK_a
Dimethylamine	11.7
Aniline	4.6
Benzylamine	9.3
Melamine	5.0
Tetraethylmelamine	6.3
Hydrazine	8.4
Phenylhydrazine	5.2
Ethylenediamine	(7.0), 9.9
Glycine	9.6
Iminodiacetic acid	9.1
N-Phenyliminodiacetic acid	5.0
Hydrazino-N,N-diacetic acid	9.3
Ethylenediamine-N,N-diacetic acid	5.6, 11.0

Table 8 contains literature values for the pK's of some compounds of interest for comparison with each other and with the model compounds in this study. The effect of an aromatic nucleus, such as the phenyl or triazine ring, on the basicity of the nitrogen is immediately apparent from a comparison of the pK values in Table 8. Some interesting correlations are also evident when Tables 7 and 8 are compared. The pK's of phenylhydrazine and 2,4-bis(dimethylamino)-6-hydrazino-s-triazine are very close, as are those of aniline and melamine. By analogy, one would expect the pK of the triazinyliminodiacetic acid to be close to that of phenyliminodiacetic acid, but, in fact, it appears to be an order of magnitude larger, and is much closer to the pK of tetraethylmelamine. The same is true for the triazinylaminoacetic acid model compound. This again suggests that the dimethylamino nitrogens in these two model compounds are the most basic, and therefore possess the proton in the zwitterion forms of these ligands.

The results of this study indicate that all four model compounds were worth further consideration for possible chelating polymer formation. In terms of both steric requirements and basicity of the donor nitrogen, the hydrazino series seems to be the most pormising and was considered first in the polymer studies.

Chelating Polymers

The studies on chelating polymers reported here are of a preliminary nature and were performed to establish the validity of the transition of the data obtained from model compounds to structurally related polymer systems. For this reason, the aldehyde-reactable β-[2,4-diamino-s-triazin-6-yl]hydrazinoacetic acid was selected as the first candidate for polymerization as a suitable analog of the model β-[2,4-bis(dimethylamino)-s-triazin-6-yl]hydrazinoacetic acid. More extensive polymerization studies are contemplated and will be performed in the near future.

Aldehyde-Reactable Monomer

Since the model compounds contained dimethylamino groups, they could not be used for polymerization reactions with formaldehyde, and it was necessary to prepare either the amino or the methylamino analogs of the model compounds for actual polymerization with formaldehyde.

β-[2,4-Diamino-s-triazin-6-yl]hydrazinoacetic acid was prepared by the same procedure as used in the preparation of the analogous model compound β-[2,4-bis(dimethylamino)-s-triazin-6-yl]hydrazinoacetic acid. The reaction of 2,4-diamino-6-chloro-s-triazine with hydrazinoethylacetate in the presence of excess base allowed both the attachment of the hydrazino function to the triazine ring and the hydrolysis of the ester. The product from this reaction exhibited amphoteric properties typical of amino acids and related compounds. The potentiometric titration curve indicates an apparent pK_a of 6.1 for this compound. This is the same value as that obtained for the analogous model compound.

The infrared spectrum of β-[2,4-diamino-s-triazin-6-yl]hydrazinoacetic acid has two strong absorption bands in the NH stretching vibration region, at 3320 and 3110 cm^{-1}. The band centered at 3110 cm^{-1} is broad, and is probably due to the NH_2^+ group. In the spectrum of the sodium salt of the ligand there are five sharp, strong bands in this region, at 3420, 3360, 3300, 3260, and 3200 cm^{-1}.

A shoulder absorption around 1710 cm^{-1} appears in the spectra of the ligand, its sodium salt, and its copper complex, as well as in the spectrum of 2,4-diamino-6-chloro-s-triazine, and therefore must not be due to the carboxyl group. In the spectra of the ligand and of 2,4-diamino-6-chloro-s-triazine there is a strong band centered at 1630 cm^{-1}. A similar band appears at 1615 cm^{-1} in the spectra of the sodium salt and of the copper complex of the ligand. These bands are probably due to the NH_2 groups.

In the spectrum of the ligand there is a broad absorption profile centered between 1530 and 1590 cm^{-1}. In the spectrum of the sodium salt of the ligand this absorption is partially resolved to show two broad bands at 1555 and 1530 cm^{-1}, respectively. The high frequency band is probably a composite of ring vibration absorption and carboxylate antisymmetric stretching vibration absorption.

The infrared spectral evidence suggests that the ligand has the expected zwitterion structure and is similar to Structure VI.

The copper complex of β-[2,4-diamino-s-triazin-6-yl]hydrazinoacetic acid was prepared in the same manner as the copper complex of the analogous model compound. The complex precipitated immediately when the ligand solution and the metal ion solution were mixed.

The infrared spectrum of the copper complex has two broad absorption bands in the NH stretching vibration region, at 3315 and 3180 cm^{-1}, which are considerably weaker than those in the spectra of the ligand and of the sodium salt of the ligand. Because of the many NH and NH_2 groups present in this ligand, it is impossible to assign a definite frequency to the NH stretching vibration of the potential donor nitrogen. However, the similarity between the spectra of the copper complex and of the ligand in the NH stretching vibration region, and the profile change in the spectrum of the copper complex as compared with the spectrum of the sodium salt of the ligand indicate the presence of metal-nitrogen interaction in the copper complex. The infrared spectrum of the copper complex is very similar to that of the sodium salt in the 1500-1600 cm^{-1} region. A shift of the high frequency band in this region from 1555 cm^{-1} in the spectrum of the sodium salt to 1570 cm^{-1} in the spectrum of the copper complex is evident, and indicates metal-carboxylate interaction in the copper complex.

Polymerization Reactions

Polymerization reactions were carried out with both the free ligand, β-[2,4-diamino-s-triazin-6-yl]hydrazinoacetic acid, and its copper complex in the presence of excess formaldehyde.

In order to prevent formaldehyde condensation at the coordinating nitrogen of the amino acid function, the polymerization of the free ligand with formaldehyde was carried out in acid solution at a pH of approximately four. At this pH the ligand should be present in the zwitterion form, and, since formaldehyde does not react with a positive nitrogen, condensation is not expected to take place at that position.

The formation of the clear, viscous solution during the course of the polymerization reaction is good evidence that some resinification occurred. The final product, a hard, glassy pellet, was typical in appearance of aminotriazine-formaldehyde polymers.

Problems were encountered in obtaining infrared spectra of the polymers by the potassium bromide disk method. Even after extensive grinding of the polymer samples the spectral absorptions were extremely weak and very poorly resolved; such spectra are typical of triazine condensation polymers.

In the spectrum of this polymer, a broad profile absorption is evident between 3200 and 3600 cm^{-1}. The band at 3110 cm^{-1} in the spectrum of the ligand is absent in the spectrum of the polymer. The CH stretching vibration absorption centered at 2920 cm^{-1} appears to be stronger and broader in the spectrum of the polymer than in the spectrum of the sodium salt of the ligand. The spectrum of the polymer has a broad absorption profile between 1500 and 1800 cm^{-1} with a maximum around 1550 cm^{-1}, and appears to be very similar to the spectrum of the ligand in this region.

Polymer Chelation Studies

These qualitative studies were designed as a preliminary investigation of the complexing ability of this polymer system with various transition metal ions. The immediate coloration of the polymer samples, and also of cloth and filter papers which had been impregnated with the polymer, and the fact that these colors did not wash out with water, are indications of metal ion-polymer interaction.

In simple ion exchange resins, where ion exchange functions according to the mass action law, metal ions such as copper(II), nickel(II), and cobalt(II) can be eluted from the resin by alkali metal ion solutions. This is amply demonstrated by the experiments carried out with the Amberlite IRC-50 cation exchange resin in this work. In the Amberlite resin the metal ion is bonded to carboxylate anions in the polymer matrix. In the experiment carried out in this work, it was found that most of the copper(II) ions were removed from the resin by 1 M sodium chloride solution.

In contrast to this behavior, transition metal ions are not removed from chelating resins by alkali metal ion solutions. For example, studies on the Dowex A-1 Chelating Resin have shown that metals which have been complexes by the resin are not eluted by concentrated salt solutions, but can be removed with mineral acid [24]. This same behavior was observed for the polymer prepared in this study. There was not evidence of metal ion removal from the resin when the complexed polymer samples were stirred in 1 M sodium chloride solution, but the metal ions were removed by 1 M mineral acid. This behavior is a good indication that the metal ions are actually chelated to the polymer, and not bonded by simple electrostatic interaction.

Polymer from the Copper Complex of β-[2,3-Diamino-s-triazine-6-yl]hydrazinoacetic Acid

As was mentioned, the polymerization reaction between the free ligand and formaldehyde was carried out in acid solution to reduce the possibility of formaldehyde condensation at the amino acid nitrogen. By the same argument one would not expect this nitrogen to condense with formaldehyde if it were already involved in the metal-nitrogen bonding. With this in mind, a polymer was prepared by the polycondensation of the copper complex of the ligand with excess formaldehyde in a slightly alkaline medium. The formation of the dark green solution during the reaction and the general appearance of the final product, a dark green, glassy pellet, are good evidence that polycondensation took place to form the polymer. Again, 1 M mineral acid was required to remove the copper ion from the polymer.

The results of these preliminary polymer studies indicate that this is a promising system for chelating polymer formation. Future work on this system will be directed towards finding the best conditions for the polymerization reaction and a more complete characterization of the polymers formed. A study of the low-molecular-weight oligomers should prove helpful in this characterization. The studies should include the determination of distribution coefficients with various metal ions as a function of pH, and experiments on the separation of various metal ion mixtures [24-26].

The model compound β-[2,4-bis(dimethylamino)-s-triazin-6-yl]hydrazino-N,N-diacetic acid is also worthy of further consideration in chelating polymer formation. Since the amino acid nitrogen in this model compound is a tertiary nitrogen, it would eliminate the possibility of the formaldehyde condensation occurring at this position.

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