Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Chelating Polymers. II. Amino Acetic Acid Chelating Polymers Derived from Hydroxyarylamino Acetic Acids

G. F. D'alelio[a]; E. T. Hofman[a]; F. J. Meyers[a]
[a] Department of Chemistry, University of Notre Dame, Notre Dame, Indiana

To cite this Article D'alelio, G. F. , Hofman, E. T. and Meyers, F. J.(1970) 'Chelating Polymers. II. Amino Acetic Acid Chelating Polymers Derived from Hydroxyarylamino Acetic Acids', Journal of Macromolecular Science, Part A, 4: 2, 361 — 439

To link to this Article: DOI: 10.1080/00222337008063155

URL: http://dx.doi.org/10.1080/00222337008063155

J. MACROMOL. SCI.–CHEM., A4(2), pp. 361-439, March, 1970

Chelating Polymers. II. Amino Acetic Acid Chelating Polymers Derived from Hydroxyarylamino Acetic Acids*

G. F. D'ALELIO, E. T. HOFMAN, and F. J. MEYERS

Department of Chemistry
University of Notre Dame
Notre Dame, Indiana 46556

SUMMARY

The prototype dimeric chelating compounds 3,3′-methylenebis-[N-(4-hydroxyphenyl) iminodiacetic acid] and 3,3′-methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid] were synthesized and characterized by composition analysis, infrared spectroscopy, and potentiometric titration data. Their chelating characteristics with Cu(II), Ni(II), Co(II), and Zn(II) ions were established by composition analysis and comparative infrared spectroscopy.

The results suggest chelation and structures of the usual iminodiacetato-metal complex type for the Ni(II), Co(II), and Zn(II) compounds of 3,3′methylenebis-[N-(4-hydroxyphenyl) iminodiacetic acid] and for the Cu(II, Ni(II), and Co(II) compounds of 3,3′-methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid]. The composition analysis of each of these compounds indicates 1:2:2 mole ratios of ligand to metal ion to water. Square planar structures are proposed wherein the two iminodiacetato-metal chelate moieties are essentially independent of each other.

The composition analysis of the Cu(II) compound of 3,3′-methylenebis-[N-(4-hydroxyphenyl) iminodiacetic acid] indicates a 1:2:1 mole ratio of

---

*Taken in part from the Ph.D. dissertation of F. J. Meyers.

ligand to metal ion to water. Structures are proposed in which some of the carboxylate groups are bridges between two metal coordination centers.

The composition analysis of the Zn(II) compound of 3,3′-methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid] indicates a 1:1 mole ratio of ligand to metal ion. A structure is proposed in which both nitrogen atoms and two of the four carboxylate groups of the dimeric ligand are coordinated to the same metal ion.

A preliminary investigation was made of oligomeric compounds analogous to the prototype dimeric compounds.

INTRODUCTION

Monomeric hydroxyarylamino acetic acids having two unsubstituted ortho positions in the ring appear to be ideal compounds for the synthesis of chelating polymers. They contain amino acid groups which are suitable chelating moieties; they are also capable of condensation reactions with formaldehyde to produce polymers.

Ashida [1] reported that a condensation product of N-(p-hydroxyphenyl) glycine and formaldehyde indicated no chelating tendencies with calcium ion. Since N-(p-hydroxyphenyl)glycine, itself, would appear to be a good chelating agent, it would be expected that, if the aminoacetic acid ligand segment had been unaltered in its incorporation into the polymer, the polymer should exhibit good chelating properties. Ashida did not characterize his condensation product, and it is likely that condensation occurred not only at the ortho positions in the benzene ring, but also with the reactive hydrogen of the amino group in the glycine function, thus producing a polymer whose chelating moiety is essentially unrelated to the model compound, N-(p-hydroxyphenyl)glycine.

In a prior publication [2], we proposed that an orderly approach to the synthesis of a chelating polymer should include the following steps:

1) Synthesis of the model compound and determination of its chelating characteristics.

2) Synthesis, characterization, and determination of the chelating characteristics of the dimer, trimer, or other low molecular weight oligomers of the model compound; then a comparison of the chelating characteristics of these compounds with the chelating characteristics of the model compound.

3) If the results of step 2) verify chelation, synthesis, characterization, and determination of the chelating capacities of the high molecular weight polymer.

Following this approach, D'Alelio, Hofman, and Zeman [2] prepared several model chelating compounds of the monomeric hydroxyarylaminoacetic acid type and then prepared some transition metal compounds of these ligand compounds and characterized them, particularly by means of infrared spectroscopy.

As a consequence of that prior investigation [2], and following the approach proposed, the objectives of our investigation were:

1) To prepare some N-substituted amino acid chelating compounds based on dimeric condensation products of para-substituted phenols with formaldehyde.

2) To prepare some transition metal complexes of these compounds and to characterize them by means of infrared spectroscopy.

3) To investigate, in a preliminary fashion, the possible adaptability of these dimeric N-substituted amino acid compounds to chelating polymer synthesis.

The chemistry of phenol-formaldehyde condensations is treated in detail in several texts [3-5]. Dimeric or bis compounds are prepared most importantly by reaction of phenolic compounds with formaldehyde in 2:1 mole ratio and in acid medium. Faith discusses a number of specific preparative methods [6]. Polymers are best prepared by adjusting the mole ratio of the phenolic compound to formaldehyde to 1:1. The condensation occurs in either acid or base medium.

In order to minimize the difficulties in the preparation of phenol-formaldehyde polymeric ligands suitable for chelation studies, the following general procedure was followed:

1) The position para to the hydroxy group on the benzene ring was blocked with a suitable nitrogen compound that is unreactive to subsequent condensation.

2) The compound synthesized in step 1) was condensed with formaldehyde under conditions appropriate to the synthesis of the compound desired.

3) The nitrogen group attached to the phenol moiety was converted to an amino acid group by chemical treatment.

EXPERIMENTAL

Physical Measurements

Melting points were determined with a Thiele melting point bath and are uncorrected.

Infrared spectra were obtained on a Perkin-Elmer 421 Grating Spectrophotometer in the range 3800-550 cm^{-1}. Wavenumber calibrations were made by comparison with polystyrene and carbon dioxide standard peaks. Samples were prepared for the infrared studies by the potassium bromide disk technique [7].

Potentiometric titrations were done using a Beckman Model 76 Expanded Scale pH meter with glass and saturated calomel electrodes. The meter was calibrated with a standard buffer. Standardized hydrochloric acid and sodium hydroxide solutions were used as titrants.

Thermogravimetric data were obtained on a duPont 950 Thermogravimetric Analyzer employing the recording system of the duPont 900 Differential Analyzer.

Molecular weights were determined using the Mechrolab Model 302 Vapor Pressure Osmometer equipped with a 37° thermostat and a 37° no-aqueous probe. The solvents used in the molecular weight determinations were acetone and p-dioxane. In each case a calibration factor characteristic of the instrument-thermostat-probe-solvent combination was obtained using recrystallized benzyl (MW210.1) as a standard solute.

Synthesis

Prototype Dimeric Compound (I): 3-3′-Methylenebis-[N-(4-hydroxyphenyl) iminodiacetic acid]. The stepwise synethesis of this compound included:

1) Synthesis of 3,3′-methylenebis-(4-hydroxynitrobenzene).

2) Synthesis of 3,3′-methylenebis-(4-hydroxyaniline hydrochloride) by catalytic hydrogenation of 3,3′-methylenebis-(4-hydroxynitrobenzene).

3) Synthesis of 3,3′-methylenebis-[N-(4-hydroxyphenyl) iminodiacetic acid] disodium salt by reacting 3,3′-methylenebis-(4-hydroxyaniline hydrochloride) with chloroacetic acid.

The details of these syntheses are given in the following procedures.

3,3′-Methylenebis-(4-hydroxynitrobenzene), $CH_2[C_6H_3(OH)NO_2]_2$. This compound was prepared according to the method of Chattaway and Goepp [8] in which p-nitrophenol is reacted with formaldehyde in acid medium. The reaction product was recrystallized twice from glacial acetic acid after treatment with charcoal and then dried in a desiccator under vacuum. Pale yellow crystals (15 g, 38% of theory) were recovered. The melting point of the crystals was 267-268°C, lit. 268°C [8]. The molecular weight of the crystals as determined by vapor pressure osmometry in acetone solution was 289; the theoretical value is 290.

Analysis calculated for $C_{13}H_{10}N_2O_6$: C, 53.79%; H, 3.45%; N, 9.66%. Found: C, 53.13%; H, 3.73%; N, 9.74%.

3,3′Methylenebis-(4-hydroxyaniline hydrochloride), $\mathbf{CH_2[C_6H_3(OH)NH_3Cl]_2}$. This compound was first prepared by the catalytic hydrogenation of 3,3′-methylenebis-(4-hydroxynitrobenzene) with Raney nickel at room temperature and at pressures of about 1500 psig. However, it was found to be simpler and more convenient to do the hydrogenation using a Parr hydrogenator at pressures of about 42 psig and with 5% palladium-on-charcoal as the catalyst. This hydrogenation was done according to the following procedure.

3,3′-Methylenebis-(4-hydroxynitrobenzene) (9.26 g, 0.0319 mole) was dissolved in 95% ethanol (260 ml) and the solution was placed in a Parr bottle with 5% palladium-on-charcoal (0.65 g). The bottle was placed on the Parr apparatus, flushed three times with hydrogen, and subjected to pressure with hydrogen (44.3 psig). The bottle and contents were shaken at room temperature for 1 hr. The hydrogen pressure dropped to 25.4 psig. The hydrogen was removed from the bottle at reduced pressure, and the flask was then flushed with nitrogen, stoppered, and removed from the apparatus. The catalyst was removed from the system by filtration under nitrogen. The filtrate was quickly poured into an Erlenmeyer flask containing a solution of hydrogen chloride (approximately 7 g) in absolute alcohol (60 ml). This flask was stoppered and allowed to stand in an ice-water bath for several hours. The heavy, faint-green, crystalline precipitate that formed was isolated by filtration and then dried in a desiccator under vacuum. The yields varied from 80 to 90% of theory. The product was recrystallized for elemental analysis from an ethanol-ethyl acetate mixture.

Analysis calculated for $C_{13}H_{14}N_2O_2\,2HCl$: C, 51.48%; H, 5.28%; N, 9.24%. Found: C, 51.36%; H, 5.53%; N, 9.68%.

3,3′-Methylenebis-[N-(4-hydroxyphenyl) iminodiacetic acid] disodium salt, $\mathbf{CH_2[C_6H_3(OH)(N_2\,\{CH_2COOH\}\,\{CH_2COONa\})]_2}$. This compound was prepared following a procedure reported in a prior publication [2] for the synthesis of the corresponding monomer, N-(4-hydroxyphenyl) iminodiacetic acid.

3,3′-Methylenebis-(4-hydroxyaniline hydrochloride) (8.00 g, 0.0264 mole) and sodium sulfite (0.25 g) were mixed with 10 ml of water in a 250-ml three-necked flask. The flask was equipped with a water condenser heating mantle, mechanical stirrer, thermometer, and a nitrogen inlet tube through which nitrogen was admitted to the flask at a slow constant rate.

To the mixture was added a solution of sodium acetate (23.9 g, 0.292 mole) in 55 ml of water. A solution of chloroacetic acid (11.2 g, 0.118 mole) in 18 ml of water was added to the reaction mixture. A brown solution formed almost immediately; the solution was stirred for 20 min without external heating, during which time the temperature rose to about 35°. The solution was refluxed for 1 hr, cooled to room temperature, and filtered. The filtrate was transferred to a beaker, and the solution pH was adjusted from 3.12 to 3.75 by adding approximately 3.5 ml of 6 M hydrochloric acid.

The reaction solution was then transferred to a flask, flushed with nitrogen, stoppered, and cooled overnight in a refrigerator at about 7°. It solidified to a white mass. A small amount of water was added, and the mixture was stirred and filtered. The residue was washed with water and with absolute ethanol, then dried over P_2O_5 in a vacuum desiccator. Approximately 2 g of tan solid (i) was recovered.

The filtrate and the water wash solution from the first residue were combined and concentrated on a flash evaporator to about one-half of the original volume, then cooled in a refrigerator. The resulting tan precipitate was filtered and recrystallized once from water and once from a 70-30 (volume per cent) ethanol-water solution. The precipitate was dried in a vacuum oven at 110° for 16 hr. A tan solid (II) (1.67 g, 12.5% of theory) was recovered.

The infrared spectra of products (I) and (II) were very similar, but the spectrum of (II) gave better resolution. Product (II) was used for analysis and subsequent preparation of the metal complexes.

Thermogravimetric analysis of product (II) indicated it to be an anhydrous compound which decomposes slowly beginning at 160° and then more rapidly above 200°.

Analysis calculated for $C_{21}H_{20}N_2O_{10}Na_2$: C, 49.81%, H, 3.98%; N, 5.53%. Found: C, 49.34%; H, 4.77%; N, 5.40%.

Metal Complexes of 3,3'-Methylenebis-[N-(4-hydroxyphenyl)iminodiacetic acid]. The procedure followed in the preparation of these complexes was a modification of the one previously published [2] for the preparation of the corresponding monomer, N-(4-hydroxyphenyl) iminodiacetic acid.

3,3'-Methylenebis-[N-(4-hydroxyphenyl) iminodiacetic acid] disodium salt (0.105 g, 0.20 mmole) was added to 1.6 ml of deionized water and stirred with warming until a clear solution formed. Metal nitrate solution (0.20 ml of 2.0 M solution) was then added. The mixture was heated on a water bath for about 10 min and then 0.20 ml of 2.0 M sodium hydroxide solution was added. The mixture was heated for about 10 min and stirred vigorously during that time. It was then allowed to stand for about 30 min. The residue formed was recovered by filtration under reduced pressure and then washed three times in cold, deionized water and once in ethyl alcohol. The product was dried in a vacuum oven at 120°C for 1 hr. The data for the metal complexes are given in Table 1.

Table 1. Metal Complexes of 3,3'-Methylenebis-[N-(4-hydroxyphenyl) iminodiacetic acid]

Formula	Color	Analysis, % C	H	N	H_2O	
$Cu_2(C_{21}H_{18}N_2O_{10})\cdot H_2O$	Olive	41.79	3.34	4.64	2.99	Calc.
		41.48	3.54	4.55	2.9	Found
$Ni_2(C_{21}H_{18}N_2O_{10})\cdot 2H_2O$	Light green	41.22	3.62	4.58	5.89	Calc.
		41.28	4.41	4.37	6.1	Found
$Co_2(C_{21}H_{18}N_2O_{10})\cdot 2H_2O$	Deep purple	41.19	3.62	4.58	5.88	Calc.
		40.77	4.33	4.51	5.8	Found
$Zn_2(C_{21}H_{18}N_2O_{10})\cdot 2H_2O$	Tan	40.34	3.55	4.48	4.76	Calc.
		40.29	4.05	4.35	5.0	Found

Prototype Dimeric Compound (II): 3,3'-Methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid. This compound was synthesized in much the same way as was prototype dimeric compound (I) by a series of steps which included:

1) Synthesis of 3,3'-methylenebis-(4-methoxynitrobenzene).
2) Synthesis of 3,3'-methylenebis-(4-methoxyaniline hydrochloride).
3) Synthesis of 3,3'-methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid] disodium salt.

3,3'-Methylenebis-(4-methoxynitrobenzene), $CH_2[C_6H_3(OCH_3)NO_2]_2$, The preparation of this compound was based on a general methylation procedure reported by Diner and coworkers [9]. 3,3'-Methylene-bis-(4-hydroxynitrobenzene) (15.0 g, 0.0517 mole) was dissolved in 100 ml of N,N-dimethylformamide which had been previously distilled and dried over calcium hydride. This solution was poured into a 250-ml three-necked flask equipped with a mechanical stirrer, water condenser, drying tube, and thermometer. Methyl iodide (19.1 g, 0.134 mole) was added, and the flask was immersed in an ice-water bath. Sodium hydride (3.63 g, 0.151 mole) was added to the flask in small portions over a 1-hr period and with continuous stirring. Gentle evolution of gas occurred with each addition, and the temperature rose slowly, but it was carefully maintained below 15°. Finally, a second portion of methyl iodide (2.54 g, 0.018 mole) was added to the flask, and the yellow solution was stirred overnight and slowly reached room temperature. After 15 hr the system became a pasty, lemon-yellow mixture. A small amount of methanol was added to neutralize the unreacted sodium hydride, but no exotherm was observed. Water (150 ml) was added to the reaction mixture, which was then stirred for ½ hr. The reaction mixture was diluted with a large amount of water, filtered under reduced pressure, and washed repeatedly with large amounts of water. The residue recovered was recrystallized from dioxane and dried in a vacuum oven at 80°C. Pale yellow crystals (14.4 g, 88% of theory) melting at 185-189°C were obtained. After a second recrystallization, the product melted at 189-190°C. The molecular weight of the product, as determined by vapor pressure osmometry in dioxane solution at 37°, was 317; the theoretical value is 318.

Analysis calculated for $C_{15}H_{14}N_2O_6$: C, 56.60%; H, 4.43%; N, 8.80%. Found: C, 56.66%; H, 4.62%; N, 8.88%.

3,3′-Methylenebis-(4-methoxyaniline hydrochloride), $CH_2[C_6H_3(OCH_3)NH_3Cl]_2$. 3,3′-Methylenebis-(4-methoxynitrobenzene) (10.0 g, 0.0315 mole) was dissolved in 140 ml of 2-(2-ethoxyethoxy)-ethanol, $C_2H_5OC_2H_4OC_2H_4OH$. This solution was poured into a Parr bottle with 5% palladium-on-charcoal (0.54 g). The bottle was placed on the Parr apparatus, flushed three times with hydrogen, and subjected to a pressure of 46.7 psig with hydrogen. The bottle and contents were shaken at room temperature for 10 hr. The hydrogen pressure dropped to 34.0 psig. The hydrogen was removed from the bottle at reduced pressure, and the bottle was flushed with nitrogen. The catalyst was removed by filtration. To the filtrate was added 100 ml of concentrated hydrochloric acid; this mixture was then allowed to stand for 36 hr. The resulting fine, white precipitate was isolated by filtration, washed with concentrated hydrochloric acid, dissolved in water, and then reprecipitated with concentrated hydrochloric acid. The product was once again isolated by filtration, washed, and dried in a vacuum oven at 80°C. There was obtained 8.79 g (84.5% of theory) of a grey-white powder.

Analysis calculated for $C_{15}H_{18}N_2O_2 \cdot 2HCl$ + 0.8% H_2O: C, 53.95%; H, 6.11%; N, 8.39%. Found: C, 53.26%; H, 6.39%; N, 8.48%; H_2O, 0.8%.

3,3′-Methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid] disodium salt, $CH_2[C_6H_3(OCH_3)(N \} CH_2COOH \} \{CH_2COONa \})]_2$. 3,3′-Methylenebis-(4-methoxyaniline hydrochloride) (10.0 g, 0.0302 mole) and sodium sulfite (0.10 g) were mixed with 25 ml of water in a 250-ml three-necked flask. The flask was equipped with a water condenser, heating mantle, mechanical stirrer, thermometer, and a gas inlet tube by means of which the reaction mixture was blanketed with a slow stream of nitrogen. To this mixture was added a solution of sodium acetate (14.8 g, 0.181 mole) in 35 ml of water. A solution of sodium chloroacetate (17.6 g, 0.151 mole) in 30 ml of water was then added. The reaction mixture was heated to 120°C, by which time a clear solution was formed. It was then refluxed at this temperature for 18 hr. After this time a solution of sodium chloroacetate (3.52 g, 0.0302 mole) in 7 ml of water was added to the reaction flask. The system was refluxed for another 26 hr, and a second identical portion of sodium chloroacetate solution was added. The refluxing was continued for an additional 46 hr, during which time the reaction solution changed gradually from orange-red to red-brown. The solution was cooled to room temperature and filtered. The filtrate, the pH of which was 3.7, was cooled in an ice-water bath. It solidified rapidly to a tan colored mass. A small amount of water was added, and the mixture was stirred. It was then allowed to stand for several hours. The residue formed was recovered by filtration and was first washed with several portions of cold, deionized water and then with several portions of cold ethyl alcohol. After the residue was dried in vacuo at 75° for 48 hr, 9.7 g (60% of theory) of a tan solid was obtained. A thermogravimetric analysis of the product showed less than 1% water loss and indicated that the compound decomposes slowly beginning at 100° and more rapidly at temperatures above 150°.

Analysis calculated for $C_{23}H_{24}N_2O_{10}Na_2$: C, 51.68%, H, 4.53%, N, 5.24%. Found: C, 51.65%; H, 5.61%; N, 5.43%.

Metal Complexes of 3,3′-Methylenebis-[N-(4-methoxyphenyl) iminodiacetic adid]. The procedure followed in the preparation of these complexes were modifications of the one previously published [2] and also used in the preparation of the complexes of prototype monomeric compound (I).

(A) Copper Complex. 3,3′-Methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid] disodium salt (0.27 g, 0.50 mmole) was dissolved in 2 ml of 50-50 (volume per cent) water-dioxane solution. Copper(II) nitrate solution (0.50 ml, 2.0 M) was added, and the resulting solution was stirred vigorously for several minutes. Sodium hydroxide solution (0.50 ml, 2.0 M) and 2 ml of water were added. The mixture was heated with constant stirring on a steam bath for 10 min. It was then allowed to stand for 1 hr. The residue that was formed was recovered by filtration under reduced pressure. It was then washed four times with cold water and twice with ethyl alcohol. The washed product was dried in a vacuum oven at 80°C for 16 hr. The data for the complex are given in Table 2.

(B) Nickel Complex. 3,3′-Methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid] disodium salt (0.274 g, 0.50 mmole) was dissolved in 2 ml of a 75-25 (volume per cent) water-dioxane solution. Nickel(II) nitrate solution (0.50 ml, 2 M) was added. Sodium hydroxide solution (0.50 ml, 2.0 M) and 2 ml of water were added successively. The mixture was stirred and warmed on a steam bath for 15 min, and then it was permitted to stand at room temperature for 16 hr before it was filtered under reduced pressure. The residue recovered was washed four times with cold water and once with ethyl alcohol. It was then dried in a vacuum oven at 80°C for 16 hr. The data for the complex are given in Table 2.

(C) Cobalt Complex. 3,3′-Methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid] disodium salt (1.10 g, 2.0 mmole) was dissolved in 8 ml of a 75-25 (volume per cent) water-dioxane solution. Cobalt(II) nitrate solution (2.0 ml, 2.0 M) was added. Sodium hydroxide solution (2.0 ml, 2.0 M) and 8 ml of water were then added successively. The mixture was stirred at room temperature for 6 hr, and then it was filtered under reduced pressure. The residue that was recovered was washed several times with cold water, once with ethyl alcohol, and once with diethyl ether. It was then dried in a vacuum oven at 80° for 16 hr. The product (I) was a grey-brown powder.

The filtrate of the above filtration was diluted with 75 ml of acetone (A.R. grade), and the mixture was stirred for several hours at room temperature. The precipitate formed was isolated by filtration under reduced pressure. It was then washed four times with diethyl ether and twice with water. The washed product was dried in a vacuum oven at 80°C for 16 hr. The dry material (II) was a red-brown powder.

The infrared spectra of (I) and (II) were quite similar. However, product (I) had a strong, sharp peak at about 3640 cm^{-1} which was presumed to be due to the OH^- group. [The spectrum of freshly

Table 2. Metal Complexes of 3,3′-Methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid]

Formula	Color	Analysis, %				
		C	H	N	H_2O	
$Cu_2(C_{23}H_{22}N_2O_{10})\cdot 2H_2O$	Deep green	42.55	4.04	4.31	5.55	Calc.
		42.55	4.43	4.76	~5	Found
$Ni_2(C_{23}H_{22}N_2O_{10})\cdot H_2O$	Yellow-green	44.42	3.88	4.51	2.90	Calc.
		46.43	5.05	5.20	~2.6	Found
$Co_2(C_{23}H_{22}N_2O_{10})\cdot 2H_2O$	Red-brown	43.14	4.09	4.37	5.60	Calc.
		40.13	3.91	4.37	~5.9	Found
$Zn(C_{23}H_{24}N_2O_{10})$	Tan	49.88	4.37	5.05	0	Calc.
		50.41	4.74	4.75	1.9	Found

precipitated cobalt(II) hydroxide also includes this peak.] Therefore, product (II), which did not include this peak, was assumed to be less contaminated with cobalt(II) hydroxide, and it was the sample used for elemental analysis. The data for the complex are given in Table 2.

(D) Zinc Complex. 3,3′-Methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid] disodium salt (0.572 g, 1.0 mmole) was dissolved in 2.5 ml of 80-20 (volume per cent) water-dioxane solution. Zinc(II) nitrate solution (1.0 ml, 2.0 M) and then 0.76 ml of 2.0 M sodium hydroxide solution and 2 ml of water were added. The mixture was stirred and heated on a steam bath for 15 min. It was then allowed to stand at room temperature for 16 hr, after which time it was filtered under reduced pressure. The residue recovered was washed several times with water and once with ethyl alcohol and then dried in a vacuum oven at 80° for 16 hr. The data for the complex are given in Table 2.

PREPARATION OF AN OLIGOMERIC SYSTEM. A PRELIMINARY INVESTIGATION FOR FUTURE CHELATING POLYMER STUDIES.

p-Nitrophenol-Formaldehyde Oligomer. The preparation of this oligomer is based upon ideas proposed by Baekeland [10] and now generally included in polymer laboratory manuals, such as the one written by D'Alelio [11].

p-Nitrophenol (140 g, 1.00 mole) was mixed with 20 ml of water and 30 ml of ethyl alcohol in a 500-ml three-necked flask equipped with a mechanical stirrer, water condenser, dropping funnel, thermometer, and heating mantle. The reaction mixture was heated to 50°C with continuous stirring, and a yellow solution was formed. Concentrated hydrochloric acid (56.5 g of 37.3% solution) was added slowly from a dropping funnel, and a yellow precipitate formed. After the mixture was heated to 60°C, paraformaldehyde powder (31.5 g, 1.05 mole) was added, and the reaction mixture was heated to the reflux temperature (104°C). At that temperature the mixture separated into two phases: a clear, orange-yellow, oil phase on the bottom and a clear, colorless phase on the top. The reaction mixture was refluxed with continuous stirring for 93 hr. During this time the oil layer gradually became darker and more viscous; eventually it became an opaque, yellow-brown resin. The aqueous layer was decanted from the mixture. After having cooled to room temperature, the resin layer was very tacky. The crude resin was washed with water and then dissolved in 400 ml of acetone. The acetone solution was filtered. Small portions of the filtrate (about 40 ml) were added slowly to 250 ml volumes of ice-water contained in an osterizer blender operating at high speed. Resin precipitated on the walls of the blender, and the aqueous-acetone layer was decanted from the system. The resin precipitated from each portion treated was washed with water and redissolved in acetone. The cycle was repeated with new portions until the entire acetone solution of the crude product was processed. The washing treatment yielded a 500-ml solution of the resin in acetone. This solution was diluted with 1 liter of water and the resin then settled from it. The recovered resin was washed ten times by stirring with 200 ml portions of water. The resin became quite tacky. Finally, the resin was dried in a vacuum oven at slowly increasing temperatures up to 60°C. Considerable foaming occurred. After the resin dried at 60°C for 12 hr, it yielded 130 g of light yellow solid. The number-average molecular weight of the solid, as determined by vapor pressure osmometry in acetone solution at 37°C, was about 400.

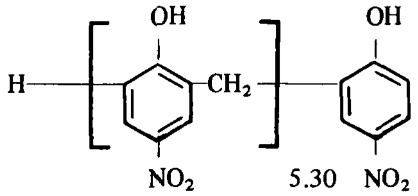
The product was ground in a mortar, dried in a vacuum oven at 110°C for 12 hr, reground, and then dried in a vacuum oven at 110°C for 20 hr. The weight decreased to 123 g, and the product was yellow-brown. The product was then washed ten times by stirring it in 150 ml portions of warm 55-45 (volume per cent) ethanol-water solution. The decantates of the washings were yellow, and the residue was dark brown. After the residue was dried in a vacuum oven at 110°C for 18 hr, there was obtained

77.5 g (50.6% of theory) of dark brown solid. The number-average molecular weight of the product, as determined by vapor pressure osmometry in acetone at 37°, was 940. The product began to decompose slowly at about 175°.

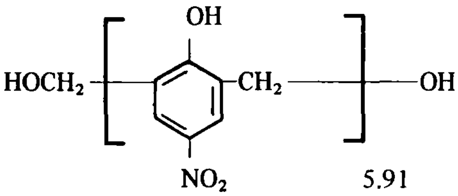
Analysis found for Sample I: C, 56.53%; H, 3.60%; N, 8.88%; for Sample II: C, 56.40%; H, 3.75%; N, 8.85%. Calculated for model structures of molecular weight = 940:

Model Structure	%C	%H	%N
A_1	55.06	3.39	9.39
B_1	54.07	3.54	8.80
C_1	56.70	3.54	8.74

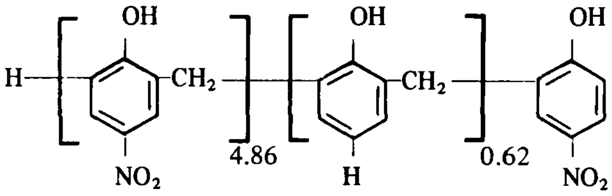
where
Model
Structure A_1 =



Model
Structure B_1 =



Model
Structure C_1 =



It may be seen that, for the above product and for the following three chain analogues of this product, the assumption of a linear, phenol-ended model structure wherein 9.6% of the phenyl rings have lost their nitro substituent (Model Structure C_1) permits a consistent correlation between calculated and observed carbon, hydrogen, and nitrogen percentages. In Model Structure C_1 the total number of chain units, or number of phenyl rings, is 6.48. This figure was chosen to give a molecular weight of 940 so the model structure would be in agreement with the observed value.

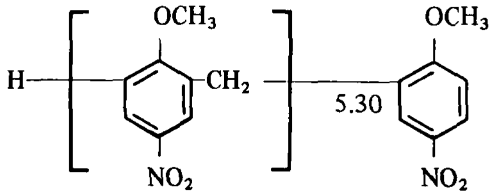
Methylation of the p-Nitrophenol-Formaldehyde Oligomer. Preparation of a p-Nitroanisole-Formaldehyde Oligomer. The preparation was based on the general methylation procedure of Diner [9] which was also used to prepare the dimeric compound, 3,3'-methylenebis-(4-methoxynitrobenzene). p-Nitrophenol-formaldehyde oligomer (number-average molecular weight = 940, 10.0 g, ~0.069 equivalents) was dissolved in 100 ml of N,N-dimethylformamide, which was previously distilled and dried over calcium hydride. The solution was contained in a 250-ml three-necked flask equipped with a mechanical stirrer, water condenser, drying tube, and thermometer. Methyl iodide (12.4 g, 0.0873 mole) was added, and the flask was immersed in an ice-water bath and stirred continuously. Sodium hydride (2.31 g, 0.0964 mole) was added to the flask in small portions over a one-half period. Gentle gaseous evolution occurred, with each addition, a yellow-orange precipitate formed, and the temperature rose slowly. However, the temperature was carefully maintained below 15°C. After all of the sodium hydride was added, the cooling bath was removed, and the reaction mixture was allowed to reach room temperature. Then a second portion of methyl iodide (1.31 g, 0.0092 mole) was added. The reaction mixture was stirred at room temperature for 12 hr. A heavy precipitate of sodium iodide formed. A small amount of methanol was added to neutralize the unreacted sodium hydride, and the reaction mixture was poured into a large beaker and diluted to a volume of 1 liter with distilled water. The pH was adjusted from about 8 to about 4 with dilute hydrochloric acid. The mixture was filtered under reduced pressure, and the residue was washed repeatedly with large amounts of water until the washings gave a negative silver nitrate test for iodide ion. The residue was then dissolved in acetone, gravity filtered, and reprecipitated with water. The precipitate was coagulated by adding a small amount of dilute hydrochloric acid to it. The precipitate was isolated by filtration under reduced pressure, and then it was washed several times with water. The residue was dried in a vacuum oven at 60°C for 12 hr. There was obtained 10.0 g (~91% of theory) of a yellow-brown solid which softens in the range of

128-150°C and melts slowly from 150-180°C. The number-average molecular weight of the product, as determined by vapor pressure osmometry in acetone at 37°, was 1015. The theoretical value from complete reaction with the proposed model (C_1) of the starting material, assuming the average number of chain units had not changed from starting material to isolated product, is 1030.

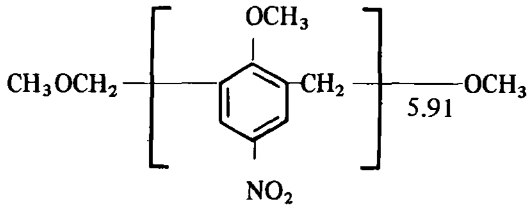
Analysis found for Sample I: C, 59.85%, H, 4.74%; N, 7.99%; for Sample II: C, 59.73%; H, 4.64%; N, 7.95%. Calculated:

Model Structure	%C	%H	%N	MW
A_2	55.70	4.32	8.57	1030
B_2	57.40	4.73	7.87	1050
C_2	59.27	4.49	7.97	1030

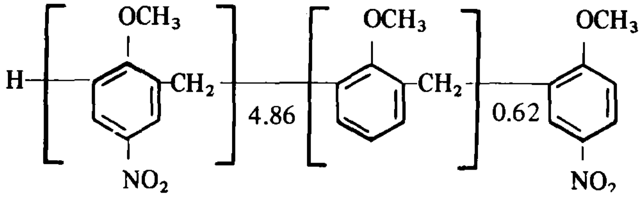
where Model Structure A_2 =



Model Structure B_2 =



Model Structure C_2 =



Model Structure C_2, which assumes a linear, phenol-ended chain of 6.48 units and a loss of 9.6% of the nitro substituents, gives the closest fit to the analysis data.

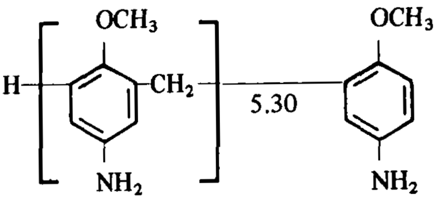
Partial Hydrogenation of the p-Nitroanisole-Formaldehyde Oligomer. Preparation of a (p-Anisidine, p-Nitroanisole)-Formaldehyde Oligomer. The procedure described below is for one of five high-pressure hydrogenation experiments performed on the p-nitroanisole-formaldehyde oligomer. In each experiment the solvent was 2-(2-ethoxyethoxy)-ethanol, $C_2H_5OC_2H_4OC_2H_4OH$, and the catalyst was Raney nickel. The hydrogenations were all conducted at a controlled temperature of 88°C (corrected) and at pressures of 1400-1700 psig. Reaction times were from 2 to 6 hr and yields of product varied from 37 to 82%. As calculated from elemental analyses of the products, the hydrogenation efficiencies, or percentages of nitro groups converted to amino groups, ranged from 65 to 83%. This general method gave the best results of a variety of catalytic hydrogenation and chemical reduction experiments conducted on both p-nitrophenol- and p-nitroanisole-formaldehyde oligomers.

p-Nitroanisole-formaldehyde oligomer (number-average molecular weight = 1015, 10.0 g, 0.058 equivalents) was dissolved in 145 ml of 2-(ethoxyethoxy)-ethanol. The solution was placed in a 300-ml hydrogenation bomb along with 2 teaspoons (approximately 10 ml) of Raney nickel-in-methanol. The bomb was sealed, flushed several times with hydrogen, and then charged with 1610 psig of hydrogen at 24°. After the bomb was rocked at 24°C for 5 min, the pressure was 1550 psig. The bomb and its contents were then rocked and heated at 88°C (corrected) for 3 hr. After the bomb and its contents were cooled to 24°C, the hydrogen pressure was 1340 psig. The total pressure drop of 210 psig after the initial rocking corresponded to 68% of the theoretical hydrogen pressure drop expected for complete reaction. The catalyst was removed by filtration through Celite; the filtrate was diluted with 1500 ml of water and allowed to stand overnight. The red-brown gelatinous precipitate which formed was isolated by filtration and then washed repeatedly with large volumes of water. The residue was dissolved in a minimum amount of dilute hydrochloric acid; the solution was gravity filtered through Celite, and the product was reprecipitated by addition of concentrated ammonium hydroxide until the mixture was strongly alkaline. The precipitate was isolated by filtration, washed thoroughly with water, and dried in a vacuum oven at 66°C for 14 hr. There was obtained 3.9 g (48% of theory) of a yellow-brown solid.

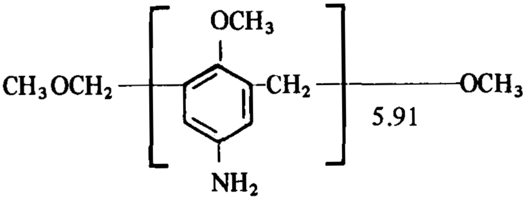
Analysis found for Sample I: C, 68.15%; H, 6.73%; N, 9.00%; O, 15.92%; for Sample II: C, 68.41%; H, 6.77%; N, 9.09%. Calculated:

Model Structure	%C	%H	%N	%O	MW
A_3	70.67	6.81	10.52	12.00	839
B_3	69.02	7.05	9.47	14.47	874
C_3	71.45	6.80	9.61	12.13	855
D_3	68.40	6.23	9.20	16.15	893

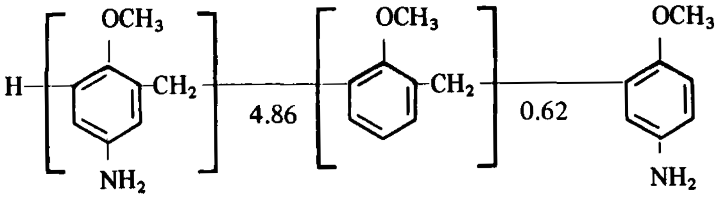
where
Model
Structure A_3 =



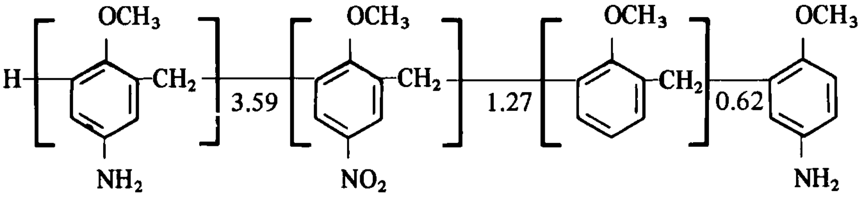
Model
Structure B_3 =



Model
Structure C_3 =



Model
Structure D_3 =



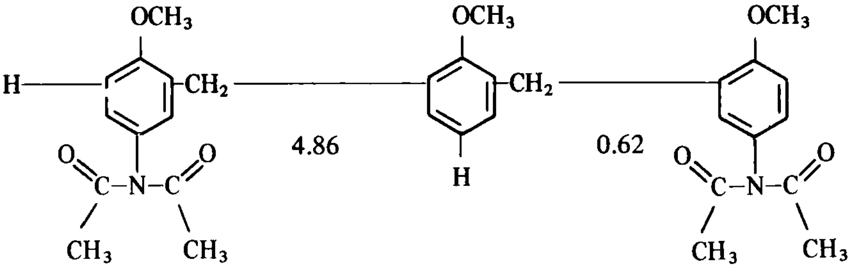
The model structure which best fits the elemental analysis is Model Structure D_3, which assumes a linear, phenol-ended chain of 6.48 units, 9.6% of which have lost the nitrogen substituent, and with 78% conversion of nitro to amino substituents.

(N,N-Diacetyl-p-anisidine, p-nitroanisole)-Formaldehyde Oligomer. The starting material for this oligomer was the partially hydrogenated p-nitroanisole-formaldehyde oligomer for which the elemental analysis indicated 78.5% conversion from nitro to amino groups. This oligomer (0.204 g, approximately 0.0010 M in amino groups) was added, together with 50 ml of dioxane and 15 ml of acetic anhydride (0.16 mole), to a 100-ml round-bottom flask which was equipped with a reflux condenser, magnetic stirrer, and heating mantle. The mixture was refluxed for 12 hr with continuous stirring and was then cooled and gravity filtered. The small residue of insoluble matter was discarded. The filtrate was diluted with four volumes of water, and the resulting solution was heated to 70°C. After the solution was cooled, a cloudy mixture was formed. This mixture was neutralized with sodium carbonate to a pH between 6 and 7. The brown precipitate which then formed was isolated by filtration under reduced pressure. It was washed with water and dried in a vacuum oven at 60°C for 18 hr. There was obtained 0.190 g of tan solid.

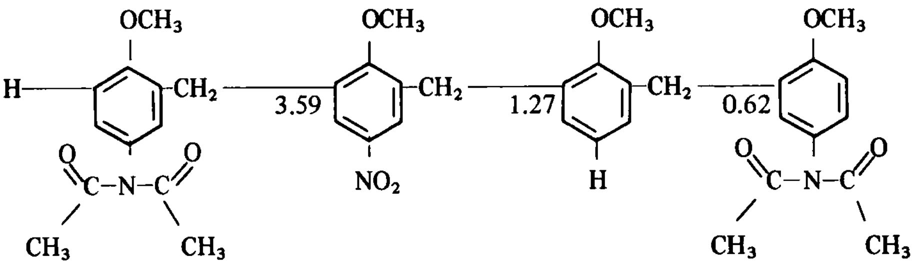
Analysis found for Sample I: C, 64.96%, H, 6.31%; N, 5.67%; O, 23.00%; for Sample II: C, 64.47%; H, 6.01%; N, 5.91%. Calculated:

Model Structure	%C	%H	%N	%O	MW
C_4	66.62	6.06	6.09	21.62	1348
D_4	65.01	5.79	6.42	22.77	1280

where Model Structure C_4 =



Model Structure D_4 =



The best fit to the elemental analysis is Model Structure D_4, which assumes a linear, phenol-ended chain of 6.48 units, 9.6% of which have lost the nitrogen substituent. Of the remaining nitrogen substituted units, 78.5% are assumed to have diacetylamino substituents and 21.5% to have nitro substituents. This structure is analogous to the assumed Model Structure D_3 of the starting material.

Reaction of the (p-Anisidine, p-Nitroanisole)-Formaldehyde Oligomer with Chloroacetic Acid. Attempted Preparation of a Chelating Oligomer. The procedure described below was the most successful one used in a large number of experiments in which chloroacetic acid was reacted with a (p-anisidine, p-nitroanisole)-formaldehyde oligomer.

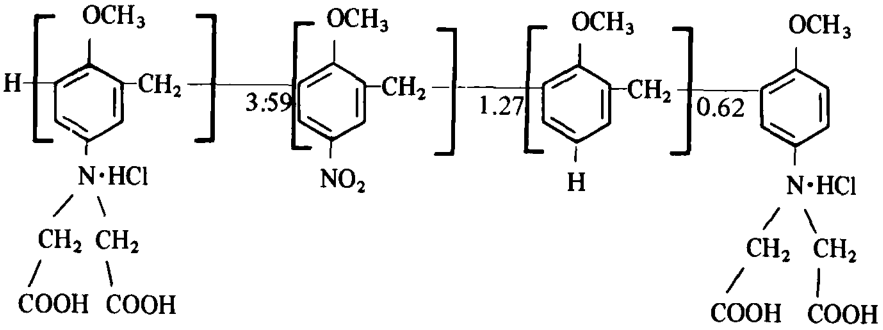
Part I. The partially hydrogenated p-nitroanisole-formaldehyde oligomer for which elemental analysis of both the oligomer and its diacetyl derivative indicated 78.5% conversion from nitro to amino groups (1.00 g, approximately 0.0046 M in amino groups) was dissolved in 100 ml of dioxane. The solution was contained in a 250-ml three-necked flask equipped with a reflux condenser, magnetic stirrer, thermometer, heating mantle, and a gas inlet tube. By means of the gas inlet tube the reaction mixture was blanketed with a slow stream of nitrogen. Sodium acetate (1.56 g, 0.1090 mole) and chloroacetic acid (1.80 g, 0.0190 mole) were reacted in 15 ml of water; the resulting solution was added to the reaction flask. The reaction solution was heated to the reflux temperature (90°) with stirring. A solution of sodium acetate (1.56 g, 0.0190 mole) in 25 ml of water was added to the reaction flask. After the reaction solution was refluxed for 7 hr, a small aliquot was removed and diluted with water. A precipitate formed; it was completely soluble in dilute sodium hydroxide solution. After the reaction solution was refluxed for a total of 8 hr, a sodium chloroacetate solution (0.726 g chloroacetic and 0.629 g. sodium acetate in 4 ml of water) was added to the reaction flask. After the reaction solution was refluxed for 22 hr, another sodium chloroacetate solution of the same composition was added. After having refluxed for 48 hr, the reaction solution was cooled to room temperature and gravity filtered. The filtrate was diluted with four volumes of water, and a tan precipitate formed. The pH of the system was 3.9. The precipitate was isolated by filtration under reduced pressure, washed with water, and dried in a vacuum desiccator over P_2O_5; 0.9 g of brown solid (I) was obtained.

Part II. Product (I) (0.300 g) was added to 25 ml of 80-20 (volume per cent) ethanol-water solution. Hydrochloric acid (2 ml, 6 M) was then added, and the system was heated until a solution formed. The solution was gravity filtered, and the filtrate was saturated with hydrogen chloride gas while it cooled in an ice-water bath. After approximately 11 g of hydrogen chloride was added, the solution was diluted with 125 ml of water and cooled in an ice-water bath. The tan precipitate which formed was isolated by filtration under reduced pressure, washed with anhydrous diethyl ether, and dried in a vacuum desiccator; 0.154 g of a tan solid (II) was obtained.

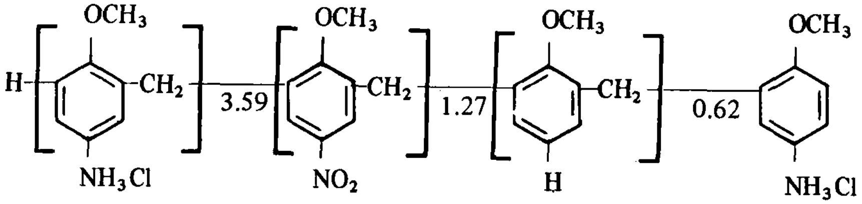
Analysis found for (II): Sample I: C, 62.39%; H, 6.21%, N, 6.11%; for Sample II: C, 62.65%; H, 6.22%, N, 6.25%. Calculated for (II):

Model Structure	%C	%H	%N	MW
D_5	52.18	4.94	5.15	1593
E_5	57.59	5.68	7.74	1061
F_5	58.30	5.20	5.76	1426
G_5	62.52	5.76	7.74	1063
H_5	62.52	5.63	7.19	1142

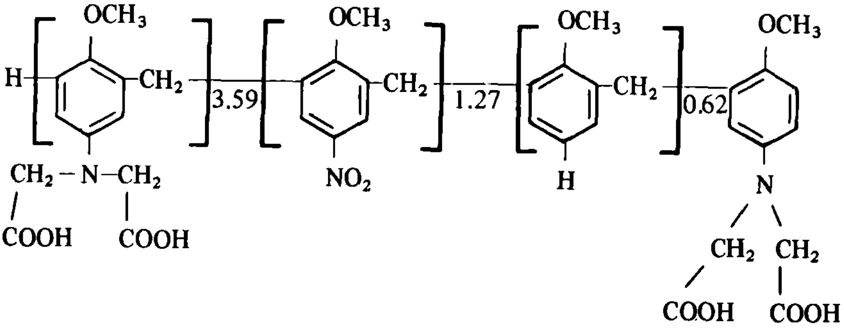
where Model Structure D_5 =



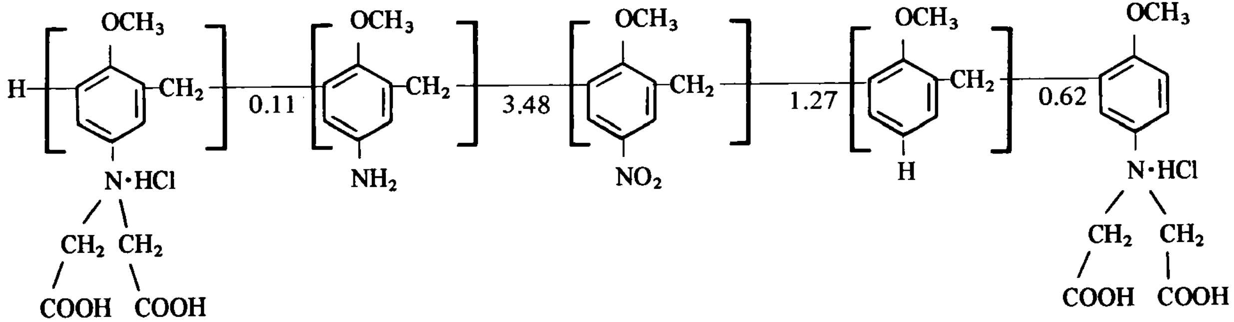
Model Structure E_5 =



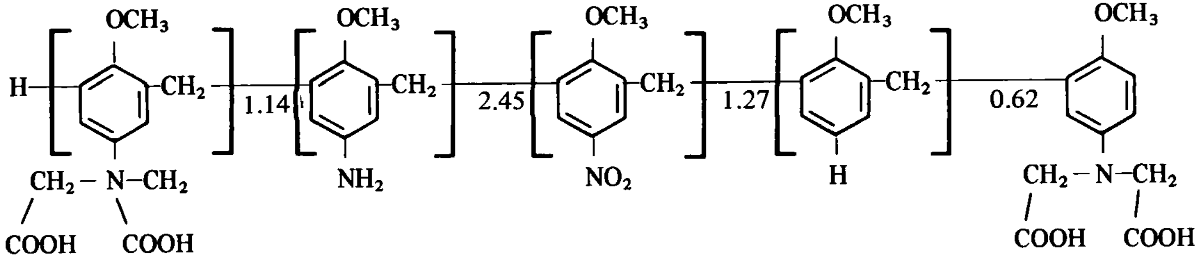
Model Structure F_5 =



Model Structure G_5 =



Model Structure H_5 =



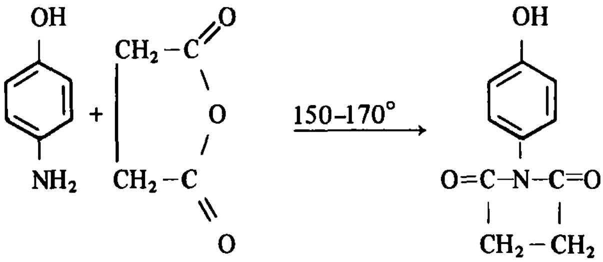
The elemental analysis values of product (II) are intermediate between the experimental values for the starting material, the (p-anisidine, p-nitroanisole)-formaldehyde oligomer, and the calculated values for possible Model Structures D_5, E_5, and F_5. Model Structure D_5 assumes complete reaction and complete hydrochloride salt formation of the iminodiacetic acid nitrogen atoms. Model Structure E_5 assumes no reaction except complete hydrochloride salt formation of the amino nitrogen atoms. Model Structure F_5 assumes complete reaction to free iminodiacetic acid functions with no hydrochloride salt formation. Best fits to the experimental data are obtained with the partial reaction models G_5 and H_5. Model Structure G_5 assumes partial reaction (24%), but with hydrochloride salt formation of the iminodiacetic acid nitrogen atoms only. Model Structure H_5 assumes partial reaction (47%) to free iminodiacetic acid functions with no hydrochloride salt formation. All of the Model Structures D_5 to H_5 assume linear, phenol-ended chains of 6.48 units, with relative segmer distributions which are analogous to that of the assumed Model Structure D_3 for the starting material.

Chelating Properties of the Oligomer. Product (I) (0.100 g, 0.18 meq) was partially dissolved in a solution of dioxane (20 ml) and water (10 ml) by stirring and heating the mixture on a steam bath. Sodium hydroxide solution (0.095 ml, 2.0 M) and copper(II) nitrate solution (0.095 ml, 2.0 M) were added. The pH of the reaction mixture was below 4; it was adjusted to 6.0 by adding 0.10 ml of 2.0 M sodium hydroxide solution. The reaction mixture was then transferred to a 100-ml three-necked flask; the mixture was washed into the flask with 10 ml of dioxane; the flask and contents were heated at 60°C for 12 hr with stirring. After the reaction mixture was diluted with 50 ml of water, the pH was 4.15. The pH was adjusted to 6.1 by adding 0.45 ml of 2 M sodium hydroxide. After the reaction mixture was stirred for 24 hr, the pH dropped to 5.0. It was adjusted to 6.0 by adding 0.20 ml of 2 M sodium hydroxide solution. The reaction mixture was diluted with 50 ml of water, allowed to stand, and then filtered under reduced pressure. The residue was washed with water and dried in a vacuum over at 60°C for 48 hr: 0.093 g of a brown solid (III) was obtained. The infrared spectrum of the product (III) is very similar to that of the starting material (I). The spectrum offers no apparent evidence for chelate formation.

DISCUSSION

This research was concerned initially with the use of indirect methods of synthesis for preparing dimers and oligomers based on the model chelating compounds reported in an earlier paper [2]. The approach followed in the synthesis was based on the use of phenolic monomers wherein the para position on the phenol ring was blocked with a suitably substituted nitrogen group that was unreactive to subsequent formaldehyde condensation.

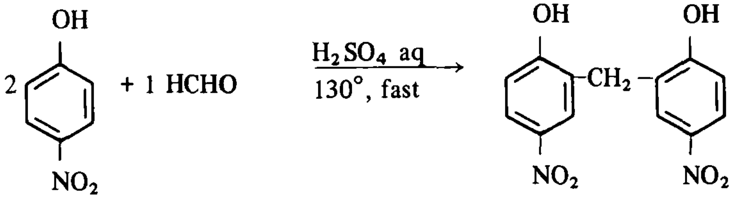
The first attempt in this research to block the para position of the phenyl ring involved the reaction of p-aminophenol with succinic anhydride to give N-(4-hydroxyphenyl) succinimide:



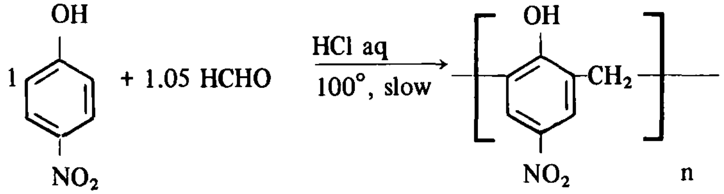
$+ H_2O$ (1)

This compound was obtained in good yield by heating an equimolar mixture of the two reactants at 150–170°C for 1 hr, according to the method of Wirths [12]. The product was purified by recrystallization, and the elemental analysis agreed closely with the calculated percentages. However, a number of attempts to prepare dimers of this compound by condensation in a 2:1 mole ratio with formaldehyde in sulfuric acid medium were unsuccessful. From these experiments only starting material and/or cross-linked, insoluble polymers were obtained. Moreover, the polymers formed appeared to be cross-linked through the para nitrogen position.

The next method employed to "block" the para nitrogen substituent involved the use of p-nitrophenol. This proved to be successful, and it was found possible to condense this compound to give soluble, characterizable products:



(2a)

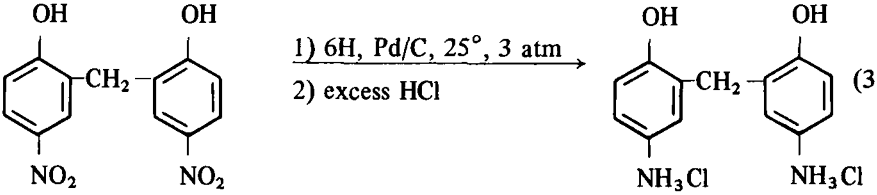


(2b)

By controlling the ratio of reactants and the nature of the catalysts, either dimers or higher molecular weight products were obtained in reasonably good yields. Also, in the case of the higher molecular weight products, it was found possible to control the molecular weight by varying the amount and degree of postheating of the condensation products.

After it was ascertained that the use of para-nitro substituents on the phenolic ring afforded a means of obtaining suitable condensation products with formaldehyde, attention was directed toward the dimeric product, 3,3′-methylenebis-(4-hydroxynitrobenzene), with the aim of converting the nitro groups by chemical treatment to amino acid groups analogous to those in the model compounds, N-(4-hydroxyphenyl) glycine and N-(4-hydroxyphenyl) iminodiacetic acid, previously reported [2].

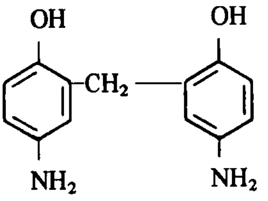
The first step involved the preparation of 3,3′-methylenebis-(4-hydroxyaniline hydrochloride) by catalytic hydrogenation of the nitro compound:



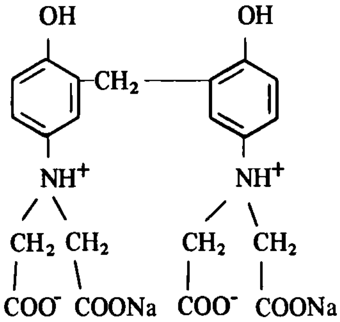
(3)

This reaction went rapidly under mild conditions to give the product in good yields (80-90%). The product was isolated in the hydrochloride salt form because the free amine was unstable to air oxidation.

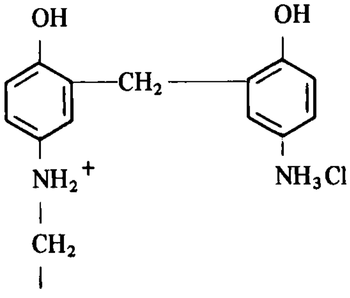
Next, a number of attempts were made to prepare 3,3′-methylenebis-[N-(4-hydroxyphenyl) glycine] by reaction of 3,3′-methylenebis-(4-hydroxyaniline hydrochloride) with chloroacetic acid in the presence of base. In these experiments, the procedures followed were patterned after those reported in the literature for the preparation of the corresponding model compound, N-(4-hydroxyphenyl) glycine [13-15]. The procedure involved the reaction of the amine hydrochloride dimer (1 mole) in aqueous medium with from 2 to 4 moles of chloroacetic acid in the presence of from 4 to 11 moles of base. The bases used were sodium hydroxide and sodium acetate. The reactions were run at temperatures from 55-100° for periods of from 5 min to 10 hr. Although reactions did occur, in none of the experiments was the desired product isolated. The only products identified from these experiments were the free amine of the starting material,



a tetrasubstituted material,



and, in one experiment, a small amount of a monosubstituted material,



The failure to isolate the desired product might be due to its oxidative instability, or to a tendency for disubstitution of one nitrogen site to form $[-R-N(CH_2COOH)_2]$ groups in preference to the monosubstitution of both nitrogen sites to form two glycine $[(-R-NH(CH_2COOH)]$ groups, or perhpas to a combination of both factors.

The tendency to form iminodiacetic acid groups in preference to glycino groups is not too surprising in consideration of the report of Galatis [14] that approximately equal yields of N-(4-hydroxyphenyl) glycine and N-(4-hydroxyphenyl) iminodiacetic acid result when equimolar amounts of p-aminophenol, chloroacetic acid, and sodium hydroxide are refluxed in aqueous medium. Also indicative of this tendency toward disubstitution is the commerical preparation of glycine from ammonia and chloroacetic acid, which requires a threefold excess of ammonia to obtain good yields [16].

Because attempts to isolate 3,3′-methylenebis-[N-(4-hydroxyphenyl) glycine] by direct condensation of the dimeric amine with chloroacetic acid were unsuccessful, a method used to prepare the model compound [17] was tried as an alternate method for the dimeric system:

$$RNH_3Cl + HCHO + KCN \longrightarrow RNHCH_2CN$$

$$RNHCH_2CN + \text{dil HCl aq} \xrightarrow{\text{heat}} RNHCH_2COOH$$

In this method, equivalent amounts of 3,3′-methylenebis-(4-hydroxyaniline hydrochloride), formaldehyde, and potassium cyanide were reacted in aqueous medium at 10-15°, and the product was refluxed in dilute hydrochloric acid solution. Infrared analysis of the reaction products indicated that some reaction had occurred, but neither the desired product, $CH_2[C_6H_3(OH)(NHCH_2COOH)]_2$, nor its nitrile intermediate,

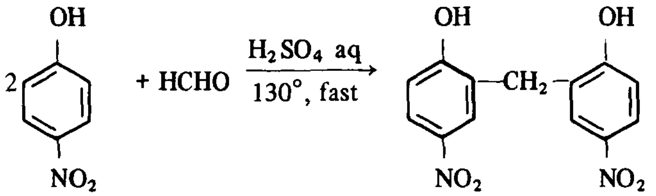
$CH_2[C_6H_3(OH)(NHCH_2CN)]_2$, could be isolated. Again, failure to isolate the desired product might be due either to its oxidative instability or to competitive disubstitution reactions leading to the formation of iminodiacetic acid groups, $[-R-N(CH_2COOH)_2]$.

After efforts to prepare the dimeric glycino compound failed, the investigation was directed toward the preparation and characterization of 3,3′-methylenebis-[N-(4-hydroxyphenyl iminodiacetic acid] and its metal complexes with divalent copper, nickel, cobalt, and zinc.

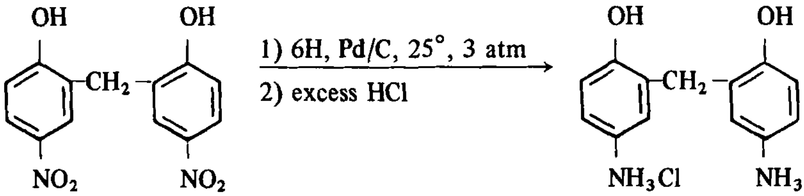
After the characterization of the dimeric system analogous to N-(4-hydroxyphenyl) iminodiacetic acid was completed, a preliminary investigation was made on the oligomeric analogues of this compound. One important result of the preliminary investigation of the oligomeric system is that it was found necessary to methylate the phenolic OH groups of the oligomeric condensation products of p-nitrophenol and formaldehyde in order for subsequent hydrogenation of the nitro groups to proceed substantially. Therefore, it was decided to prepare and characterize the dimeric compound, 3,3′-methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid], and its metal complexes for comparison with both the methylated oligomeric system and the nonmethylated dimer, 3,3′-methylenebis-[N-(4-hydroxyphenyl) iminodiacetic acid].

Prototype Dimeric Compound (I): 3,3′-Methylenebis-[N-(4-hydroxyphenyl) iminodiacetic acid] and Metal Complexes

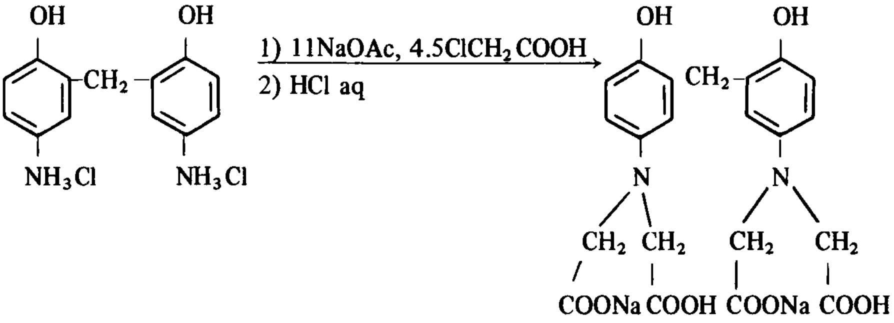
This compound was obtained, in the disodium salt form, from a three-step synthesis beginning with p-nitrophenol and formaldehyde:



(2a)



(3)

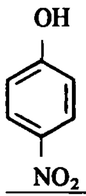
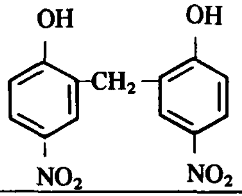
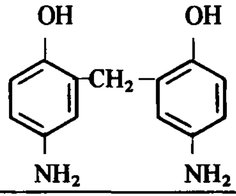
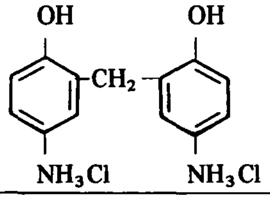


(4)

Because of the similarity in composition of p-nitrophenol ($C_6H_5NO_3$, %C = 51.80) and its condensation products with formaldehyde (e.g., dimer = $C_{13}H_{10}N_2O_6$, %C = 53.80; trimer = $C_{20}H_{15}N_3O_9$, %C = 54.42, etc.), elemental analysis alone does not establish conclusively the dimeric nature of the reaction products. In order to prove that dimerization had occurred, as in Eq. (2a), the molecular weights of the starting material, p-nitrophenol, and its 2-to-1 condensation product with formaldehyde were determined by vapor pressure osmometry in acetone solution at 37°C. The experimental molecular weights obtained for these compounds were 141 and 289, respectively. These are in good agreement with the theoretical values, 139 for n-nitrophenol, and 290 for 3,3′-methylenebis-(4-hydroxynitrobenzene). Other evidence supporting the dimerization includes the increase in melting point from 114°C for the monomer to 268°C for the dimer, and the general decrease in solubility for the dimer in comparison to the monomer.

The infrared spectra of p-nitrophenol and its dimer with formaldehyde are quite similar, as would be expected. Important assignments for the spectra of these two compounds, and for the spectra of the corresponding free amine and amine hydrochloride of Dimer System I, are given in Table 3. The only distinguishing difference between the spectra of p-nitrophenol and its dimer with formaldehyde is the absorptions due to C–H out-of-plane bending vibrations. p-Nitrophenol and other related monomers studied in this research show a peak between 800 and 860 cm^{-1}, which is characteristic of 1,4-substituted benzenes [18]. The corresponding dimers display two peaks in the ranges 800-860 cm^{-1} and 860-915 cm^{-1} which are characteristic of 1,2,4-substituted benzenes. These absorptions are attributed to C–H out-of-plane bending vibrations involving either two adjacent–or one isolated–free ring hydrogen atom(s) [18].

Table 3[a]. Some Characteristic Infrared Absorption Frequencies (cm^{-1}) and Tentative Assignments[b] for *p*-Nitrophenol and Related Dimeric Compounds

Compound				
				Tentative assignment
3340 (s,b)	3330 (s,b)		3345(s)	ν (OH)
		3370(s), 3300(s)		ν_{asym} and $\nu_{sym}(NH_2)$, ν (OH)
			2940(vs,vb)	ν (NH_3^+)
1505 (s)	1511 (s)			ν asym (NO_2)
1330 (vs)	1335 (vs)			ν sym (NO_2)
1280 (s)	1274 (s)	1229 (s)	1279 (s)	ν ($C_{aromatic}$—O)
	910 (m)	910 (m)	891 (m), 881 (m)	δ (CH out-of-plane, 1 isolated H)
843 (s)	830 (m)	812 (s)	824 (s), 816 (s)	δ (CH out-of-plane, 2 adjacent H's)

[a] Abbreviations used for this and following spectral tables: s = strong, m = medium, w = weak, b = broad, sh = shoulder, v = very, ν = stretching vibration, δ = deformation vibration, sym = symmetric, asym = antisymmetric, arom = aromatic, aliph = aliphatic.

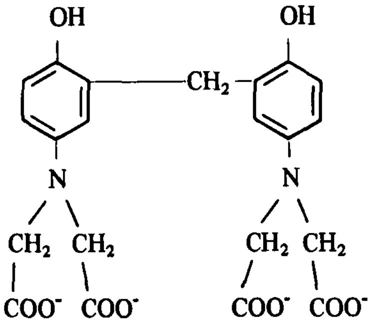
[b] Based on similar assignments in the following references: general: Bellamy [18], Nakanishi [19], Rao [20], and Colthup et al. [21]; C_{arom}—O stretching vibrations: Hadzi and Sheppard [22], Davies and Jones [23], Briggs et al. [24], and Ritschl [25].

The conversion of the dimeric nitro compound to the corresponding amine hydrochloride by catalytic hydrogenation (Eq. 3) is established not only by the good agreement of the product elemental analysis data with calculated values but also by the changes in the infrared spectra. For example, the characteristic strong absorptions at 1511 and 1335^{-1}, due to the antisymmetric and symmetric stretching vibrations of the nitro group, do not appear in the spectrum of the product; and a new, very strong, broad absorption appears near 2940 cm^{-1}. This absorption is attributed to the NH_3^+ stretching vibration. Moreover, the spectrum of the free amine of Dimer System I shows peaks at 3370 and 3300 cm^{-1} which may be assigned to the NH_2 antisymmetric and symmetric stretching vibrations, although these absorptions are most likely mixed with the O–H stretching peak in the same region.

The final step in the preparation of Prototype Dimer I was the reaction of the amine hydrochloride dimer in aqueous medium with a slight excess of chloroacetic acid in the presence of an excess of sodium acetate (Eq. 4). Hydrochloric acid solution was added to adjust the pH to the isoionic point of the disodium salt form of the product, which is approximately pH 3.75 in concentrated solution. The product was isolated in the disodium salt form because of the difficulties encountered in attempts to isolate the free acid.

The elemental analysis of the ligand disodium salt shows high results for hydrogen and low results for carbon. This might be expected to be due to absorbed water; however, thermogravimetric analysis of the compound indicated it to be anhydrous. It might be pointed out that deviations of this type are not uncommon for sodium salts of amino acids, which are often difficult to characterize [26].

The potentiometric curve for Prototype Dimer I shown in Fig. 1 was obtained from data for the titration of an approximately 0.006 M aqueous solution at room temperature; standard hydrochloric acid and sodium hydroxide solutions were used as titrants. In this plot, when "n" represents the number of moles of base added per mole of ligand free acid, two inflection points are distinguishable, at n = 2 (pH = 4.4) and n = 4 (pH 8.1). These inflections correspond to the isoionic points of the species $(H_2L_I)^{2-}$ and $(L_I)^{4-}$, respectively, where the symbol $(L_I)^{4-}$ represents the tetranegative ion of Prototype Dimer I:



From this curve, the pH's corresponding to n = 2.5 (i.e., pH 5.3) and n = 3.5 (i.e., pH 6.4) may be taken to represent apparent pK_a values for the ionizations

$$H_2L_I^{2-} + H_2O \rightleftharpoons H_3O^+ + HL_I^{3-} \qquad (pK_{1,2} = 5.3)$$

$$HL_I^{3-} + H_2O \rightleftharpoons H_3O^+ + L_I^{4-} \qquad (pK_1 = 6.4)$$

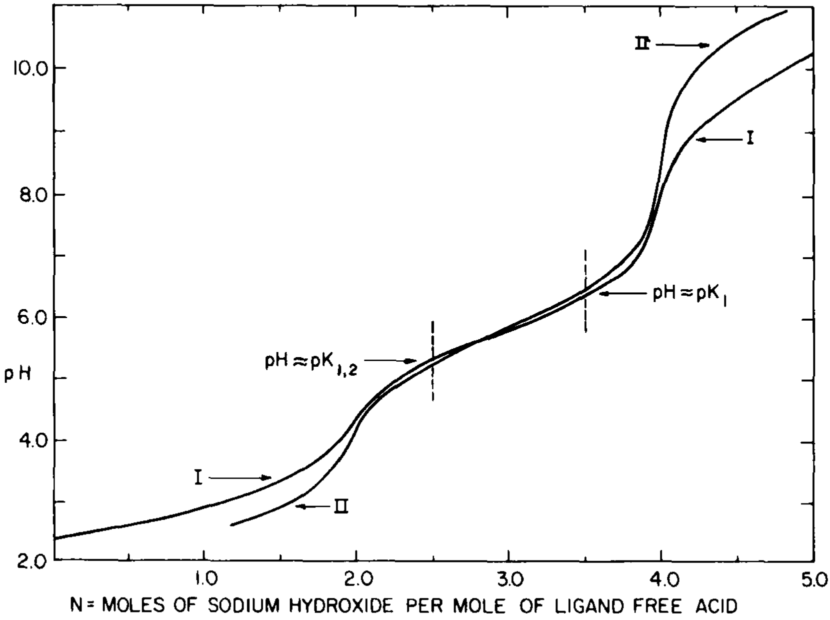
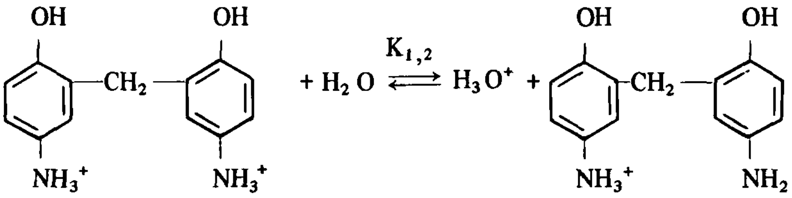


Fig. 1. Potentiometric titration curves. I: 3,3′-methylenebis-[N-(4-hydroxyphenyl) iminodiacetic acid]; ~0.006 M; H_2O as solvent. II: 3,3-methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid]; ~0.006 M; ~85-15 (vol%) H_2O-dioxane as solvent.

Since in aqueous solution the protons involved in these ionizations, i.e., the more basic protons, are normally associated with the nitrogen atoms (zwitterion form), these uncorrected pK_a values may be taken to be approximate indications of the basicity of the nitrogen atoms.

These apparent pK_a values may be compared with recorded pK_a values for analogous systems given in Table 4. From an examination of Table 4 one can see the decreased nitrogen basicity (evidenced by smaller pK_a values corresponding to larger acidic ionizations) in going from compounds with nitrogen atoms which have only aliphatic substituents to anologous compounds wich have aromatic substitutents on nitrogen (cf. EDTA with o-phenylenediamine-N,N,N′,N′-tetraacetic acid, or N-methyliminodiacetic acid with N-phenyliminodiacetic acid). The pK_a data also suggest that, for aromatic-substituted nitrogens, an electron releasing group para to the nitrogen effects a measurable increase in the nitrogen basicity (cf. N-phenyliminodiacetic acid, $pK_1 = 4.96$, and N-(p-carboxyphenyl)iminodiacetic acid, $pK_1 = 5.20$). In summary, the apparent pK_a values of 6.4 and 5.3 obtained for Prototype Dimer I indicate that its nitrogen atoms are considerably less basic than those of EDTA or IMDA, but that the nitrogens are similar in basicity to those of other aromatic substituted nitrogen derivatives.

The apparent pK_a values were obtained similarly for the amine hydrochloride dimer, $CH_2[C_6H_3(OH)(NH_3Cl)]_2$, of Dimer System I; values of 4.8 for $pK_{1,2}$ and 5.9 pK_1 were obtained corresponding to the ionizations



and

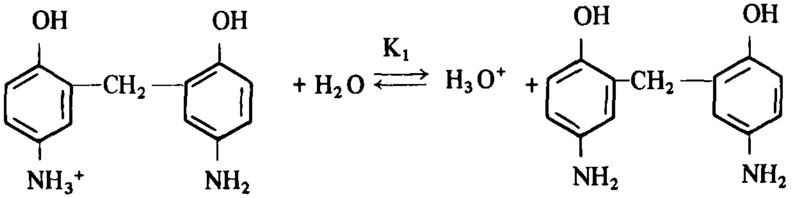


Table 4. Literature pK_a Values for Some Substituted Amino Acids [27]

Compound	pK_1	$pK_{1,2}$	Temperature °C
Ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA)	10.26	6.16	20
Hexamethylenediamine-N,N,N′,N′-tetraacetic acid	10.65	9.75	20
o-Phenylenediamine-N,N,N′,N′-tetraacetic acid	6.7	4.8	30
Iminodiacetic acid (IMDA)	9.89	2.98	20
N-Phenyliminodiacetic acid	4.96	2.40	20
N-Methyliminodiacetic acid	9.65	2.12	20
N-(p-Carboxyphenyl)iminodiacetic acid	5.20	4.28	20

The lower pK_a values for the amine hydrochloride dimer indicate its lower nitrogen basicity in comparison with the prototype dimeric ligand itself, in which each of the nitrogens is disubstituted with carboxymethyl groups.

Infrared spectra of the ligand were recorded for samples isolated at five different pH's, for which the predominant species are as follows:

pH	Predominant species
<1	$(H_6L_I)^{2+}\ Cl_2{}^{2-}$
~2.3	H_4L_I
3.4	$Na_2H_2L_I$, NaH_3L_I
4.6	$Na_2H_2L_I$
8.1	Na_4L_I

Important absorptions for these species are tabulated in Table 5.

The spectrum at pH < 1 shows a very strong peak at 1735 cm^{-1}, which is assigned to the C=O stretching vibration of the un-ionized carboxyl group. This peak shifts to a lower frequency (1705 cm^{-1}) and becomes weaker in intensity as the pH increases, but the absorption is still present at pH 4.6 at moderate intensity. The peak disappears at pH 8.1. Two other peaks at 1410 and 1190 cm^{-1}, at pH < 1, similarly become gradually weaker in intensity as the pH increases to 4.6, and these peaks also disappear at pH 8.1. They are attributed to interacting in-plane O–H deformation and C–O stretching vibrations of the un-ionized carboxyl group [21].

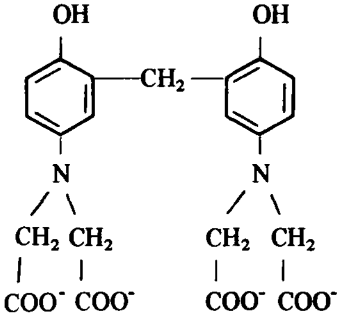
For the ligand sample isolated at pH < 1, the spectrum shows strong, broad absorptions near 3000 and 2600 cm^{-1} which are probably due to NH^+ stretching. At pH 2.3 the higher frequency peak is considerably weaker and at pH 4.6 has virtually disappeared. The peak at 2600 cm^{-1} is present at weaker intensity up to pH 4.6. Both peaks are absent at pH 8.0.

An absorption band appears near 1660 cm^{-1} at pH 2.3; it shifts to 1609 cm^{-1} at pH 3.4. At pH 8.0 the band is broad and strong, and it absorbs near 1585 cm^{-1}. Another band, near 1397 cm^{-1}, begins to appear at pH 3.4 and is broad and strong at pH 8.0. These peaks are attributed to the carboxylate antisymmetric and symmetric stretching vibrations, respectively.

Table 5. Some Characteristic Infrared Absorption Frequencies (cm^{-1}) for Species of 3,3′-Methylenebis-[N-(4-hydroxyphenyl)iminodiacetic acid] at Various pH's

pH	<1	~2.3	3.4	4.6	8.1
Predominant species	$H_6L_IC l_2$[a]	H_4L_I	$Na_2H_2L_I$ NaH_3L_I	$Na_2H_2L_I$	Na_4L_I
Absorptions, cm^{-1}	~3000 (s,b)	~3000 (m)	~3000 (w)	~3000 (vw)	–
	~2600 (s,b)	~2600 (m)	~2600 (m)	~2600 (m)	–
	1735 (vs)	1705 (s)	1705 (s,b)	1710 (m)	–
	–	1660 (s)	1609 (s)	1585 (s,b)	1585 (vs,b)
	1410 (s,b)	1410 (sh)	1396 (m,b)	1403 (m)	–
	–	–		1397 (m)	1397 (s,b)
	1278 (s)	1255 (sh)	1255 (s)	1253 (s)	1250 (sh)
	1190 (s)	1190 (sh)	1190 (sh)	1190 (sh)	–

[a] In this and Tables 6 and 7, "L_I" represents the tetranegative ion of Prototype Dimer I:



The persistence of the 1705 cm^{-1} peak at pH 4.6, which is slightly above the isoionic point for $Na_2H_2L_I$, together with the corresponding disappearance of the peak at 3000 cm^{-1} at this same pH, indicates that in the solid state of the $Na_2H_2L_I$ species, the protons are associated primarily with the carboxyl groups rather than with the nitrogen atoms (zwitterion form). This type of behavior, however, is not unusual, since nitrilotriacetic acid has been shown to have all three carboxyl groups un-ionized with no N^+H absorption in the solid state [28], and the disodium salt of EDTA also exhibits infrared absorption characteristic of un-ionized carboxyl groups [29].

Metal complexes of Prototype Dimer I with divalent copper, nickel, cobalt, and zinc were prepared by reacting the ligand disodium salt in aqueous solution in a 1:2 mole ratio with the metal ion in the presence of 2 moles of sodium hydroxide. The copper complex precipitated almost immediately; the cobalt, nickel, and zinc complexes precipitated after the aqueous solutions were heated and cooled.

The analytical results for the complexes are in reasonably good agreement with the empirical formula for the 1:2 mole ratios of ligant-to-metal ion, although the nickel, cobalt, and zinc complexes show high hydrogen results paralleling those obtained for the ligand disodium salt. The analytical results also indicate that the copper complex is a monohydrate, whereas the other three complexes are dihydrates.

These results are supported by the data given in Table 6 which were derived from the thermogravimetric curves of the complexes. The estimated weight losses (from the curves) prior to decomposition correspond well to the theoretical water percentages for the assigned hydrate formulas. In the thermogravimetric determinations, the metal complexes were heated under nitrogen at a rate of 3°/min. For each complex, the procedural initial decomposition temperature is taken to be the temperature at which the weight loss curve begins to drop below the slope because of the water loss. The results indicate that the cobalt, nickel, and zinc complexes are thermally stable in nitrogen to about 300°C, whereas the copper complex and ligand disodium salt begin to decompose near 160°C.

The important infrared spectral assignments for the metal complexes of Prototype Dimer I are given in Table 7.

The spectra of the metal complexes all show absorption in the 3400 cm^{-1} region, which is due to water and to the phenolic OH group. For the cobalt and nickel complexes, the spectra of which are virtually identical, this absorption is very strong, very broad, and centered near 3360 cm^{-1}. For the zinc complex, this absorption is split into two broad bands which are centered at 3450 and 3190 cm^{-1}. For the tetrasodium salt, this absorption is

Table 6. Thermogravimetric Data for 3,3′-Methylenebis-[N-4-hydroxyphenyl) iminodiacetic acid] Disodium Salt and Its Metal Complexes

Compound	Initial weight, mg	Suppression, mg	Estimated weight loss, %	Theoretical loss, % water	Procedural initial decomposition temperature, °C
$Na_2H_2L_I$	11.25	9.25	0.0	0.0	160
$Cu_2L_I{\cdot}H_2O$	10.02	8.02	~2.9	2.99	160
$Co_2L_I{\cdot}H_2O$	5.00	4.00	5.8	5.88	300
$Ni_2L_I{\cdot}2H_2O$	10.55	8.55	6.1	5.89	310
$Zn_2L_I{\cdot}2H_2O$	10.44	8.44	5.0	5.76	320

Table 7. Some Characteristic Infrared Absorption Frequencies (cm^{-1}) and Tentative Assignments[a] for the Tetrasodium Salt and Metal Complexes of 3,3′-Methylenebis-[N-(4-hydroxyphenyl) iminoacetic acid]

Compound					
$Na_4L_I \cdot nH_2O$	$Cu_2L_I \cdot H_2O$	$Co_2L_I \cdot 2H_2O$	$Ni_2L_I \cdot 2H_2O$	$Zn_2L_I \cdot 2H_2O$	Tentative assignment
3400 (s,b)	3400 (m)	3360 (vs,vb)	3360 (vs,vb)	3450 (m,b) 3190 (m,b)	$\nu\,(H_2O)^b$
1585 (vs,b)	1608 (vs), 1559 (vs)	1581 (vs,b)	1585 (vs,b)	1570 (vs,b)	ν asym $(COO^-)^b$
1397 (s)	1372 (s) 1409 (s)	1399 (s)	1404 (s)	1409 (s)	ν sym (COO^-)
188	(236)(150)	182	181	161	$\Delta\nu$ asym-sym (COO^-)
1250 (sh)	1273 (s)	1259 (m,b)	1262 (m)	1264 (s,b)	$\nu\,(C_{arom}\text{—}O)$

[a] Assignment of carboxylate stretching peaks based on similar assignments given in Refs. 2, 18, 28, 30-39. Assignment of C_{arom}—O *stretching vibrations* based on similar assignments given in Refs. 21-25.

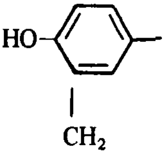
[b] Estimated centers of absorption maxima for broad bands.

centered at 3400 cm^{-1} and is intermediate in intensity between the cobalt or nickel complex and the copper complex. For the copper complex, this absorption is the narrowest and weakest of the group and is centered at 3400 cm^{-1}.

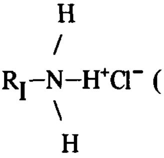
In the spectra of these complexes, the absorptions due to the antisymmetric stretching vibration of the carboxylate groups occur in the region near 1580 cm^{-1}, and are broad and very strong. Values for this peak listed in Table 7 represent estimated centers of the absorption maxima, because the absorptions are spread over 30 to 40 cm^{-1} ranges in the cobalt, nickel, and zinc complexes, as well as in the tetrasodium salt. The occurrence of ring skeletal vibrations near the same frequency, the possibility of water interaction, and the broadness of the absorption maxima make absolute assignment of the carboxylate antisymmetric vibration frequencies for these complexes of questionable value. The copper complex spectrum is unique in that its carboxylate peaks are split. For this complex, two strong bands are observed for both the antisymmetric and symmetric modes of the carboxylate stretching vibration. The antisymmetric peaks occur at 1608 and 1559 cm^{-1}.

The absorptions due to the carboxylate symmetric stretching vibration, in the 1400 cm^{-1} region, are also strong for these complexes; however, the bands are considerably narrower than the antisymmetric absorptions. Again the copper complex shows two peaks, at 1409 and 1372 cm^{-1}. As can be seen from Table 7, the tetrasodium salt anomalously shows a greater frequency separation between the antisymmetric and symmetric carboxylate stretching modes than do the cobalt, nickel, or zinc complexes, with the order of separation for the series being $Cu > Na > Co \approx Ni > Zn$. Since the relative spearation of the carboxylate antisymmetric and symmetric stretching frequencies has been taken as an indication of the relative covalent nature of the carboxylate-metal interaction, one must conclude that, for these complexes, this interaction is essentially electrostatic in nature, although the copper complex is a possible exception.

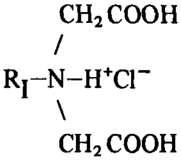
There is no direct evidence in the spectra of the metal complexes of Prototype Dimer I either to support or to contradict nitrogen-to-metal interaction based on a trend in the absorption in the 1260 cm^{-1} region by the compounds and metal complexes of this system. An examination of the frequency values of this absorption, for the compounds listed in Tables 3, 5, and 7, reveals an apparent dependence of these frequencies on the electron densities of the nitrogen atoms in the compounds. Thus, if one considers only one-half the dimeric molecule and if one allows R_I to represent the aromatic substituent on the nitrogen,



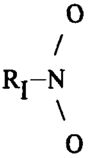
then the following order can be written for the "1260 cm^{-1} peak" in Dimer System I:



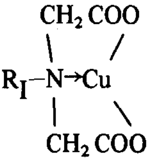
$R_I\text{-}\underset{H}{\overset{H}{N}}\text{-}H^+Cl^-$ (1279)



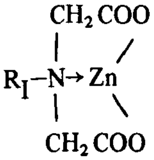
$R_I\text{-}\underset{CH_2COOH}{\overset{CH_2COOH}{N}}\text{-}H^+Cl^-$ (1278)



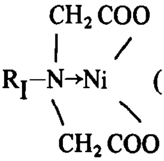
$R_I\text{-}\underset{O}{\overset{O}{N}}$ (1274)



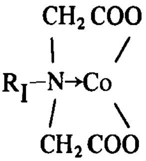
$R_I\text{-}\underset{CH_2COO}{\overset{CH_2COO}{N}}\rightarrow Cu$ (1273)



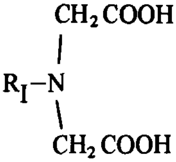
$R_I\text{-}\underset{CH_2COO}{\overset{CH_2COO}{N}}\rightarrow Zn$ (1264)



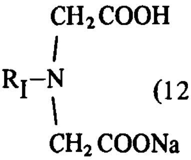
$R_I\text{-}\underset{CH_2COO}{\overset{CH_2COO}{N}}\rightarrow Ni$ (1262)



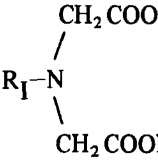
$R_I\text{-}\underset{CH_2COO}{\overset{CH_2COO}{N}}\rightarrow Co$ (1259)



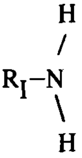
$R_I\text{-}\underset{CH_2COOH}{\overset{CH_2COOH}{N}}$ (1255)



$R_I\text{-}\underset{CH_2COONa}{\overset{CH_2COOH}{N}}$ (1253)



$R_I\text{-}\underset{CH_2COONa}{\overset{CH_2COONa}{N}}$ (1250)



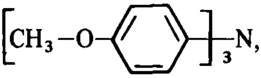
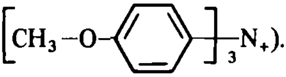
$R_I\text{-}\underset{H}{\overset{H}{N}}$ (1229)

As can be seen, the order of decreasing frequency appears to be paralleled by an order of increasing electron density on nitrogen. As Tables 3, 5, and 7 indicate, these absorptions are generally of strong intensity.

Davies and Jones [23] observe a strong peak at 1250 cm^{-1} in a solution spectrum of phenol, and they note that the frequency shifts only slightly on deuteration; they assign this absorption to the $\mathrm{C}\underset{\mathrm{arom}}{\text{—}}\mathrm{O}$ stretching vibration. Mecke and Rossmy [40] also observe a strong peak at 1253 cm^{-1} for phenol which shifts to 1242 cm^{-1} upon deuteration; similarly for p-nitrophenol, they observe a strong peak at 1277 cm^{-1} which shifts to 1271 cm^{-1} upon deuteration. These authors, however, do not associate this peak with the $\mathrm{C}\underset{\mathrm{arom}}{\text{—}}\mathrm{O}$ stretching vibration; they merely attribute it to a fundamental vibration of the ring skeleton without further discussion of the assignment. Colthup et al. [21], in reviewing the work of other authors, assign a strong absorption at 1260-1180 cm^{-1} in the solid state spectra of phenols to the $\mathrm{C}\underset{\mathrm{arom}}{\text{—}}\mathrm{O}$ stretching vibration; they point out that this vibration interacts somewhat with a medium-intensity OH deformation vibration at 1390-1330 cm^{-1}, and that these bands shift to lower frequencies in solution.

The similarity in frequency and intensity of the observed spectral values with those cited in the literature suggest that the "1260 cm^{-1} peak" in Dimeric System I is associated with the $\mathrm{C}\underset{\mathrm{arom}}{\text{—}}\mathrm{O}$ stretching absorption. It should be pointed out, however, that absorptions in this region of the infrared spectrum seldom represent pure vibrations. In addition to its possible interaction with the O–H bending mode, the $\mathrm{C}\underset{\mathrm{arom}}{\text{—}}\mathrm{O}$ stretching vibration might also be expected to mix with other absorptions in this region, such as the $\mathrm{C}\underset{\mathrm{arom}}{\text{—}}\mathrm{N}$ stretching and CH deformation vibrations, ring skeletal vibrations, and combination bands [25]. The latter three absorptions are usually weak, but the $\mathrm{C}\underset{\mathrm{arom}}{\text{—}}\mathrm{N}$ stretching peak is generally of strong intensity. Colthup et al. [21] assign the $\mathrm{C}\underset{\mathrm{arom}}{\text{—}}\mathrm{N}$ stretching vibration in tertiary anilines to a strong absorption in the 1380-1265 cm^{-1} range.

Jungbauer and Curran [41] observe a decrease in frequency for the C–N stretching vibration in aniline upon complex formation, in line with a decrease in C=N double bond character. On the other hand, a decrease in electron density of a nitrogen substituent para to an OH group would be expected to increase the double bond character and stretching vibration frequency of the $\mathrm{C}\underset{\mathrm{arom}}{\text{—}}\mathrm{O}$ bond, in line with an increase in the resonance of the OH group into the ring. Ritschl [25] has compared the infrared spectra of some triparasubstituted triarylamines with the spectra of the corresponding amminium radical perchlorates; he observes that the $\mathrm{C}\underset{\mathrm{arom}}{\text{—}}\mathrm{X}$ stretching frequencies ($-\mathrm{X} = -\mathrm{F}$, $-\mathrm{OCH_3}$, $-\mathrm{NH_2}$ and $-\mathrm{N(CH_3)_2}$) increase by about 25 cm^{-1} in going from the amine to the amminium radical (e.g., the $\mathrm{C}\underset{\mathrm{arom}}{\text{—}}\mathrm{O}$ stretching vibration, which absorbs at 1240 cm^{-1}

in , shifts to 1270 cm^{-1} in ).

The observed order of the "1260 cm^{-1} peak" in Dimeric System I, then, is consistent with its assignment to the $\mathrm{C}\underset{\mathrm{arom}}{-\!\!-\!\!-}\mathrm{O}$ stretching vibration, but is contrary to what would be expected for a $\mathrm{C}\underset{\mathrm{arom}}{-\!\!-\!\!-}\mathrm{N}$ stretching vibration.

In view of the higher frequencies of the assigned $\mathrm{C}\underset{\mathrm{arom}}{-\!\!-\!\!-}\mathrm{O}$ stretching vibrations for the metal complexes in comparison with the ligand species, it seems reasonable to conclude that nitrogen-to-metal interaction is probable for the metal complexes of Prototype Dimer I, with the following order for the magnitude of the N-M interaction: Cu > Zn > Ni > Co. However, the small differences between the zinc, nickel, and cobalt frequencies suggest that the interaction is nearly equal for these complexes, with a somewhat stronger interaction expected for the copper complex.

If nitrogen-metal bonding does take place, then Structure A (Fig. 2) seems reasonable for the cobalt, nickel, and zinc complexes.

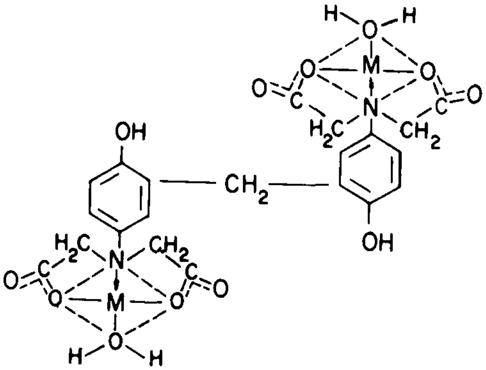


Fig. 2. Structure A.

In Structure A, three coordination positions of each metal are filled by a nitrogen and two carboxylate oxygens, while the fourth position in the plane is occupied by a water molecule. The trans-octahedral positions may be occupied by the carbonyl oxygens of adjacent complexes in the crystal lattice. Similar structures have been proposed for transition metal complexes of iminodiacetic acid [28] and N-substituted iminodiacetic acids [42].

No attempt has been made in Fig. 2 to depict the over-all three-dimensional character of the molecule; however, it is highly unlikely that the phenyl rings are coplanar either with each other or with the adjacent coordination planes of the metals.

Although intramolecular interaction between the two metal-iminodiacetate groups is possible, such interaction would not be expected to be strong for the following reasons:

1) An examination of space-filling models suggests that the two metal-chelate moieties should be directed away from each other in order to minimize unfavorable steric interactions between the two phenyl ring systems, and between their substituents.

2) Intramolecular interaction between the two metal-chelate moieties would result in the formation of extremely large rings (at least ten members) whereas numerous stability studies have shown that the affinity of a ligand for a metal decreases sharply when the ring size exceeds five members. Schwartzenbach and Ackermann [43], for example, have studied some homologs of EDTA in which the number of methylene groups between the nitrogen atoms is increased progressively from two to five; they note that an increase in distance between the nitrogen atoms is accompanied by a rapid increase in the tendency to form chelates containing two metal ions per mole of ligand. Hence, when the two iminodiacetate groups in EDTA homologs are separated sufficiently, they tend to act independently of each other and to form metal complexes analogous to Structure A.

The structure of the copper complex is thought to differ from that of the other complexes of Dimeric System I for the following reasons:

1) Elemental and thermogravimetric analyses of the copper complex indicate a monohydrate composition.

2) Thermogravimetric analysis indicates a much reduced thermal stability relative to the other complexes.

3) The infrared spectrum of the copper complex exhibits band splitting for both the antisymmetric and symmetric carboxylate stretching absorptions.

With regard to the latter point, it is interesting to note that the carboxylate band splittings are not observed for a sample of the copper complex which was dried in vacuo for 1 hr at room temperature. The spectrum of this sample is similar to those of the cobalt, nickel, and zinc complexes dried at 120°; it shows strong, broad water absorption centered at 3200 cm^{-1} (with a shoulder near 3400 cm^{-1}) plus typical carboxylate absorptions centered at 1587 and 1395 cm^{-1}. Only after drying the copper complex for a long period at room temperature or for 1 hr at 120°C is the carboxylate band splitting observed. Nakamoto et al. [28] report somewhat similar behavior for spectra of a 1:2 copper(II) complex with iminodiacetic acid; in deuterium oxide solution they observe only one band, at 1596 cm^{-1}, in the carboxylate antisymmetric stretching region. In the crystalline state of the complex they observe two bands, at 1632 and 1590 cm^{-1}. These authors attribute this band splitting either to distortion of the octahedral configuration or to intermolecular interactions in the crystalline state.

The complexity of the molecule makes the assignment of a structure for the copper complex of Prototype Dimer I rather arbitrary in the absence of more definitive information; however, either the dimeric Structure B (Fig. 3) or the polymeric Structure C (Fig. 4) would seem to be reasonable on the basis of the information available. In view of the spectral evidence offered above, it seems likely that the copper complex, when initially formed in aqueous solution, has a "normal" dihydrate structure similar to the other complexes, i.e., Structure A. The subsequent formation of the dimeric

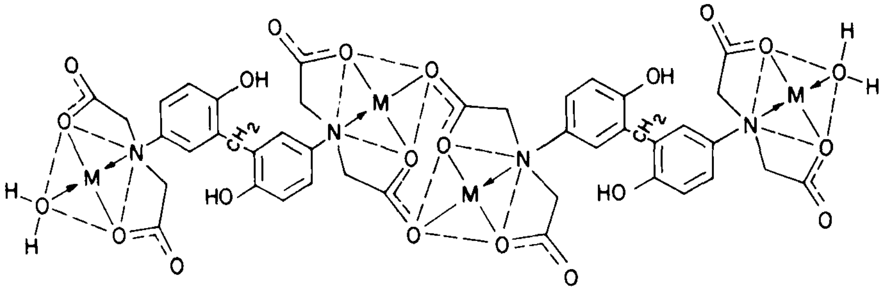


Fig. 3. Structure B

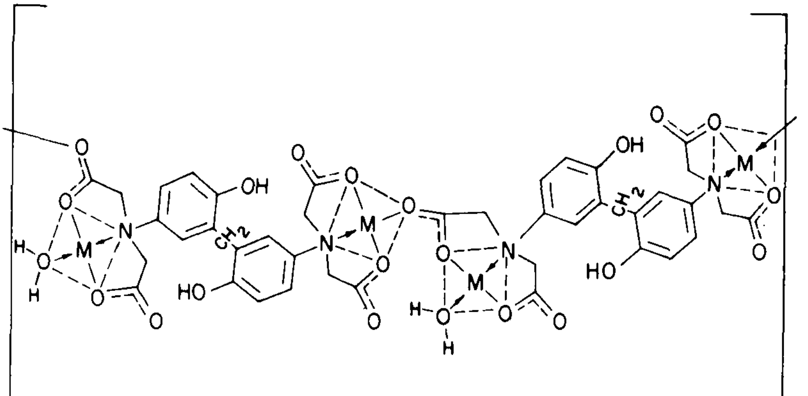


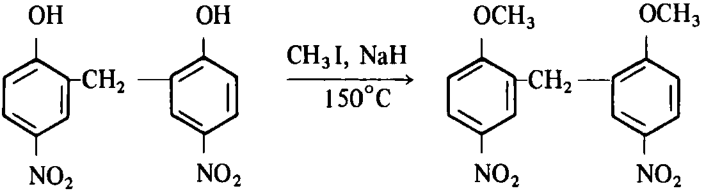
Fig. 4. Structure C

Structure B could be formally pictured as occurring by intermolecular interaction between two adjacent "normal" dihydrate molecules in the crystal lattice resulting in the displacement of two adjacent water molecules by carbonyl oxygens. Similarly, a series of intermolecular interactions between adjacent "normal" dihydrate molecules in the crystal lattice could produce the polymeric Structure C through displacement of alternate water molecules by carbonyl oxygens. In either structure, the presence of both bridging carboxylate groups could account for the observed band splittings.

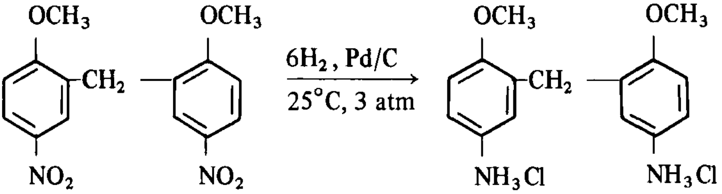
Again, no attempt has been made in the figures to depict the over-all three-dimensional character for Structures B and C.

Prototype Dimeric Compound (II): 3,3′-Methylenebis-[N-(4-methoxyphenyl)iminodiacetic acid] and Metal Complexes

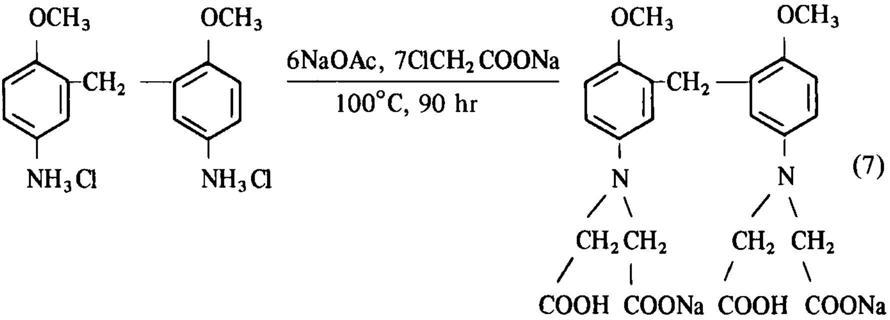
This compound was obtained, in the disodium salt form, from a three-step synthesis beginning with 3,3′-methylenebis-(4-hydroxynitrobenzene):



(5)



(6)



(7)

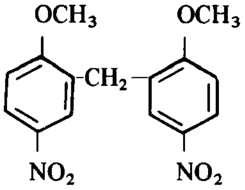
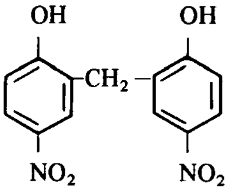
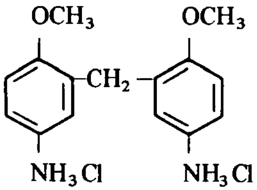
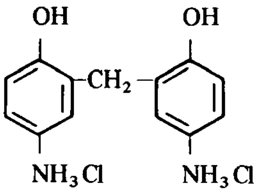
The methylation of the nitro compound from Dimer System I (Eq. 5) was accomplished rather easily, and in good yield, according to a general methylation procedure reported recently by Diner et al. [9]. The elemental analysis values for the product are in good agreement with the calculated values. As expected, the product (Nitro Dimer II) exhibits a lower melting point (189-190°C) than the more polar Nitro Dimer I (268°C). The experimental molecular weight value for the product (317), which was determined by vapor pressure osmometry in dioxane solution at 37°C, is in good agreement with the theoretical value (318).

The next step in the synthesis, the preparation of Amine Hydrochloride Dimer II, was accomplished by low-pressure catalytic hydrogenation of Nitro Dimer II (Eq. 6). The procedure used was similar to the one employed in Dimer System I; however, the reduced solubility of the methoxy compound necessitated a change of solvents, and a much longer reaction time was then required. The product was obtained in good yield (84%). The elemental analysis values for Amine Hydrochloride Dimer II indicate the presence of water. This is confirmed by thermogravimetric analysis, which shows 0.8% weight loss for the compound prior to decomposition. The decomposition begins near 200°C and proceeds rapidly above 250°C.

Some characteristic absorption frequencies and tentative assignments for the infrared spectra of Nitro Dimer II, Amine Hydrochloride Dimer II, and Dimer System I are given in Table 8. The methylation of the phenolic OH group is strongly substantiated by comparison of the infrared spectrum of the product with that of the starting material for this reaction. The strong O–H stretching absorption near 3330 cm^{-1} disappears, and new peaks appear near 2827 and 1020 cm^{-1}; moreover, the peak near 1260 cm^{-1}, which was assigned previously to the $\mathrm{C}\underset{\text{arom}}{\text{---}}\mathrm{O}$ stretching vibration in Dimer System I, shifts to lower frequency by about 15 cm^{-1} upon methylation. Similar peaks have been observed by Briggs et al. [24] who have studied the infrared spectra of a large number of compounds which contain methoxy groups attached to aromatic nuclei. They observe a number of absorptions which they attribute to the methoxy linkage, including two peaks near 2850 and 1028 cm^{-1} said to be diagnostic of the methoxy group. These peaks are assigned to the C–H symmetric stretching and the $\mathrm{C}\underset{\text{aliph}}{\text{---}}\mathrm{O}$ stretching vibrations of the methoxy group. In addition, these authors assign a strong peak near 1250 cm^{-1} to the $\mathrm{C}\underset{\text{arom}}{\text{---}}\mathrm{O}$ stretching vibration, but they note that this peak also occurs in phenols and other compounds.

The conversion of Nitro Dimer II to Amine Hydrochloride Dimer II is also substantiated by changes in the infrared spectra. Similar to previous

Table 8. Some Characteristic Infrared Absorption Frequencies (cm^{-1}) and Tentative Assignments[a] for Some Methylated and Nonmethylated Dimers

Compound				
				Tentative assignment
		3400 (w)		(H_2O)
	3330 (s)		3345 (s)	(OH)
		2860 (vs, vb)	2940 (vs, vb)	(NH_3^+)
2827 (m)		(masked by 2860 peak)		asym(CH of CH_3O-
1512 (s)	1511 (s)			asym(NO_2)
1336 (s)	1335 (s)			sym(NO_2)
1260 (s)	1274 (s)	1264 (s)	1279 (s)	$(C\underset{\text{arom}}{\text{——}}O)$
1013 (s)		1020 (s)		$(C\underset{\text{aliph}}{\text{——}}O$ of $CH_3O-)$

[a] Based on similar assignments in the following references: general, 18-22; $C\underset{\text{arom}}{\text{——}}O$ and $C\underset{\text{aliph}}{\text{——}}O$ stretching vibrations, 22-25.

observations for Dimer System I, the disappearance of the antisymmetric and symmetric stretching peaks of the nitro groups from the spectrum of the hydrogenated product is accompanied by the appearance of a very strong, broad absorption near 2860 cm^{-1}, which is assigned to the NH_3^+ stretching vibration.

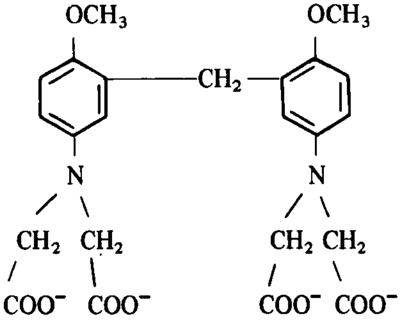
Amine Hydrochloride Dimers I and II can also be differentiated on the basis of their infrared spectra. The strong O–H stretching absorption, near 3345 cm^{-1} for the hydroxy compound, is not observed for the methoxy compound, but a new peak appears at 1020 cm^{-1} due to the C_{aliph}—O stretching vibration. Again, the C_{arom}—O stretching peak at 1264 cm^{-1} has decreased 15 cm^{-1} from its frequency for the hydroxy compound. The weak absorption near 3400 cm^{-1} for Amine Hydrochloride Dimer II is presumed to be due to absorbed water, as was indicated previously by elemental and thermogravimetric analysis data.

The final step in the preparation of Prototype Dimer II was the reaction of Amine Hydrochloride Dimer II in aqueous medium with an excess of sodium chloroacetate in the presence of sodium acetate (Eq. 7). In order to assure complete carboxymethylation of the amine nitrogens, the reaction was continued for a long time (90 hr). The sodium chloroacetate was added portionwise, at extended intervals, because of its tendency to hydrolyze [44]. The product was isolated near the isoionic point of its disodium salt form, which is near pH 3.7 in concentrated solution. Attempts to crystallize the free acid form were unsuccessful. Difficulties were also encountered in attempts to recrystallize the disodium salt. These difficulties might be related to the low decomposition point of the product (100°C).

The elemental analysis of the unrecrystallized disodium salt of the ligand shows good agreement for carbon and nitrogen, but the hydrogen analysis is high; a similar result was noted for the hydrogen analysis of Prototype Dimer I. Thermogravimetric analysis of the product indicates less than 1% water loss, which would be insufficient to account for the disparity in the hydrogen values.

A potentiometric curve for Prototype Dimer II shown in Fig. 1 was obtained from data for the titration of an approximately 0.006 M solution at room temperature; standard hydrochloric acid and sodium hydroxide solutions were used as titrants. Because of the low solubility of the ligand in water, it was necessary to use an approximately 85-15 (volume per cent) water-dioxane solution for the titration medium. However, a comparison of the resulting curve with one obtained from titration of an aqueous dispersion of the ligand suggests that the dioxane has only a very slight effect on the shape and position of the curve. Hence, a qualitative comparison between the curves for Prototype Dimers I and II seems justified.

The close similarity between the titration curves of the two ligands, particularly at intermediate pH's, is readily apparent from an examination of the plots. As was noted previously with Prototype Dimer I, two inflection points are distinguishable for the potentiometric curve of Prototype Dimer II at n = 2 (pH 4.2) and n = 4 (pH 8.5). These inflection points correspond to the isoionic points of the species $(H_2 L_{II})^{2-}$ and $(L_{II})^{4-}$, respectively, where the symbol $(L_{II})^{4-}$ represents the tetranegative ion of Prototype Dimer II:



Again, the pH's corresponding to n = 2.5 (i.e., pH 5.3) and n = 3.5 (i.e., pH 6.5) represent apparent pK_a values for the ionizations

$$H_2L_{II}^{2-} + H_2O \rightleftharpoons H_3O^+ + HL_{II}^{3-} \qquad (pK_{1,2} = 5.3)$$

and

$$HL_{II}^{3-} + H_2O \rightleftharpoons H_3O + L_{II}^{4-} \qquad (pK_1 = 6.5)$$

As was noted previously, these uncorrected pK_a values may be taken to be rough indications of the basicity of the nitrogen atoms; therefore, the close agreement of these values with those of Prototype Dimeric Ligand I suggests similar nitrogen basicities in these two compounds.

It may be seen that the close similarity of the two curves prevail in the region between n = 2 and n = 4, or between pH ~4 and pH ~8. Below pH 4, Prototype Dimer II appears to be slightly more acidic, perhaps because the nitrogens opposite to para-methoxy substituents have slightly lower basicity than those opposite to more strongly electron-releasing para-hydroxy groups. Above pH 8, Prototype Dimer I is significantly more acidic, presumably because of the ionization of the phenolic OH groups in this pH region.

Infrared spectra of Prototype Dimer II were recorded for three species of this ligand: $Na_2H_2L_{II}$, H_4L_{II}, and Na_4L_{II}. The spectrum of the disodium salt was recorded for the analytical sample which was crystallized from aqueous solution. The spectra of the latter two species were recorded for samples which were obtained by stoichiometric reaction of the disodium salt in aqueous solution with hydrochloric acid or sodium hydroxide. The solutions were then evaporated to dryness; therefore, the isolated samples are crude. The free acid sample most likely contains sodium chloride impurities; however, this is not expected to affect the infrared spectrum significantly. Important absorption frequencies and tentative assignments for the species of Prototype Dimer II are given in Table 9.

The spectrum of the free acid (H_4L_{II}) shows a very broad absorption profile between 2600 and 2150 cm^{-1}, which is attributed to the NH^+ stretching vibration together with overtones and combination bands [19]. The absorption is stronger and at considerably lower frequency than the corresponding absorption for the free acid of Prototype Dimer I; this suggests a stronger dipolar (zwitterion) character for H_4L_{II}. The profile absorption does not appear in the spectra of the species $Na_2H_2L_{II}$ and Na_4L_{II}.

The medium intensity peak at 1716 cm^{-1} in the spectrum of the free acid of Prototype Dimer II is assigned to the C=O stretching vibration of the un-ionized carboxyl group. This peak also appears in the spectrum of the disodium salt; the persistence of this peak and the loss of the NH^+ stretching absorption indicate a lack of zwitterion character for the species $Na_2H_2L_{II}$, at least in the solid state. The weak absorption at 1720 cm^{-1} in the spectrum of Na_4L_{II} is probably carbonyl absorption resulting from incomplete conversion to the tetrasodium salt form or from impurities.

The medium intensity peak at 1658 cm^{-1} in the spectrum of the free acid is assigned to the carboxylate antisymmetric stretching vibration. This is quite high compared to the usual assignment, but a similar frequency (1660 cm^{-1}) was observed for this absorption in the free acid of Prototype Dimer I. In a prior publication [2] a carboxylate antisymmetric stretching vibration frequency was assigned at 1650 cm^{-1} for the monomer N-(4-hydroxyphenyl) iminodiacetic acid. This high frequency was attributed to an inductive effect towards the un-ionized carboxyl group in the iminodiacetic acid function. The carboxylate antisymmetric frequency decreases to 1585 and 1583 cm^{-1} for the disodium and tetrasodium salt species of Prototype Dimer II. The absorptions for these

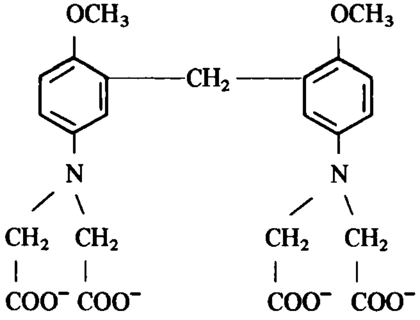
Table 9. Some Characteristic Infrared Absorption Frequencies (cm^{-1}) and Tentative Assignments[a] for Species of 3,3′-Methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid

Predominant species			Tentative assignment
H_4L_{II}[b]	$Na_2H_2L_{II}$	Na_4L_{II}	
2600–2150 (vb)			(NH^+) profile
1716 (m)	1700 (sh)	1720 (w)	ν (C═O of COOH)
1658 (m)	1585 (s,b)	1583 (s,b)	$\nu_{asym}(COO^-)$
1400 (w)	1460–1400 (vb)	1423 (m,b)	$\nu_{sym}(COO^-)$
1258 (s)	1241 (s)	1236 (s)	ν (C_{arom}—O)
1022 (s)	1030 (s)	1025 (m)	ν (C_{aliph}—O of CH_3O—)

---

[a] Based on similar assignments in the following assignments: general, 2, 18, 28, 30-39; C_{arom}—O and C_{aliph}—O stretching vibrations, 22-25.

[b] In this and in Tables 10 and 11, "L_{II}" represents the tetranegative ion 3,3′-methylenebis-[N-(4-methoxyphenyl) iminodiacetate] =



species are broad and strong, and they are generally similar to the corresponding absorptions of Prototype Dimer I.

The absorption profiles for the Prototype Dimer II species near 1400 cm^{-1} are broad and weak; hence, the carboxylate symmetric stretching frequency is not easily assigned. The probable frequency for this vibration in the Na_4L_{II} species is 1423 cm^{-1}.

The $C_{\overline{arom}}O$ stretching peaks are stronger than those observed for the species of Prototype Dimer I. For $Na_2H_2L_{II}$ and Na_4L_{II}, the frequencies are 12 and 14 cm^{-1} lower than for the corresponding hydroxy compounds, in line with the usual decrease of about 15 cm^{-1} observed previously for the methoxy compounds. However, the frequency for the free acid, 1258 cm^{-1}, is slightly higher than that observed for H_4L_{II}; this supports the previous assumption of greater zwitterion character for H_4L_{II}.

The species of Prototype Dimer II can easily be distinguished from those of Prototype Dimer I in three general areas of their infrared spectra: (1), Near 3400 cm^{-1} the hydroxy dimer species absorb strongly due to the O–H stretching vibration; and (2) and (3), near 2830 and 1025 cm^{-1} the methoxy dimer species show C–H stretching and $C_{\overline{arom}}O$ stretching peaks which are due to the CH_3O- function.

Metal complexes of Prototype Dimer II with divalent copper, nickel, cobalt, and zinc were prepared by reacting the disodium salt of the ligand in aqueous-dioxane solution in a 1:2 mole ratio with the metal ion. The preparations were carried out in the presence of from 1.5 to 3.0 moles of sodium hydroxide. Except for the copper complex, the metal complexes of this system were more difficult to isolate, and the yields and purities of the products obtained were generally lower than for the complexes of Dimer System I. These isolation difficulties are believed to arise either from a low stability for the metal complexes or from their high solubility in the water-dioxane solvent system. Because of the ligand's low water solubility, it was necessary to use water-dioxane mixtures in order to dissolve the ligand prior to formation of the complexes. As a result, the copper, nickel, and zinc complexes were isolated from media containing from 10 to 20% by volume of dioxane, rather than from strictly aqueous media. For the cobalt complex it was necessary to add a large excess of acetone in order to precipitate the product.

The analytical results support a 1:2 mole ratio of ligand to metal ion and a dihydrate structure for the copper, nickel, and cobalt complex. For the zinc complex, the analyses of three separately prepared samples all indicate a 1:1 complex, and either an anhydrous or a monohydrate structure.

Variable amounts of sodium hydroxide were required in the preparations in order to isolate the complexes free from impurities. When stoichiometric amounts (2 moles) of base were used, satisfactory analyses were obtained fro the copper and zinc complexes; the observed pH's were 5.2 and 6.4, respectively. However, for the cobalt complex, low analysis results were obtained when two moles of base were used (pH 7.0); presumably, the low results were caused by coprecipitation of cobalt(II) hydroxide. For the nickel complex, high results were obtained when 2 moles of base were used (pH 6.7) the high results are thought to be caused by the coprecipitation of unreacted ligand. For the same complex, the use of 3 moles of base (pH 7.8) produced low analysis results. An intermediate amount of base, 2.2 moles (pH 6.9), produced the best agreement of analysis results with the calculated values for the nickel complex.

An assumption that the low analysis results obtained for the cobalt and nickel complexes at high pH's are due to metal hydroxide impurities permits correction of the observed values to within good agreement with the theoretical values for the 1:2 dihydrate structures. Moreover, the results obtained from a titration of the nickel complex for nickel(II) hydroxide appear to support the assumption of metal hydroxide impurity in the complex.

Table 10 contains data derived from the thermogravimetric curves of the disodium salt and metal complexes of Prototype Dimer II. It can be seen that the observed and theoretical water losses do not agree as closely as do those for the complexes of Prototype Dimer I (Table 6). However, the observed weight losses for the Prototype Dimer II complexes coincide best with dihydrate structures for the copper, nickel, and cobalt complexes, a monohydrate structure for the zinc complex, and an anhydrous structure for the ligand disodium salt. The thermogravimetric determinations were carried out in the same manner as described previously for the Prototype Dimer I complexes. From a comparison of the procedural initial decomposition temperatures listed in Table 10 with those in Table 6, it can be seen that the order of thermal stability in nitrogen for the complexes of the methoxy ligand parallels the one observed previously for the hydroxy ligand complexes. Initial decomposition occurs about 60° lower for the methoxy series; the ligand disodium salt and copper complex begin to decompose near 100°C and the other complexes near 240°C.

Some characteristic infrared absorption frequencies and tentative assignments for the metal complexes of Prototype Dimer II are given in Table 11.

The metal complexes all exhibit very broad water absorption profiles in

Table 10. Thermogravimetric Data for 3,3′-Methylenebis-[N-(4-methoxyphenyl) *iminodiacetic acid*] Disodium Salt and Its Metal Complexes

Compound	pH of Isolation	Initial weight, mg	Suppression, mg	Estimated weight loss, %	Theoretical loss, % water	Procedural initial decomposition temperature, °C
$Na_2H_2L_{II}$	3.7	11.48	9.48	0.9[a]	0.00	100
$Cu_{II}L_{II} \cdot 2H_2O$	5.2	10.63	8.63	5[a]	5.55	95
$Ni_2L_{II} \cdot 2H_2O$	7.8			5.7	5.6[b]	230
	6.7			2.6	2.9[c]	
	6.9	11.29	9.29	4.6	5.6	260
$Co_2L_{II} \cdot 2H_2O$	7.0	10.53	8.53	5.9	5.6[b]	235
ZnH_2L_{II}	6.3			1.9	0.00	195
	6.4			3.2	3.15[c]	240
	5.8	10.06	8.06	2.0	0.00	240

[a] Crude estimate of weight loss percentage for sample with low decomposition point.

[b] Calculated water percentage neglecting metal hydroxide impurity.

[c] Calculated water percentage assuming monohydrate structure.

Table 11. Some Characteristic Infrared Absorption Frequencies (cm^{-1}) and Tentative Assignments[a] for Metal Complexes of 3,3′-Methylenebis-[N-(4-methoxyphenyl) iminodiacetic acid]

Complex and pH of isolation					
$Na_4L_{II} \cdot nH_2O$	$Cu_2L_{II} \cdot 2H_2O$ (pH 5.2)	$Ni_2L_{II} \cdot 2H_2O$ (pH 6.9)	$Co_2L_{II} \cdot 2H_2O$ (+ 7% $Co(OH)_2$) (pH 7.0)	ZnH_2L_{II} (pH 5.8)	Tentative assignment
3600-3100 (w,b)	3600-3100 (m,b)	3600-3100 (m,b)	3600-3100 (m,b)	3600-3100 (m,b)	$\nu\ (H_2O)$
1583 (s,b)	1593 (s,b)	1599 (s,b)	1589 (s,b)	1585 (s,b)	$\nu_{asym}(COO^-)^b$
1423 (m,b)	1375 (m,b)	1400 (m)	1397 (m,b)	1405 (m)	$\nu_{sym}(COO^-)$
160	218	199	192	180	$\Delta\nu_{asym\text{-}sym}(COO^-)$
1236 (s)	1252 (s)	1242 (s)	1242 (s)	1248 (s)	$\nu\ (C \underset{arom}{\text{——}} O)$
1025 (m)	1019 (m)	1023 (m)	1018 (m)	1023 (m)	$\nu\ (C \underset{aliph}{\text{——}} O)$

[a] References given in Table 9.

[b] Estimated centers of absorption maxima for broad bands.

the 3600-3100 cm^{-1} region. The absorption is considerably weaker than that observed for the Prototype Dimer I complexes, which also have phenolic OH groups absorbing in this region.

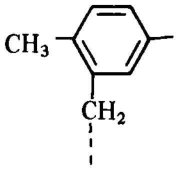
The absorptions due to the carboxylate antisymmetric stretching vibrations occur near 1590 cm^{-1} for the metal complexes of Prototype Dimer II; the absorptions are broad and strong, although weaker than those of the Prototype Dimer I complexes. The frequencies listed for this absorption in Table 11 represent estimated centers of the absorption maxima because the absorptions are spread over about 30 cm^{-1} ranges. As was noted previously in the discussion of the Prototype Dimer I complexes, and absolute assignment of the carboxylate antisymmetric stretching frequencies is precluded by the broadness of the absorption maxima, the possibility of water interaction, and the occurrence of ring skeletal vibrations in the same frequency region.

The absorptions due to the carboxylate symmetric stretching vibrations occur near 1400 cm^{-1}; the intensities of these absorptions are considerably lower than those observed for the complexes of the hydroxy series.

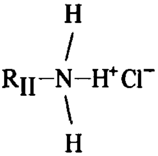
The tentative frequency separation between the antisymmetric and symmetric carboxylate stretching absorptions for the Prototype Dimer II complexes is in the following order: Cu > Ni > Co > Zn > Na. The greater separation for the metal complexes relative to the tetrasodium salt indicates metal-carboxylate interaction in these complexes; however, the small magnitudes of the observed separations suggest that the metal-carboxylate interaction is essentially electrostatic.

The splitting of the carboxylate peaks, seen previously for the copper complex of Prototype Dimer I, is not observed for the copper complex of Prototype Dimer II, even after prolonged drying of the complex at 80°C.

The spectra of the metal complexes of Prototype Dimer II do not provide any direct evidence of nitrogen-to-metal bonding, as was also the case for the Prototype Dimer I complexes. However, the observed frequency order for the $C \underset{\text{arom}}{—} O$ stretching absorption may again be taken as indirect evidence of nitrogen-to-metal interaction. An examination of the observed frequencies for this absorption for the Dimer System II compounds, given in Tables 8, 9, and 11, reveals an inverse relationship between the $C \underset{\text{arom}}{—} O$ stretching frequency and the apparent election density on nitrogen. Thus, by considering only one-half of the dimeric molecule and by allowing R_{II} to represent the aromatic substituent on the nitrogen,

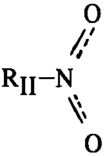


one can represent the order of the "1250 cm^{-1} peak" in Dimer System II as follows:



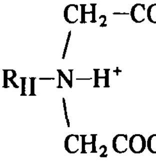
$R_{II}-\overset{H}{\underset{H}{N}}-H^+Cl^-$

(1264)



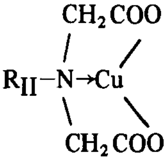
$R_{II}-N\overset{O}{\underset{O}{\lessgtr}}$

(1260)



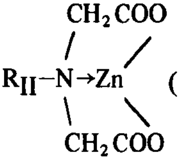
$R_{II}-\overset{CH_2-COOH}{\underset{CH_2COO^-}{N}}-H^+$

(1258)



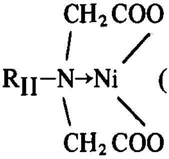
$R_{II}-\overset{CH_2COO}{\underset{CH_2COO}{N}}\rightarrow Cu$

(1252)



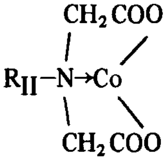
$R_{II}-\overset{CH_2COO}{\underset{CH_2COO}{N}}\rightarrow Zn$

(1248)



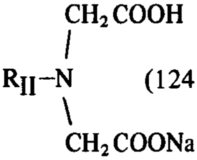
$R_{II}-\overset{CH_2COO}{\underset{CH_2COO}{N}}\rightarrow Ni$

(1242)



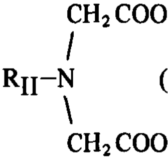
$R_{II}-\overset{CH_2COO}{\underset{CH_2COO}{N}}\rightarrow Co$

(1242)



$R_{II}-\overset{CH_2COOH}{\underset{CH_2COONa}{N}}$

(1241)



$R_{II}-\overset{CH_2COONa}{\underset{CH_2COONa}{N}}$

(1236)

The assignment of this absorption to the $C_{\overline{arom}}O$ stretching vibration is based on the evidence proposed earlier for the same assignment of the "1260 cm^{-1} peak" in the spectra of Dimer System I compounds. Briggs et al. [24] have made an identical assignment for a strong peak near 1250 cm^{-1} in the spectra of aromatic methoxy compounds.

The stretching vibration frequency (and the double bond character) of the $C_{\overline{arom}}O$ bond would be expected to decrease in the observed manner as the electron density of the nitrogen substituent para to the CH_3O- group is increased, in line with a decreased resonance of the methoxy group into the ring. Moreover, a comparison of the frequency values for the two dimer series reveals that the $C_{\overline{arom}}O$ frequencies of the methoxy series compounds are lower than those of the corresponding hydroxy series compounds by 16 ± 5 cm^{-1}. The lone exception—as noted previously—is the H_4L_{II} species, for which the frequency is slightly higher than that of the H_4L_I species in line with the proposed stronger zwitterion character of H_4L_{II}.

In summary, the higher frequency of the $C\underset{\mathrm{arom}}{\text{—}}O$ stretching vibration for the metal complexes, in comparison with the tetrasodium salt of Prototype Dimer II, suggests probable nitrogen-to-metal interaction with the following order for the magnitude of this interaction: $\mathrm{Cu} > \mathrm{Zn} > \mathrm{Ni} = \mathrm{Co}$. The smaller frequency differences between the complexes and the tetrasodium salt for this series suggest a weaker N-M interaction than that expected for the Prototype Dimer I complexes; this should be especially true for the cobalt and nickel complexes of the methoxy ligand, which are also the most difficult to isolate.

If nitrogen-to-metal bonding does occur, then it seems reasonable that the copper, nickel, and cobalt complexes of Prototype Dimer II would have a structure similar to the proposed Structure A for the zinc, nickel, and cobalt complexes of Prototype Dimer I.

The results for the zinc complex of Prototype Dimer II are puzzling. Although the elemental analyses of three separately prepared samples all indicate a 1:1 complex with two extra hydrogens to preserve charge balance, no evidence can be found in the infrared spectra for NH^+ or COOH groups. In fact, the spectra of the zinc complexes are quite similar to those of the other three complexes of this system. Moreover, the high frequency of the $C\underset{\mathrm{arom}}{\text{—}}O$ peak and its lack of splitting or broadening in the spectrum of the zinc complex indicates that both nitrogens are probably coordinated to the metal.

In view of the above evidence, and despite the lack of spectral evidence for COOH groups, it would seem that Structure D (Fig. 5) is the most probable arrangement for the zinc complex.

The three-dimensional character of the molecule in proposed Structure D has not been fully depicted; however, an examination of space-filling models suggests that in such a structure the planes of the benzene rings must be tilted somewhat both from a coplanar relationship with each other and from perpendicular relationships with the metal coordination plane. The trans octahedral position below the coordination plane would be free for occupation by a water molecule, but the position above the plane appears to be effectively blocked by the benzene ring structures. Alternatively, a structure might be proposed in which a water molecule does occupy the trans octahedral position above the metal atom, and a

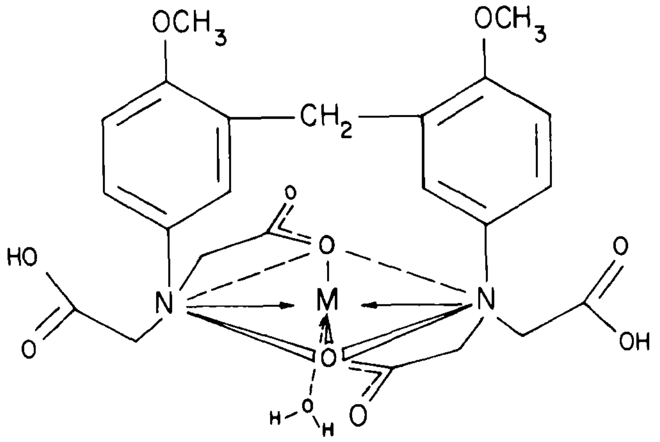


Fig. 5. Structure D

carboxyl group from another ligand bonds to the metal atom from below to complete the octahedron.

CONCLUSIONS

Stability studies are needed before any quantitative evaluation of the relative chelating abilities and selectivities of Prototype Dimers I and II can be made. Even in the ideal situation, infrared spectroscopy in the 3800-600 cm^{-1} region can give only limited information regarding metal-nitrogen and metal-oxygen bonds. Because of the complexity of the molecules in this study, only general inferences concerning actual chelate structure can be deduced from the infrared spectra. These spectra, however, should prove valuable for comparison with the spectra of the oligomers and polymers and their complexes in future studies of these systems for chelating polymer formation.

The spectral studies of the complexes of both prototype dimers indicate carboxylate-metal interaction; this interaction appears to be essentially electrostatic in nature. The COO-M interaction in each system appears to be strongest for the copper complex and weakest for the zinc complex.

The increase in the $\mathrm{C}\underset{\mathrm{arom}}{-\!\!-\!\!-}\mathrm{O}$ stretching frequencies upon complex formation suggests nitrogen-to-metal interaction in these complexes; the interaction is probably stronger for the complexes of Prototype Dimer I.

The N-M interaction in each system appears to be strongest for the copper complex and weakest for the cobalt and nickel complexes.

The basicity of the donor nitrogen is one of the main factors in determining the stability of metal complexes with this type of ligand. The apparent pK_a data derived from potentiometric titration curves of the prototype dimers indicate that the two ligands have similar nitrogen basicities. Comparison of this pK_a data with literature values of pK_a's for analogous known compounds reveals that the aromatic rings effect a substantial decrease in the nitrogen basicities, but the nitrogen basicities of the prototype dimers compare favorably with those of the other chelating compounds which contain aromatic-substituted nitrogens.

The results of this study indicate that both the Prototype Dimers I and II are worthy of further consideration for possible chelating polymer formation. The hydroxy system seems to be the more promising of the two, but the methoxy system should prove useful at least for comparison purposes. If possible, stability studies should be carried out in order to characterize the complexes better. Also, the possibility of improving the basicity of the donor nitrogens, by separating them from the aromatic ring with other atoms, should be investigated further.

A Preliminary Investigation of an Oligomeric System for Future Chelating Polymer Studies

In preparation for future chelating polymer studies, a preliminary investigation was made of an oligomeric system analogous to Dimer Systems I and II. The purpose of this investigation was to explore the possibilities of obtaining suitable higher molecular weight chelating compounds by appropriate modifications of the synthesis procedures which were used to prepare Prototype Dimers I and II.

In the system which was studied, the molecular chain compounds contain an average of about six or seven repeating units, or segmers, and the number-average molecular weights ($\overline{MW_n}$) are of the order of about 1000. Hence, the system is more properly described as oligomeric, rather than polymeric, in nature. Oligomeric compounds usually show greater solubility than their higher molecular weight analogues [45]. For this and other reasons, the characterization and chemical modification of oligomeric compounds are generally done more easily than are those for higher molecular weight compounds. However, a comparison of the properties of the oligomeric chelating system with those properties observed for the corresponding monomeric and dimeric chelating systems should reflect possible interferences which might arise from the polymerization process. As a result of the polymerization, the subsequent chemical incorporation of the chelating function into the system may conceivably be hindered and the chelate-forming ability of the system may also be significantly reduced. But if the results for the oligomeric system prove promising, then the synthesis and characterization of the corresponding high polymer chelating system may be approached with some greater expectation of success.

The first step in the preparation of the oligomeric system was the preparation of the p-nitrophenol-formaldehyde oligomer. In phenolic compounds, the electron-releasing phenolic OH groups activate the ortho and para positions of the phenyl rings, thus facilitating polycondensation with formaldehyde at these positions. In p-nitrophenol, the strongly electrophilic nitro substituent not only blocks the para position from formaldehyde condensation, but it also counteracts somewhat the activating effect of the phenolic OH groups on the ortho positions of the phenyl ring. Thus, the polycondensation of p-nitrophenol with formaldehyde is slow and requires strong acid or base catalysts.

Only a few references to polymerizations involving p-nitrophenol and formaldehyde are found in the literature [46-48], and the details are not available. The first attempt to prepare a polymeric condensation product of p-nitrophenol and formaldhyde in this research involved a modification of the procedure used to prepare the dimer. This reaction was carried out in a 1:1 mole ratio in aqueous medium, with about 40% by weight of sulfuric acid as catalyst. The reaction proceeded vigorously, but the product charred and decomposed when moderate heating was applied. Oligomeric products were obtained from prolonged refluxing of a slight excess of formaldehyde with p-nitrophenol in aqueous medium when about 20% by weight of oxalic acid was used at catalyst. Oligomeric products were also obtained from the following two-step process:

1) p-Nitrophenol was refluxed for a prolonged period with a slight excess of formaldehyde in aqueous medium. Sodium hydroxide, comprising about 10% of the system weight, was used as catalyst.

2) The isolated product from step 1) was treated with a large excess of concentrated hydrochloric acid. The resulting mixture was refluxed for a prolonged period in aqueous medium.

Step 2) was accompanied by some decomposition of the product.

The most successful polycondensation experiments reported for this research were those involving the following steps:

1) p-Nitrophenol was refluxed for a prolonged period of time with a slight excess of formaldehyde in a mixed water-ethanol medium. Hydrochloric acid, comprising about 7.5% of the system weight, was used as catalyst.

2) The condensation products from step 1) were isolated from the starting materials and catalyst by repeated washings with water and precipitations from acetone-water solutions.

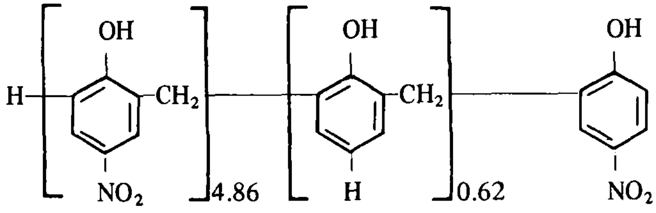
3) The condensation products were heated in vacuo for a prolonged period of time. The temperature was increased gradually to a maximum of 110°C. At various intervals in the heating process, the product was temporarily removed from the vacuum oven and pulverized.

4) The product was extracted repeatedly with ethanol-water mixtures in order to remove lower condensation products.

At various intervals in the procedure, the number-average molecular weight ($\overline{MW}_n$) of the product was determined by vapor pressure osmometry in acetone solution at 37°C; these determinations indicate that the $\overline{MW}_n$ is increased by each of the four steps in the procedure. Moreover, the $\overline{MW}_n$ appears to be dependent on the time of refluxing (step 1) and/or on the time of drying (step 3). For example, the procedure involved 93 hr of refluxing and 50 hr of drying in vacuo at 110°C to obtain a final product of $\overline{MW}_n = 940$; a similar procedure, but rather with 140 hr of refluxing and 90 hr of drying, yielded a final product of $\overline{MW}_n = 1240$.

As expected, the oligomeric product ($\overline{MW}_n = 940$) differs in its physical properties from the corresponding monomer (MW = 139) and dimer (MW = 290). The oligomer is dark brown, whereas the monomer and dimer are light yellow. The oligomer begins to decompose slowly at about 175°C; the monomer melts sharply at 114°C; the dimer melts at 268°C and decomposes near its melting point. The oligomer also shows diminished solubility; it is insoluble in glacial acetic acid, very slightly soluble in ethanol, and more soluble in acetone and ethyl acetate.

The elemental analysis values of the p-nitrophenol-formaldehyde oligomer ($\overline{MW}_n = 940$) are not consistent with the calculated values for an expected linear, phenol-ended Model Structure A_1. On the basis of Model Structure A_1, the analysis indicates low nitrogen and high carbon and hydrogen percentages; similar results are noted for the analogous oligomer of $\overline{MW}_n = 1240$, and also for the p-nitroanisole-formaldehyde oligomer of $\overline{MW}_n = 1015$. These results are consistent with a partial loss of nitro groups. The proposed Model Structure, C_1



(not ordered)

gives a close fit to the observed carbon, hydrogen, and nitrogen percentages. Model Structure C_1 assumes a linear, phenol-ended chain of 6.48 units, a molecular weight of 940, and a loss of 9.6% of the nitro substituents.

It is not known if, or how, the nitro groups are actually lost. Some possible explanations for the deviations from the expected composition are:

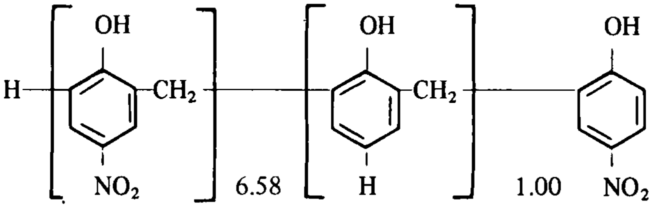
1) The starting material is contaminated with phenol. This seems highly unlikely, especially in view of the sharp melting point of the sample used (114°C).

2) Nitro groups are not lost, but some side reaction leading to a modification of the oligomer structure, or some impurity, causes the deviation from the expected composition.

3) Nitro groups are lost through some decompositon reaction which probably occurs during the prolonged refluxing in the strong acid medium.

The elemental analysis values of the p-nitrophenol-formaldehyde oligomer and its derivatives are all fairly consistent with the calculated values for the analogous Model Structures C_1, C_2, D_3, and D_4. This suggests that the loss of nitro groups through decomposition during the prolonged refluxing in strong acid medium is the most likely explanation, since all four Model Structures assume a loss of 9.6% of the nitro groups.

Because the initial attempt at polymerization of p-nitrophenol and formaldehyde in 40% sulfuric acid led to decomposition, the theory of partial loss of nitro groups during reflux in 7.5% hydrochloric acid appears to be supported. The elemental analysis values of the p-nitrophenol-formaldehyde oligomer of $\overline{MW}_n = 1240$ would also seem to support this theory. For this oligomer, which was obtained from a procedure involving 140 hr of reflux in 7.5% hydrochloric acid (or approximately 1.5 times as long as for the oligomer of $\overline{MW}_n = 940$), the elemental analysis values are: C = 57.22%, H = 3.77%, N = 8.82%. These results agree well with the calculated values for a Model Structure which assumes 11.6% loss of nitro groups:



(not ordered)

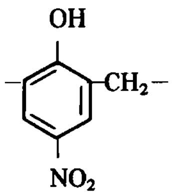
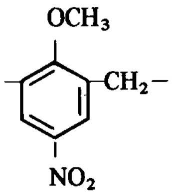
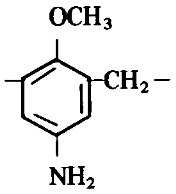
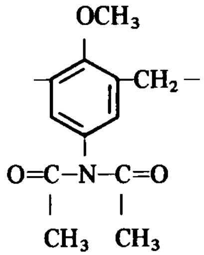
MW = 1240, C = 57.22%, H = 3.57%, N = 8.57%. Some characteristic absorption frequencies and tentative assignments for the p-nitrophenol-formaldehyde oligomer and other derived oligomers are given in Table 12.

The infrared spectrum of the p-nitrophenol-formaldehyde oligomer ($\overline{MW}_n$ = 940) is very similar to the spectrum of the corresponding dimer, 3,3′-methylenebis-(4-hydroxynitrobenzene); this can be seen by comparison of the spectra and of their assignments in Tables 12, and Table 3. The strong, broad OH stretching absorption (3360 cm^{-1}), the strong anti-symmetric and symmetric stretching absorptions of the nitro group (1512 and 1335 cm^{-1}), and the strong $C_{\overline{arom}}O$ stretching absorption (1272 cm^{-1}) are all quite similar to the corresponding absorptions for the dimer.

The only important changes in the spectrum of the oligomer in comparison to the dimer spectrum, apart from broadening of some of the peaks, are an increase in intensity of absorption in the C–H stretching region (3100-2800 cm^{-1}) and a change in the relative intensities of the C–H out-of-plane deformation peaks. In the oligomer spectrum the peak at 900 cm^{-1}, which is characteristic of one isolated, free, ring hydrogen atom, has grown stronger relative to the peak at 815 cm^{-1}, which is characteristic of two adjacent, free ring hydrogen atoms. This change is in line with the increased ring substitution of the oligomer in comparison with the dimer. Of course, the infrared spectrum can offer no good evidence to support the theory that 9.6% of the nitro groups are missing, but this is not surprising since no major changes in the spectrum would be expected.

The next phase in the study of the oligomeric system involved attempts to prepare a p-aminophenol-formaldehyde oligomer by hydrogenation or chemical reduction of a p-nitrophenol-formaldehyde oligomer. These efforts met with very limited success. Even for the most successful

Table 12. Some Characteristic Infrared Absorption Frequencies (cm^{-1}) and Tentative Assignments for Some Oligomeric Compounds Derived from p-Nitrophenol and Formaldehyde

Oligomer, principal segmer, and proposed model structure				Tentative assignment and references
p-Nitrophenol-formaldehyde oligomer, $\overline{MW}_n = 940$	p-Nitroanisole-formaldehyde oligomer, $\overline{MW}_n = 1015$	(p-Anisidine, p-nitroanisole)-formaldehyde oligomer	(N,N-Diacetyl-p-anisidine, p-nitroanisole)-formaldehyde oligomer	
				
(Cl, MW = 940	(C_2, MW = 1030)	(D_3, MW = 893)		
		3420 (sh), 3350 (s)		ν asym and sym(NH_2) [18, 19-21]

3360 (s,vb)				ν (OH) [18, 19-21]
	2840 (m)	2830 (m)	2830 (m)	ν_{asym}(CH of CH_3O-) [19, 20, 24]
			1753 (m,b), 1714 (sh) 1703 (vs), 1657 (m,b)	ν (C=O) [20, 21, 53, 54]
1512 (s)	1507 (s)	–	–	$\nu_{asym}(NO_2)$ [18, 19-21]
–	–	–	1360 (s)	δ_{sym}(CH_3 of CH_3-CO-) [19, 21]
1335 (vs)	1335 (vs)	1335 (w)	–	$\nu_{sym}(NO_2)$ [18, 19-21]
1272 (s)	1258 (s)	1222 (s)	1229 (vs,b)	ν ($C\underset{arom}{\text{——}}O$) [19-25, 57]
	1011 (m)	1005 (m)	1020 (m,b)	ν ($C\underset{aliph}{\text{——}}O$) [19-21, 24]
900 (m)	899 (m)	853 (m)	900-865 (m,vb)	δ (C–H out-of-plane, 1 isolated H) [18]
815 (m,b)	811 (m,b)	800 (m)	805 (m,b)	δ (C–H out-of-plane, 2 adjacent H's) [18]

of the experiments which were conducted, elemental analysis indicated that less than 40% of the nitro groups were converted to amino groups. The efforts to prepare a p-aminophenol-formaldehyde oligomer can be divided into three groups: low-pressure hydrogenations, chemical reductions and high-pressure hydrogenations. In all these experiments the starting material was the p-nitrophenol-formaldehyde oligomer of $\overline{MW}_n = 1240$.

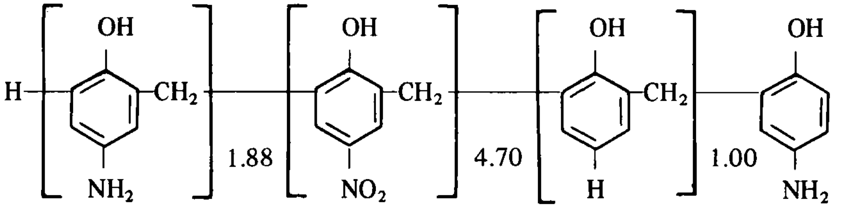
The low-pressure hydrogenation experiments were conducted in a Parr hydrogenator at room temperature and at approximately 3 atm hydrogen pressure. In each case the catalyst used was 5% palladium-on-charcoal. Approximately 1% solutions (by weight) of the p-nitrophenol-formaldehyde oligomer were used. The following solvents and mixed solvent combinations were tried: p-dioxane, ethyl acetate, 2-(2-ethoxyethoxy)-ethanol, N,N-dimethylacetamide, 70-30 (volume per cent) ethanol-ethyl acetate, 70-30 ethanol-N,N-dimethyl-acetamide, and 40-60 ethanol-2-(2-ethoxyethoxy)-ethanol. Catalyst weights of up to 100% of the oligomer weight and agitation times of from 10 to 100 hr were employed. The catalyst was added in gradually increasing portions and at various intervals during the experiments. The observed total decreases in hydrogen pressure in these experiments constituted, at most, only small factions of the theoretical pressure drops for complete reaction. Moreover, the infrared spectra of the isolated products showed little or no change from the spectrum of the starting material; in every case the symmetric stretching absorption of the nitro group (1335 cm^{-1}) remained the strongest peak in the product spectrum.

Two chemical reduction experiments were conducted on the p-nitrophenol-formaldehyde oligomer of $\overline{MW}_n = 1240$. In the first of these a suspension of the nitro oligomer in aqueous ammoniacal sodium hydrosulfite ($Na_2S_2O_4$) was refluxed for 3 days, according to the method described by Bachman et al. [49] for the reduction of nitropolystyrenes. The isolated product from this experiment was not soluble in dilute mineral acids. The infrared spectrum of the product indicated that only partial reduction had occurred; the nitro group symmetric stretching absorption at 1335 cm^{-1} remained the strongest peak in the product spectrum. The other chemical reduction attempt on the p-nitrophenol-formaldehyde oligomer was a modification of a zinc dust amalgam reduction method described by Buckler [50]. In this procedure the nitro oligomer was refluxed for 20 hr in a mixed 2-(2-ethoxyethoxy)-ethanol-water solvent in the presence of large excesses of zinc dust amalgam and acetic acid. The isolated product was insoluble in dilute mineral acids, and the infrared spectrum indicated that little or no reduction had occurred.

Two high-pressure hydrogenation experiments were conducted on the p-nitrophenol-formaldehyde oligomer of $\overline{MW}_n = 1240$. In each experiment, an approximately 3% (by weight) solution of the oligomer in 2-(2-ethoxyethoxy)-ethanol was added to a 300-ml hydrogenation bomb, the catalyst was added, and the bomb was sealed, flushed with hydrogen, and pressured with hydrogen to about 1100 psig (about 75 atm).

The first experiment employed 5% palladium-on-charcoal as catalyst in an amount approximately three times that of the oligomer weight. The bomb and contents were rocked at room temperature for 1 hr. The observed decrease in hydrogen pressure, which occurred within the first 20 min of rocking, corresponded to about 30% of the theoretical drop for complete hydrogenation of the nitro groups. The isolated product showed very little change in its infrared spectrum from that of the starting material; the symmetric stretching absorption of the nitro group at 1335 cm^{-1} remained the strongest peak in the spectrum of the product.

The second high-pressure hydrogenation experiment was the most successful of all the attempts in this research to prepare a p-aminophenol-formaldehyde oligomer. This experiment employed Raney nickel as catalyst in an amount approximately two times that of the oligomer weight. The bomb and contents were rocked at a controlled temperature of 88°C for 2 hr. The observed decrease in hydrogen pressure, which was completed before the 88°C temperature was reached, corresponded to about 40% of the theoretical drop for complete hydrogenation of the nitro groups. The isolated product differed from the starting material in that the product was insoluble in acetone. The infrared spectrum of the product, when compared with that of the starting material, indicated that partial hydrogenation had occurred. Increased absorption was observed near 3500 cm^{-1} [ν (NH_2)], 1600 cm^{-1} [δ (NH_2)], and 1220 cm^{-1} [ν ($C \underset{\text{arom}}{—} O$ para to NH_2]. However, the symmetric stretching absorption of the nitro group at 1335 cm^{-1} remained the strongest peak in the spectrum of the product. The elemental analysis results for the product are: C = 61.5%, H = 4.46%, N = 9.14%. The results are consistent with the calculated values for the following Model Structure, which assumes 38.0% hydrogenation of the nitro groups:



(not ordered)

Calculated: MW = 1154, C = 61.51%, H = 4.34%, H = 4.34%, N = 9.20%.

This Model Structure is analogous to the one which was proposed previously for the starting material. Each Model Structure assumes a linear, phenol-ended chain, which contains an average of 8.58 units, and from which 11.6% of the nitro substituents are missing.

The best result in attempts to convert the nitro groups of the p-nitrophenol-formaldehyde oligomer to amino groups was one which corresponded to only 38% conversion; therefore, it was decided to methylate the phenolic OH groups of the p-nitrophenol-formaldehyde oligomer and then to hydrogenate the methylated product. It is believed that the poor results in the catalytic hydrogenation experiments on the p-nitrophenol-formaldehyde oligomer might be related to a competition between the phenolic OH group and the nitro groups for the surface of the hydrogenation catalyst. Assuming this to be the case, then the reduction in polarity to be gained by methylation should facilitate the contact of the nitro groups with the catalyst surface, and hence should also improve the efficiency of the hydrogenation. If necessary, it should be possible afterwards to cleave the methoxy groups of the hydrogenated product in strong acid medium in order to restore the phenolic OH groups.

In the first attempt at methylation of the p-nitrophenol-formaldehyde oligomer ($\overline{MW}_n$ = 1240), the general method of Buck [51] was employed. In this method, the hydroxy compound is treated with an excess of dimethyl sulfate and sodium hydroxide in aqueous medium. The product obtained by this procedure is shown by its infrared spectrum to be only partially methylated. The absorption in the phenolic OH stretching region, ca. 3400 cm^{-1}, is of somewhat decreased intensity in comparison with the starting material. However, considerable absorption occurs in this region even in the spectrum of the product. This indicates that the product contains some nonmethylated OH groups. A slightly modified dimethylsulfate–sodium hydroxide methylation procedure, in which a mixed N,N-dimethylformamide–water solvent was used, also produced an only partially methylated product. Another related procedure, in which the sodium salt of the p-nitrophenol-formaldehyde oligomer was first isolated and then treated with excess dimethylsulfate, also yielded a partially methylated product.

Treatment of the p-nitrophenol-formaldehyde oligomer ($\overline{MW}_n$ = 940) with sodium hydride and methyl iodide, according to the method of Diner et al. [9], resulted in a fully methylated product, i.e., a p-nitroanisole-formaldehyde oligomer.

The infrared spectra of the p-nitroanisole-formaldehyde and p-nitrophenol-formaldehyde oligomers are similar in most respects. However, the two oligomers may be differentiated by the following characteristics of the spectrum of the methylated product (Table 12):

1) The lack of absorption in the OH stretching region (ca. 3400 cm^{-1}).

2) The appearance of new peaks at 2840 and 1011 cm^{-1} due to the antisymmetric CH stretching- and the $C_{\overline{aliph}}O$ stretching-absorptions of the CH_3O group, respectively.

3) The shift of the $C_{\overline{arom}}O$ stretching frequency to 1258 cm^{-1} (from 1272 cm^{-1} in the spectrum of the starting material).

The methylated product may also be differentiated from the starting material by the lower alkali solubility of the product. Moreover, the methoxy oligomer melts without apparent decomposition between 150 and 180°C, whereas the hydroxy oligomer begins to decompose without melting near 175°C.

The $\overline{MW}_n$ of the product, as determined by vapor pressure osmometry in acetone at 37°C, is 1015. This result is in good agreement with a theoretical value of 1030, which is based on the proposed Model Structure C_1 for the starting material and which assumes no change in the average number of chain units from starting material to isolated product.

The elemental analysis values for the p-nitroanisole-formaldehyde oligomer are in reasonably good agreement with the calculated values for the proposed Model Structure C_2. This Model Structure incorporates the same assumptions as does Model Structure C_1 for the starting material; i.e., a linear, phenol-ended chain of 6.48 units and a loss of 9.6% of the nitro substitutents.

The first attempt to hydrogenate the p-nitroanisole-formaldehyde oligomer employed the low-pressure, room temperature technique. The solvent was 2-(2-ethoxyethoxy)-ethanol and the catalyst was 5% palladium-on-charcoal. After 2 hr agitation, no decrease in hydrogen pressure was observed. The infrared spectrum of the isolated product showed no apparent change from that of the starting material.

The high-pressure hydrogenation method which is described in the experimental section of this paper was the most successful method found in this research for hydrogenation of the nitro groups of the oligomeric systems. This general method has been shown to yield a product in which an estimated 38% of the nitro groups are converted to amino groups when the starting material is the p-nitrophenol-formaldehyde oligomer of $\overline{MW}_n$ = 1240. When the method is applied to the p-nitroanisole-formaldehyde oligomer of $\overline{MW}_n$ = 1015, the estimated percentage of nitro groups which are converted to amino groups range from 65 to 83%.

The procedure described in this paper represents a typical hydrogenation experiment in which an estimated 78% of the nitro groups in the p-nitroanisole-formaldehyde oligomer are converted to amino groups. The product is completely soluble in dilute mineral acids and is insoluble in basic media. The carbon, nitrogen, and oxygen analyses of the purified product agree very well with the calculated values for the Model Structure D_3. This Model Structure incorporates the assumptions of the proposed Model Structure C_2 for the starting material, i.e., a linear, phenol-ended chain of 6.48 units and a loss of 9.6% of the nitro substitutents. Model Structure D_3 also assumes that 78% of the nitro groups have been converted to amino groups. The slightly high hydrogen analysis could be the result of a small amount of ring hydrogenation.

Characteristic frequencies and tentative assignments of the infrared spectrum of the partial hydrogenation product or (p-anisidine, p-nitroanisole)-formaldehyde oligomer are given in Table 12.

The hydrogenation product can be differentiated from the p-nitroanisole-formaldehyde oligomeric starting material by the following characteristics of the infrared spectrum of the product:

1) The disappearance of the characteristic, strong nitro group peaks at 1507 and 1335 cm^{-1}; in addition, other lower frequency nitro peaks disappear.

2) The appearance of typical absorptions of the NH_2 group, such as the two NH_2 stretching absorptions near 3400 cm^{-1}, and the NH_2 bending absorption near 1600 cm^{-1}.

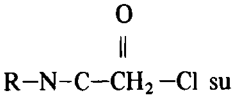
3) The shifting of the $C\underset{\text{arom}}{\text{——}}O$ stretching peak to 1222 cm^{-1} (from 1258 cm^{-1} in the spectrum of the starting material).

4) The shifting of the C–H out-of-plane deformation absorptions which occur at 899 and 811 cm^{-1} for the starting material, to 853 and 800 cm^{-1}, respectively, for the product.

In order to substantiate the proposed Model Structure D_3 for the (p-anisidine, p-nitroanisole)-formaldehyde oligomer, the N,N-diacetyl derivative was prepared according to the general method of Sudborough [52]. The carbon and oxygen analysis values of the derivative are in good agreement with the calculated values for the proposed Model Structure D_4, which is analogous to Model Structure D_3 for the starting material. The low results for nitrogen and the high results for carbon could be due to impurities, since the diacetyl derivative was not recrystallized before analysis. The N,N-diacetyl nature of the derivative is verified by the multiplicity of carbonyl (C=O) absorptions [53, 54]. The derivative also displays a new peak at 1360 cm^{-1} which is assigned [19, 21] to the symmetric deformation of the CH_3 group that is attached to the carbonyl carbon.

Although a large number of experiments were performed on the (p-anisidine, p-nitroanisole)-formaldehyde oligomers, no good method could be found for the incorporation of the iminodiacetic acid chelating function into the oligomeric system. One of the major difficulties in this phase of the investigation was the relatively low solubility of the (p-anisidine, p-nitroanisole)-formaldehyde oligomer in most common solvents. The number of solvents or solvent systems which will dissolve this oligomer and also fulfill other requirements of the chloroacetic acid reaction procedure appears to be very limited. The solvent system for this procedure should also dissolve 1) chloroacetic acid, or sodium chloroacetate, or some similar salt of chloroacetic acid, 2) some suitable base or basic salt which can react with the HCl which is eliminated by the primary reaction, and 3) intermediate reaction products of the oligomer and chloroacetic acid. Among some of the complicating factors in the carboxymethylation procedure are:

1) A tendency of sodium chloroacetic to undergo hydrolysis in aqueous medium [44] which destroys the reactive C–Cl bond.

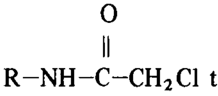
2) An apparent tendency, under certain conditions, for the amino groups to react with the carboxyl end of the chloroacetic acid molecule which produces undesired  $R-N-\overset{\overset{O}{\|}}{C}-CH_2-Cl$ substituents.

3) A tendency of chloroacetic acid to react with certain common solvents.

The following experimental examples illustrate some of the problems mentioned above:

1) The (p-anisidine, p-nitroanisole)-formaldehyde oligomer is soluble in a chloroacetic acid-water mixture, but the introduction of a basic salt, sodium acetate, causes immediate precipitation of the oligomer and inhibits further reaction.

2) The performance of the reaction in a basic organic solvent obviates the necessity of using an inorganic base or basic salt. But the oligomer is not soluble in such basic organic solvents as dimethylaniline or acetonitrile. The oligomer is soluble in pyridine, but chloroacetic acid apparently reacts with pyridine. (Chloroacetic acid also apparently reacts with another solvent for the oligomer, N,N-dimethylacetamide.)

3) The oligomer is soluble in molten chloroacetic acid itself. However, treatment of the oligomer with this solvent-reactant and with sodium chloroacetate apparently produces a cross-linked product. Possibly linkages of the  $R-NH-\overset{\overset{O}{\|}}{C}-CH_2Cl$ type form, which then react with other amino

groups through the C—Cl bond to produce a cross-linked product. Cross-linking apparently also occurs when the oligomer is reacted with chloroacetic acid and triethylamine in dioxane medium at elevated temperatures.

4) The (p-anisidine, p-nitroanisole)-formaldehyde oligomer samples which have lower percent conversions (or greater ratios of nitro-to-amino groups) than the sample described in the experimental section of this paper also display lower solubility in certain solvents, e.g., in the procedure which is described in the experimental section of this paper, the use of the mixed dioxane–water solvent system resulted in nearly complete solubility throughout the experiment of the oligomer with an estimated 78% hydrogenation. However, when duplication of the procedure was attempted using an oligomer with an estimated 65% hydrogenation, the oligomer could not be dissolved in dioxane–water mixtures.

5) In one procedure a solution of the oligomer in N,N-dimethylformamide was treated first with sodium hydride and then with chloroacetic acid. However, the sodium hydride did not dissolve in the solvent and very little reaction with chloroacetic acid occurred.

As indicated by its solubility in dilute aqueous sodium hydroxide and by appearance of carbonyl absorption in its infrared spectrum, the product (I) represented the most successful effort in this research to prepare a chelating oligomer. Of all the solvents and solvent combinations that were investigated, the mixed dioxane-water solvent system showed the best capacity to maintain complete solution of the reactants during the reaction of the (p-anisidine, p-nitroanisole)-formaldehyde oligomer with sodium chloroacetate in the presence of sodium acetate. The product (I), which was isolated at pH = 3.9, differs from the starting material in that (I) is soluble in both acidic and basic media. The product was isolated for analytical purposes from strong acid medium (II).

The elemental analysis value of (II) for carbon is too high for any of the Model Structures which assume complete reaction (D_5, E_5, or F_5). Of the two Model Structures which assume partial reaction, H_5, which assumes partial reaction (47%) to a free iminodiacetic acid structure with no hydrochloride salt formation, gives the better agreement of calculated values with the elemental analysis values. However, both G_5 and H_5 give a rather poor fit to the nitrogen analysis value.

In comparison with the starting material–the (p-anisidine, p-nitroanisole)-formaldehyde oligomer–the infrared spectra of both products (I) and (II) show new absorption in the carbonyl region of their infrared spectra (1750-1650 cm^{-1}). The spectrum of (I) shows a broad band of medium intensity centered at 1670 cm^{-1} with a broad shoulder near 1720 cm^{-1}.

Moreover, the absorption in the NH_2 stretching region (ca. 3400 cm^{-1}) has decreased in intensity from starting material to product (I). In the spectrum of product (II), the absorption maximum in the carbonyl region is a strong, broad band centered at 1735 cm^{-1}. Moreover, the absorption in the region 3200-2300 cm^{-1} has increased in intensity from the starting material to product (II); this indicates some $N\text{-}H_n^+$ structure and probable hydrochloride salt formation for II, although the absorption pattern is of considerably weaker intensity than that observed, e.g., for hydrochloride salts of the Prototype Dimers. For both of the products (I) and (II), the spectral bands are generally broader and weaker than those observed for the starting material.

The changes in composition, solubility properties, and infrared spectral patterns of the products (I) and (II) with respect to the (p-anisidine, p-nitroanisole)-formaldehyde oligomer indicate that some reaction with sodium chloroacetate has occurred. However, the analytical results do not facilitate any definite conclusions about the structures of these partial reaction products.

Part III of the experimental procedure describes an attempt to prepare a copper complex of the product (I). The infrared spectrum of the product (III) of this attempt shows very little change from the spectrum of (I), other than more broadening of the absorption maximum. In view of the high (supposed) carboxylate frequency (1670 cm^{-1}) that was observed for the potential ligand (I), little change would be expected in this frequency upon complex formation. Therefore, neither complex formation nor the lack of complex formation can be concluded from the spectrum of III.

The results of this preliminary investigation of an oligomeric system indicate that the synthetic procedures which were employed in the preparation of the Prototype Dimers can be appropriately modified to prepare characterizable higher molecular weight materials which contain amino functions in the desired positions on the polymeric chains. However, suitable conditions for a substantial reaction of the amino functions with chloroacetic acid have not yet been found. Hence, definite conclusions concerning the potential of this system for chelating polymer formation cannot be drawn on the basis of this preliminary study

Any future work on this sytem should be directed initially toward finding the best procedure for incorporation of the chelating function onto the polymer backbone. If good conditions for substantial reaction of the amino groups on the polymer with chloroacetic acid can be determined, then efforts should also be made to 1) avoid or minimize the loss of nitro groups by varying the conditions of the polymerization step, 2) improve the efficiency of the hydrogenation procedure, and 3) determine the possibility of cleaving the methoxy groups after hydrogenation in order to restore the phenolic OH groups.

Although it may be possible to find suitable conditions for a substantial reaction of the amino groups in the polymer with chloroacetic acid, other snythesis approaches to the problem might also be considered. If the synthesis problems for the oligomeric chelating system can be solved, then its chelating properties should be determined and compared with those of the corresponding monomeric and dimeric ligands. If the results are promising, then, and only then, should studies of higher molecular weight analogues be approached. The best way to prepare a cross-linked chelating polymer using the synthetic approach worked out in this paper may be to crosslink the fully synthesized chelating oligomer since it is rather doubtful if the methylation and catalytic hydrogenation procedures could be applied efficiently to an insoluble, cross-linked, nitrophenol-formaldehyde polymer.

However, in view of the synthesis difficulties that were encountered in this and in earlier studies [2] of phenol-formaldehyde chelating polymer systems, and also in consideration of the relative ease of synthesis and apparent successes with chelating polymer systems based on triazine-formaldehyde condensation products [42] and on glycidyl methacrylate addition products to be reported in future publications [55, 56], it might be concluded that the phenol-formaldehyde condensation system would be a poor choice for future chelating polymer studies and might be abandoned in favor of further studies of the other systems.

REFERENCES

[1] K. Ashida, *Chem. High Polymers* (Japan), **10**, 121 (1953).

[2] G. F. D'Alelio, E. T. Hofman and J. R. Zeman, *J. Macromol. Sci.–Chem.*, **A3**, 959 (1969).

[3] J. S. Carswell, *Phenoplasts: Their Structure, Properties, and Chemical Technology* (Vol. VII, *High Polymers*), (Wiley)Interscience, New York, 1947.

[4] N. J. L. Megson, *Phenolic Resin Chemistry*, Academic, New York, 1958.

[5] R. W. Martin, *The Chemistry of Phenolic Resins*, Wiley, New York, 1957.

[6] H. E. Faith, *J. Amer. Chem. Soc.*, **72**, 837 (1950).

[7] M. M. Stimson and M. J. O'Donnell, *J. Amer. Chem. Soc.*, **74**, 1805 (1952).

[8] F. D. Chattaway and R. M. Goepp, *J. Chem. Soc.*, **1933**, 699.

[9] U. E. Diner, F. Sweet, and R. K. Brown, *Can. J. Chem.*, **44**, 1591 (1966).

[10] L. H. Baekeland, *J. Ind. Eng. Chem.*, **1**, 149 (1909).

[11] G. F. D'Alelio, *Experimental Plastics and Synthetic Resins*, Wiley, New York, 1946.

[12] W. Wirths, *Arch. Pharm.* **234**, 622 (1896).

[13] R. Mendola, H. S. Foster, and R. Brightman, *J. Chem. Soc.*, **111**, 552 (1917).

[14] L. Galatis, *Helv. Chem. Acta*, **4**, 575 (1921).

[15] A. Terentiev and S. Chernin, *Khim. Farm. Prom.*, **1933**, 18.

[16] P. Q. Brewster and W. E. McEwen, *Organic Chemistry*, 3rd ed., Prentice-Hall, Englewood Cliffs, N. J., 1961, p. 421.

[17] K. Shimo, *Bull. Chem. Soc. Japan*, **1**, 202 (1926).

[18] L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, Wiley, New York, 1958, pp. 234-245, 259-260.

[19] K. Nakanishi, *Infrared Absorption Spectrscopy*, Holden-Day, San Francisco, 1962.

[20] C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic, New York, 1963.

[21] N. B. Colthup, L. H. Daly, and S. E. Silberly, *Introduction to Infrared and Raman Spectroscopy*, Academic, New York, 1964.

[22] D. Hadzi and N. Sheppard, *Trans. Faraday Soc.*, **50**, 911 (1954).

[23] M. M. Davies and R. N. Jones, *J. Chem. Soc.*, **1954**, 120.

[24] L. H. Briggs, L. D. Golebrook, H. M. Fales, and W. C. Wildman, *Anal. Chem.*, **29**, 904 (1957).

[25] F. Ritschl, *Spectrochim. Acta*, **23A**, 655 (1967).

[26] S. R. Palit, *Anal. Chem.*, **18**, 246 (1946).

[27] L. C. Sillen and A. E. Martell, *Chem. Soc. (London), Special Pub.* No. **17** (1964).

[28] K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, **84**, 2081 (1962).

[29] D. Chapman, *J. Chem. Soc.*, **1955**, 1766.

[30] E. T. Hofman, Ph.D. Dissertation, University of Notre Dame, Notre Dame, Indiana, 1962.

[31] G. F. Svatos, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **77**, 6159 (1955).

[32] K. Nakomoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 4528 (1961).

[33] A. J. Saraceno, I. Nakagawa, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **80**, 5018 (1958).

[34] D. N. Sen, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **77**, 211 (1955).

[35] D. Segnini, S. Curran, and J. V. Quagliano, *Spectrochim. Acta,* **16**, 540 (1960).

[36] R. J. Hooper, Ph.D. Dissertation, University of Notre Dame, Notre Dame, Indiana, 1962.

[37] D. H. Busch and J. C. Bailar, *J. Amer. Chem. Soc.*, **75**, 4574 (1953).

[38] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 1963, pp. 201-210.

[39] F. A. Cotton, *Modern Coordination Chemistry*, Wiley(Interscience), New York, 1960, p. 387.

[40] R. Mecke and G. Rossmy, *Z. Electrochem.*, **59**, 866 (1955).

[41] M. A. J. Jungbauer and C. Curran, *Spectrochim. Acta,* **21**, 641 (1965).

[42] W. W. Cuthbertson and J. S. Moffat, *J. Chem. Soc.*, **1948**, 561.

[43] G. Schwartzenbach and H. Ackermann, *Helv. Chim. Acta,* **31**, 1029 (1948).

[44] G. Senter, *Trans. Chem. Soc.*, **91**, 466 (1907).

[45] G. F. D'Alelio, *Fundamental Principles of Polymerization,* Wiley, New York, 1952, p. 19.

[46] J. P. Losev, A. S. Tevlina, and E. B. Trostyanskaya, *Teoriya i Prakt. Priminen Ionoobmen. Materialov, Sbornik Statei,* **1955**, 35.

[47] K. Nakazawa, Y. Ogami, and Y. Mizatani, Japanese Patent 3399 (1957); *Chem. Abstr.*, **52**, 6671C (1958).

[48] N. Guivitchi, *J. Rech. Centre Natl. Rech. Sci. Lab., Bellevue,* **14**, 73 (1963).

[49] G. B. Bachman, H. Hillman, K. R. Robinson, R. W. Finholt, E. J. Kahler, L. J. Filar, L. V. Heisley, L. L. Lewis, and D. D. Micucci, *J. Org. Chem.*, 12, 108 (1947).

[50] R. T. Buckler, Ph.D. Dissertation, University of Notre Dame, Notre Dame, Indiana, 1964, p. 22.

[51] J. S. Buch, in *Organic Syntheses, Collective Volume II,* (A. H. Blatt, ed)., Wiley, New York, 1943, p. 619.

[52] J. S. Sudborough, *J. Chem. Soc.*, **79**, 533 (1901).

[53] R. A. Abramovitch, *J. Chem. Soc.*, **1957**, 1413.

[54] J. Uno and K. Machida, *Bull. Chem. Soc. Japan,* **34**, 545, 551 (1961).

[55] W. F. Strazik, Unpublished results, Thesis Research, University of Notre Dame, Notre Dame, Indiana.

[56] D. P. O'Brien, Unpublished results, Thesis Research, University of Notre Dame, Notre Dame, Indiana.

[57] G. K. Goldman, H. Lehman, and C. N. R. Rao, *Can. J. Chem.*, **38**, 171 (1960).

Accepted by editor August 6, 1969
Received for publication October 17, 1969