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Chelating Polymers. I.
Monomeric Hydroxyarylaminoacetic Acids as Prototype Chelating Compounds†

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SUMMARY

The model chelating compounds, N-(p-hydroxyphenyl)glycine, N-(p-methoxyphenyl)glycine, N-methyl-N-(p-hydroxyphenyl)glycine, N-(p-hydroxyphenyl)iminodiacetic acid, N-(p-hydroxybenzyl)glycine, and N-(p-hydroxyphenylethyl)iminodiacetic acid, were synthesized and characterized by composition analysis and infrared spectroscopy. 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 glycine metal complex type for the Cu(II), Ni(II), Co(II), and Zn(II) complexes of N-(p-hydroxyphenyl)glycine, N-(p-methoxyphenyl)glycine, and N-(p-hydroxybenzyl)glycine. Only metal-carboxylate interaction is indicated in the spectra of the Cu(II), Ni(II), Co(II), and Zn(II) compounds of N-(p-hydroxyphenyl)iminodiacetic acid and of N-(p-hydroxyphenylethyl)-iminodiacetic acid. However, there was no evidence for coordination in the Cu(II) and Zn(II) compounds of N-methyl-N-(p-hydroxyphenyl)-glycine.

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†Taken in part from the Ph.D. dissertation of E. T. Hofman and the Master's Thesis of J. R. Zeman.

INTRODUCTION

Griessbach [1] in 1939 and Mellor [2] in 1950 suggested that a chelating group attached to a cross-linked polymer should exhibit highly selective absorption activity toward metal ions. Apparently, the first synthesis of such a selective chelating polymer was the substituted polystyrene of Skogseid [3] which contained a dipicrylamine structure. Skogseid reported that his polymer was selective for potassium ion. Since then, many chelating polymers have been synthesized, to which various degrees of selectivity have been attributed. Reviews on chelating polymers have been prepared by Hale [4], Millar [5], Nickless and Marshall [6], Schmuckler [7], and Blasius and Brozio [8]. More recently, a number of new chelating polymers have been reported [9-28].

Schmuckler [7] enumerates three main properties of a chelating polymer that distinguish it from an ion-exchange polymer in behavior toward metal ions: (1) greater selectivity, (2) higher metal-to-polymer bond energy, and (3) slower kinetics.

Blasius and Brozio [8] point out that, in addition to the selectivity required in a chelating polymer, the practical application of the polymer dictates other minimal requirements, namely: (1) sufficient mechanical and chemical stability, especially toward acids and bases which are used to regenerate the polymer, (2) an effective exchange capacity of at least 1 meq of metal ion per gram of polymer, and (3) a relatively high rate for the complexation reaction.

Gregor et al. [29] suggest the following conditions for the successful synthesis of a chelating polymer:

(1) The chelating group should be capable either of polymer formation or of substitution in the polymer matrix. In the former case, the chelating group should be sufficiently stable to withstand the polymerization reaction, and the chelating function should not be altered by the polymerization reaction.

(2) The chelating group should be compact so as not to be sterically hindered by the dense polymer matrix.

(3) Both arms of the chelate structure should be present on the same "monomer" in proper spatial configuration, so that the specific arrangement of the ligand will be preserved in the polymer.

In view of these considerations, Blasius and Brozio [8] concluded that it was unlikely that many known chelating agents could be incorporated into polymers without loss of their selective properties. In particular, they believed that all chelating agents that do not form 1:1 complexes, such as anthranilic acid and 8-hydroxyquinoline, would be unsuitable. Also unsuitable [8] would be long-chain chelating agents, such as ethylenediaminetetraacetic acid (EDTA), because of the improbability that the chelate configurations, formed in aqueous solution, could be maintained or established on a cross-linked polymer. It becomes apparent, then, that it is reasonable to conclude that in an effective chelating polymer, the behavior of the chelating group in the polymer should be very similar to that of the chelating group in its monomeric segment; such a segment can be construed to be the model compound for the chelating polymer. We propose 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, trimers, 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.

Such an approach should help to prevent erroneous interpretation of the structure and properties of polymers assumed to be chelating polymers. In some cases observed effects have been erroneously attributed to chelation, and in other cases potentially good chelating polymers have been discarded because of failure to detect correctable features.

Monomeric hydroxyarylaminoacetic 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 [30] reported that a condensation product of N-(p-hydroxyphenyl)glycine and formaldehyde indicated no chelation 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.

We have undertaken investigations of a number of chelating polymers having various polymeric matrices, all of which contain amino acid ligands. This paper is the first in the series. Following the approach proposed above, the objective of our investigation was 1) to prepare several model chelating compounds of the monomeric hydroxyarylaminoacetic acid type, and 2) to prepare some transition metal complexes of these compounds and to characterize these complexes particularly by means of infrared spectroscopy since profile changes and band shifts in the N—H stretching vibration region and in the carboxylate stretching vibration regions of the spectra offer evidence for metal-nitrogen and metal-oxygen interaction, respectively.

The synthesis, characterization, and chelating properties of the oligomeric condensation products structurally related to the model compounds of this paper are the subject of a subsequent publication [31].

EXPERIMENTAL

Physical Measurements

All melting points were determined with a Fisher-Johns melting point apparatus calibrated against the U.S.P. reference melting point standards. Decomposition points are recorded as the temperatures at which decomposition was initially observed.

Infrared spectra were obtained on 1) a Perkin-Elmer Model 221 infrared spectrophotometer with a grating from 4000 to 1420 cm^{-1} and with sodium chloride optics in the region 1420-650 cm^{-1}; 2) a Perkin-Elmer Model 21 infrared spectrophotometer with soidum chloride optics in the region 5000-650 cm^{-1}; 3) a Perkin-Elmer Infracord Model 137 with sodium chloride optics from 4000-650 cm^{-1}. Wave number calibrations were made by comparison with polystyrene standard peaks. Samples were prepared for the infrared studies by the potassium bromide disk technique [32].

Synthesis

Model Compound (I): N-(p-Hydroxyphenyl)Glycine. **$HOC_6H_4NHCH_2COOH$.** This compound, purchased from the Eastman Organic Chemicals Department, was recrystallized from boiling water, mp 241°C dec.

Metal Complexes of N-(p-Hydroxyphenyl)Glycine. N-(p-hydroxyphenyl)-glycine (1.84 g, 0.011 mole) was dissolved in 10 ml of 1 N sodium hydroxide solution. This solution was then added to a solution containing 0.005 mole of metal nitrate in 5 ml of water. The system was stirred vigorously for a few minutes and then allowed to stand for 2 hr. The precipitate formed was recovered by filtration under reduced pressure and then washed with several portions of hot, deionized water. It was dried for 24 hr in vacuo over P_2O_5. The date for the metal complexes are summarized in Table 1.

Model Compound (II): N-(p-Methoxyphenyl)Glycine. $CH_3OC_6H_4NHCH_2COOH$. This compound was prepared by the reaction of p-anisidine with chloroacetic acid in sodium hydroxide solution according to the procedure of Halberkann [33]; the yield was 39% of theory. The decomposition point of the recrystallized product was about 152°C (lit. [33] 154-157°C).

Anal: Calculated for $CH_3OC_6H_4NHCH_2COOH$: C, 59.66; H, 6.14: N, 7.74. Found: C, 59.65; H, 6.12; N, 7.70.

Metal Complexes of N-(p-Methoxyphenyl)Glycine. N-(p-methoxyphenyl)glycine (1.99 g, 0.011 mole) was dissolved in 10 ml of 1 N sodium hydroxide solution. This solution was then added to a solution containing 0.005 mole of metal nitrate in 5 ml of water. The system was stirred vigorously for a few minutes and then allowed to stand for 2 hr. The precipitate formed was recovered by filtration under reduced pressure and then washed with several portions of hot, deionized water. It was dried for 24 hr in vacuo over P_2O_5. The data for the metal complexes prepared are summarized in Table 2.

Model Compound (III): N-Methyl-N-(p-Hydroxyphenyl)Glycine Monohydrate. $HOC_6H_4N(CH_3)CH_2COOH \cdot H_2O$. This compound was prepared by the reaction of p-methylaminophenol sulfate with chloroacetic acid in sodium hydroxide solution according to the procedure given in an Agfa patent [34]. The yield was 50% of theory. The decomposition point of the recrystallized material was 109°C (lit. [34] 115°C).

Anal: Calculated for $HOC_6H_4N(CH_3)CH_2COOH \cdot H_2O$: C, 54.26; H, 6.56; N, 7.05. Found: C, 54.37; H, 6.60; N, 7.12.

Metal Compounds of N-Methyl-N-(p-Hydroxyphenyl)Glycine. N-methyl-N-(p-hydroxyphenyl)glycine monohydrate (2.34 g, 0.011 mole) was dissolved

Table 1. Metal Complexes of N-(p-Hydroxyphenyl)Glycine

Formula	Color	Analysis, % C	H	N	
$Cu(HOC_6H_4NHCH_2COO)_2$	Deep green	48.54	4.04	7.10	Calc.
		48.36	4.10	7.13	Found
$Ni(HOC_6H_4NHCH_2COO)_2 \cdot 2H_2O$	Gray-green	44.99	4.72	6.55	Calc.
		44.99	4.93	6.75	Found
$Co(HOC_6H_4NHCH_2COO)_2 \cdot 2H_2O$	Rose	44.98	4.72	6.55	Calc.
		44.89	4.70	6.59	Found
$Zn(HOC_6H_4NHCH_2COO)_2 \cdot H_2O$	Light tan	46.25	4.31	6.74	Calc.
		45.93	4.04	6.43	Found

Table 2. Metal Complexes of N-(p-Methoxyphenyl)Glycine

Formula	Color	Analysis, % C	Analysis, % H	Analysis, % N	
$Cu(CH_3OC_6H_4NHCH_2COO)_2$	Deep green	51.00	4.76	6.61	Calc.
		51.02	4.71	6.30	Found
$Ni(CH_3OC_6H_4NHCH_2COO)_2$	Light blue	51.59	4.81	6.68	Calc.
		52.19	5.06	6.62	Found
$Co(CH_3OC_6H_4NHCH_2COO)_2$	Pink	51.56	4.81	6.68	Calc.
		51.90	4.97	6.79	Found
$Zn(CH_3OC_6H_4NHCH_2COO)_2 \cdot H_2O$	White	48.71	4.99	6.31	Calc.
		49.11	4.73	6.10	Found

Table 3. Metal Compounds of N-Methyl-N-(p-Hydroxyphenyl)Glycine

		Analysis, %			
Formula	Color	C	H	N	
$Cu(HOC_6H_4N(CH_3COO)_2 \cdot H_2O$	Deep green	48.92	5.05	6.38	Calc.
		49.01	5.21	6.34	Found
$Zn(HOC_6H_4N(CH_3)CH_2COO)_2 \cdot H_2O$	Tan	48.72	4.97	6.31	Calc.
		48.48	5.11	6.29	Found

Table 4. Metal Complexes of N-(p-Hydroxyphenyl)Iminodiacetic Acid, Prepared by Method A

Formula	Color	Analysis, %			
		C	H	N	
$Cu(HOC_6H_4N(CH_2COO)_2)$	Deep green	41.89	3.16	4.89	Calc.
		42.20	3.70	4.21	Found
$Ni(HOC_6H_4N(CH_2COO)_2) \cdot 2H_2O$	Blue-green	37.78	4.12	4.41	Calc.
		36.66	3.74	3.72	Found
$Co(HOC_6H_4N(CH_2COO)_2) \cdot 2H_2O$	Violet	37.75	4.12	4.40	Calc.
		37.14	3.48	3.66	Found
$Zn(HOC_6H_4N(CH_2COO)_2) \cdot 2H_2O$	White	37.00	4.04	4.32	Calc.
		36.71	3.74	3.69	Found

in 10 ml of 1 N sodium hydroxide solution. This solution was then added to a solution containing 0.005 mole of metal nitrate in 5 ml of water. The system was stirred vigorously for a few minutes and then allowed to stand for 2 hr. The precipitate formed was recovered by filtration under reduced pressure and then was washed with several portions of hot, deionized water. It was dried for 24 hr in vacuo over P_2O_5. The data for the metal complexes are summarized in Table 3.

Model Compound (IV): N-(p-Hydroxyphenyl)Iminiodiacetic Acid. $HOC_6H_4N(CH_2COOH)_2$. p-Aminophenol hydrochloride (1.46 g, 1 mole) and 10 g of sodium sulfite were mixed in 375 ml of water. To the mixture was added a solution of 240 g (6 moles) of sodium hydroxide in 375 ml of water. Chloroacetic acid (285 g, 3 moles) was added portionwise slowly. The mixture was stirred at the temperature of the reaction (about 90°C) for 20 min and without external heating. It was then transferred to a beaker and allowed to cool in an ice bath to approximately 10°C. The mixture was filtered under reduced pressure, and the residue was transferred to a beaker. Then, 100 ml of water and 100 ml of concentrated hydrochloric acid were added. The system was stirred until a thick paste formed. It was allowed to stand for 30 min and then 100 ml of water were added. The slurry was filtered under reduced pressure and the residue recrystallized from boiling water. The recrystallized product was dried in vacuo over P_2O_5. The yield was 38%, and the decomposition point was 148°C.

Anal: Calculated for $HOC_6H_4N(CH_2COOH)_2$: C, 53.33; H, 4.92; N, 6.22. Found: C, 53.38; H, 5.08; N, 6.41.

Metal Complexes of N-(p-Hydroxyphenyl)Iminodiacetic Acid. *Method A.* N-(p-hydroxyphenyl)iminodiacetic acid (2.25 g, 0.01 mole) was stirred into 40 ml of hot water. This mixture was added to a solution containing 0.01 mole of metal nitrate in 5 ml of water. The resulting mixture was heated on a water bath until a clear solution was formed and then 5 ml of 4 N sodium hydroxide were added. The mixture was cooled to room temperature and allowed to stand for 2 hr. The precipitate formed was recovered by filtration under reduced pressure and then was 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 summarized in Table 4.

Method B. N-(p-hydroxyphenyl)iminodiacetic acid (2.25 g, 0.01 mole) was stirred into 10 ml of 2 N sodium hydroxide solution. To this solution was then added 0.005 mole of metal nitrate. The mixture was stirred vigorously and heated over a water bath for several minutes. It was then cooled and allowed to stand at room temperature for 2 hr. The precipitate formed was recovered by filtration under reduced pressure and then washed three times in cold, deionized water and twice in ethyl alcohol. The product was dried in a vacuum oven at 120°for 1 hr. The data for the metal complexes are summarized in Table 5.

Model Compound (V): N-(p-Hydroxybenzyl)Glycine. $HOC_6H_4CH_2NHCH_2COOH$. This compound was prepared by a procedure which is a modification of the one reported by Takano and Tauruta [35]. In this procedure p-hydroxybenzyl alcohol, p-saligenin, is reacted with glycine in sodium hydroxide solution. The p-hydroxybenzyl alcohol used in the preparation was prepared by the reduction of p-hydroxybenzaldehyde according to the procedure reported by Von Auwers and Daecke [36]. The yield of N-(p-hydroxybenzyl)glycine was 36% of theory. The decomposition point of the recrystallized product was approximately 230°C (lit. [35] 230°C).

Metal Complexes of N-(p-Hydroxybenzyl)Glycine. N-(p-hydroxybenzyl)-glycine (0.500 g, 0.0025 mole) was added to 2.50 ml of 1 N sodium hydroxide solution. Water (2.50 ml) and then 1.25 ml of 1 N metal nitrate solution (0.0012 mole of metal nitrate) were added. The system was stirred vigorously and then allowed to stand at room temperature overnight. The precipitate formed was recovered by filtration under reduced pressure, and the residue was washed several times in warm, deionized water and twice in ethanol. The product was dried in vacuo over P_2O_5. The data for the metal complexes are summarized in Table 6.

Model Compound (VI): N-(p-Hydroxyphenylethyl)Iminodiacetic Acid. $HOC_6H_4CH_2CH_2N(CH_2COOH)_2$. This compound was prepared following a procedure that is a modification of the one used in the preparation of model compound (IV). Tyramine, $HOC_6H_4CH_2CH_2NH_2$ (4.00 g, 0.0292 mole), was mixed with 10 ml of water, and then 0.01 g, 0.007 mole of sodium sulfite was added. To this mixture was added a solution containing 8.280 g, 0.0876 mole of chloroacetic acid dissolved in 14.8 ml of 6 N sodium hydroxide solution. Distilled water was then added until the total volume of the mixture was 30 ml. This mixture was refluxed in a 100-ml, three-necked, round-bottom flask at 90°C for 1 hr. Then 9.74 ml of 6 N sodium hydroxide solution diluted to 15 ml were added slowly and dropwise into the refluxing solution. Approximately 1 hr was required for this

Table 5. Metal Complexes of N-(p-Hydroxyphenyl)Iminodiacetic Acid, Prepared by Method B

Formula	Color	Analysis, %			
		C	H	N	
$Cu(HOC_6H_4N(CH_2COO)_2)$	Deep green	41.89	3.16	4.89	Calc.
		41.92	3.52	4.99	Found
$Ni(HOC_6H_4N(CH_2COO)_2) \cdot 2H_2O$	Blue-green	37.78	4.12	4.41	Calc.
		38.62	4.21	3.87	Found
$Co(HOC_6H_4N(CH_2COO)_2) \cdot 2H_2O$	Violet	37.75	4.12	4.10	Calc.
		38.72	4.25	3.75	Found
$Zn(HOC_6H_4N(CH_2COO)_2) \cdot 2H_2O$	White	37.00	4.04	4.32	Calc.
		36.71	3.74	3.69	Found

Table 6. Metal Complexes of N-(p-Hydroxybenzyl)Glycine

Formula	Color	Analysis, %			
		C	H	N	
$Cu(HOC_6H_4CH_2NHCH_2COO)_2$	Purple-blue	50.98	4.72	6.62	Calc.
		50.54	4.92	6.38	Found
$Ni(HOC_6H_4CH_2NHCH_2COO)_2$	Light blue	51.56	4.80	6.70	Calc.
		51.81	5.07	6.63	Found
$Co(HOC_6H_4CH_2NHCH_2COO)_2$	Rose	51.53	4.78	6.69	Calc.
		51.85	4.97	6.55	Found
$Zn(HOC_6H_4CH_2NHCH_2COO)_2$	White	50.80	4.72	6.56	Calc.
		49.23	5.09	6.06	Found

Table 7. Metal Complexes of N-(p-Hydroxyphenylethyl)Iminodiacetic Acid

		Analysis, %			
Formula	Color	C	H	N	
$Cu(HOC_6H_4CH_2CH_2N(CH_2COO)_2 \cdot H_2O$	Blue	43.31	4.55	4.21	Calc.
		42.57	4.71	4.23	Found
$Ni(HOC_6H_4CH_2CH_2N(CH_2CCO)_2 \cdot H_2O$	Green	43.95	4.61	4.28	Calc.
		42.46	4.82	4.10	Found
$Co(HOC_6H_4CH_2CH_2N(CH_2COO)_2 \cdot H_2O$	Rose	43.91	4.60	4.26	Calc.
		44.06	4.64	4.20	Found
$Zn(HOC_6H_4CH_2CH_2N(CH_2COO)_2 \cdot H_2O$	Tan	43.07	4.52	4.19	Calc.
		42.81	4.55	4.03	Found

addition. The system was refluxed for an additional 5.5 hr and then allowed to stand at room temperature. The solution formed was made acidic to a pH of 3 by the addition of 6 N hydrochloric acid. It was then cooled, with stirring, in an ice bath. A tan precipitate was formed. This precipitate was recovered by filtration under reduced pressure, recrystallized from boiling water, and dried in vacuo at room temperature. The yield was 52% of theory, and the product decomposed at 210°C.

Anal: Calculated for $HOC_6H_4CH_2CH_2N(CH_2COOH)_2 \cdot H_2O$: C, 53.13; H, 6.31; N, 5.16. Found: C, 51.90; H, 6.45; N, 4.72.

The tyramine used in the preparation of the N-(p-hydroxyphenylethyl)-iminodiacetic acid was prepared according to the procedure reported by Johnson and Daschavsky [37]. The yield was 70%, mp 160-161°C (lit. [37] 160-161°C).

Metal Complexes of N-(p-Hydroxyphenylethyl)Iminodiacetic Acid. N-(p-hydroxyphenylethyl)iminodiacetic acid (0.375 g, 0.00148 mole) was dissolved in 2.96 ml of 1 N sodium hydroxide solution (0.00296 mole). To this solution were added 1.48 ml of 1 N metal nitrate solution (0.00148 mole). The mixture was stirred vigorously for a few minutes, then allowed to stand at room temperature for approximately 36 hr, then filtered to recover the residue which was washed several times with warm, deionized water. It was then dried in a vacuum desiccator over P_2O_5 for 18 hr at room temperature. The data for the metal complexes prepared are summarized in Table 7.

DISCUSSION

The key compound in this investigation is model compound (I): N-(p-hydroxyphenyl)glycine. However, because it is impossible to distinguish sufficiently between OH and NH stretching vibration absorptions in the 3500-3300 cm^{-1} region in the spectra of N-(p-hydroxyphenyl)glycine and its metal complexes, N-(p-methoxyphenyl)glycine and its metal complexes were prpeared and their infrared spectra were studied in advance of those of the N-(p-hydroxyphenyl)glycine compounds.

Model Compound (II): N-(p-Methoxyphenyl)Glycine and Its Metal Complexes

The infrared spectrum of N-(p-methoxyphenyl)glycine indicates strong absorption (characteristic of the CH_3O^- group) at 2835 cm^{-1}, and carboxylate antisymmetric and symmetric stretching vibration absorptions at 1560 and 1370 cm^{-1}, respectively. The NH_2^+ stretching vibration absorption expected in the 3000 cm^{-1} region is too broad to permit interpretation.

Because of the difficulty in preparing the sodium salt of N-(p-methoxyphenyl)glycine, the NH stretching vibration frequency of sodium-dl-prolinate, 3880 cm^{-1}, are reported by Segnini et al. [38], was used as the reference for determining the frequency shifts in the spectra of the metal complexes.

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

Bis-(N-(p-methoxyphenyl)glycino)-copper (II), 3150 cm^{-1}
Bis-(N-(p-methoxyphenyl)glycino)-nickel (II), 3167 cm^{-1}
Bis-(N-(p-methoxyphenyl)glycino)-cobalt (II), 3175 cm^{-1}
Bis-(N-(p-methoxyphenyl)glycino)-zinc (II), 3160 cm^{-1}

The shift toward a lower frequency (compared with the uncoordinated salt) is, in each case, an indication of nitrogen-to-metal bonding of some covalent character. The frequencies are not significantly different for the various complexes, although the copper-to-nitrogen bond appears to be of somewhat greater covalent character than the other nitrogen-to-metal bonds. The water in the zinc compound obscures the bond slightly, but the frequency is most probably 3160 cm^{-1}.

The carboxylate antisymmetric stretching vibration frequencey of the ligand is taken to be 1560 cm^{-1}. The NH_2^+ scissors absorption, however, occurs in the same region (1610 cm^{-1}), and it is possible that the peak may be a composite of the two interactions.

The carboxylate antisymmetric stretching vibration frequencies of the metal complexes are:

Bis-(N-(p-methoxyphenyl)glycino)-copper (II), 1608 cm^{-1}
Bis-(N-(p-methoxyphenyl)glycino)-nickel (II), 1590 cm^{-1}
Bis-(N-(p-methoxyphenyl)glycino)-cobalt (II), 1585 cm^{-1}
Bis-(N-(p-methoxyphenyl)glycino)-zinc (II), 1600 cm^{-1}

The shifts toward a higher frequency indicates, in each case, that in the absence of other interfering effects the carboxylate-to-metal bonds are of greater covalent character than those for uncoordinated salts. This effect is thought to be a result of different degrees of double bond character of the two carbon-to-oxygen bonds. The evidence indicates apparently greatest covalent character in the copper-to-carboxylate bonding and apparently quite similar bonding in the nickel and cobalt complexes. The broad peak in the zinc complex is probably due to water interaction.

The carboxylate symmetric stretching vibration frequency in the ligand is taken to be 1370 cm^{-1} with a shoulder at 1395 cm^{-1}. It is possible that this absorption might be a composite of the carboxylate and CH_3 absorptions.

The assigned carboxylate symmetric stretching vibration frequencies for the metal complexes are:

Bis-(N-(p-methoxyphenyl)glycino)-copper (II), 1365 cm^{-1}
Bis-(N-(p-methoxyphenyl)glycino)-nickel (II), 1430 cm^{-1}
Bis-(N-(p-methoxyphenyl)glycino)-cobalt (II), 1438 cm^{-1}
Bis-(N-(p-methoxyphenyl)glycino)-zinc (II), 1375 cm^{-1}

The expected decrease in frequencies does not appear for all compounds, and no good correlation can be made. This deviation is, however, not uncommon.

The carboxylate stretching absorption indicates the zwitterion structure for the ligand:

$$CH_3OC_6H_4NH_2^+CH_2COO^-$$

The shifts in the NH stretching and carboxylate antisymmetric stretching frequencies in the spectra of the metal complexes, as compared with those of the reference absorptions, indicate chelate structure of the common glycine type in which the glycine ligands are arranged in a transplanar form about the central metal ion [39], as shown in Fig. 1.

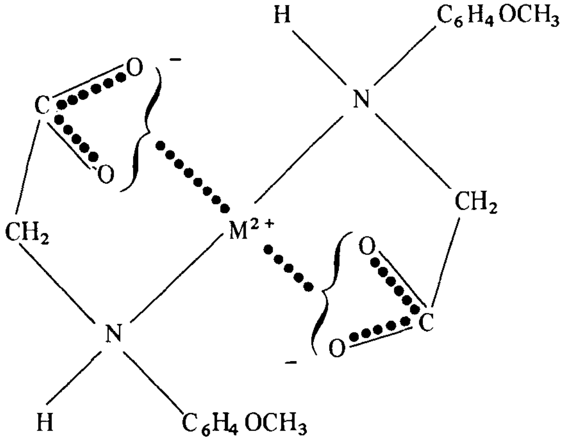


Fig. 1. Structure of complexes of N-(p-methoxyphenyl)glycine.

Graddon [40], on the basis of visible and ultraviolet absorption studies, proposed a similar structure for bis-(N-(p-ethoxyphenyl)glycino)-copper (II) and certain other N-aryl-glycine compounds. The structure of bis-(N-(p-methoxyphenyl)glycino)-zinc (II) monohydrate is probably similar to that of bis-(glycino)-zinc (II) monohydrate as reported by Low et al. [41] on the basis of X-ray investigations. According to this report, the glycine ligands are arranged in a transplanar form about the central zinc ions, and the water molecules occupy transoctahedral positions "sandwiched" between zinc ions.

Model Compound (I): N-(p-Hydroxyphenyl)Glycine and Its Metal Complexes

Possible OH absorption and possible water interaction (in the nickel, cobalt, and zinc complexes) make it impossible to draw, from the spectra of the compounds in this series, conclusions regarding NH stretching vibration absorption and related frequency shifts. It might be pointed out, however, that there is in the spectrum of the ligand a profile effect in the 3000-2500 cm^{-1} region, which is probably due to the NH_2^+ group, but which is lost in the spectrum of the copper complex and considerably changed in the spectra of other complexes. Further, there is no reason to believe that the nitrogen-to-metal bonding in this series of complexes is significantly different from that of the complexes in the N-(p-methoxyphenyl)glycine series. It may be postulated, then, that the nitrogen is coordinated to the metal ions in the N-(p-hydroxyphenyl)glycine metal complexes investigated.

The probable carboxylate antisymmetric stretching frequency in the spectrum of N-(p-hydroxyphenyl)glycine is 1572-1570 cm^{-1}. This may, however, be a composite with the NH_2^+ scissor absorption which occurs at a frequency of 1602 cm^{-1} and which is quite broad.

The carboxylate antisymmetric stretching vibration frequencies for the metal complexes are:

Bis-(N-(p-hydroxyphenyl)glycino)-copper (II), 1592 cm^{-1}
Bis-(N-(p-hydroxyphenyl)glycino)-nickel (II) dihydrate, 1592 cm^{-1}
Bis-(N-(p-hydroxyphenyl)glycino)-cobalt (II) dihydrate, 1585 cm^{-1}
Bis-(N-(p-hydroxyphenyl)glycino)-zinc (II) monohydrate, 1590 cm^{-1}

Although water interaction might affect the spectra of the hydrated complexes in this frequency range, the shift toward a higher frequency in the spectrum of each of the metal complexes gives evidence for a carboxylate group coordinated to a metal ion. The difference in the shift for the various metal complexes is not significant.

The carboxylate symmetric stretching vibration frequency assigned to N-(p-hydroxyphenyl)glycine is 1390-1375 cm^{-1} (broad, split.) The corresponding frequencies assigned to the metal complexes are:

Bis-(N-(p-hydroxyphenyl)glycino)-copper (II), 1373 cm^{-1}
Bis-(N-(p-hydroxyphenyl)glycino)-nickel (II) dihydrate, 1378 cm^{-1}
Bis-(N-(p-hydroxyphenyl)glycino)-cobalt (II) dihydrate, 1378 cm^{-1}
Bis(N-(p-hydroxyphenyl)glycino)-zinc (II) monohydrate, 1390-1388 cm^{-1} (broad)

Because of the broadness of the band in the spectrum of the ligand, no definite relationship can be established for this assignment. It appears, however, that there is no difference in the carboxylate symmetric vibration frequency in the spectra of the metal complexes as compared with that of the ligand.

The carboxylate stretching vibration absorptions in the spectrum of the ligand indicate the zwitterion structure, $HOC_6H_4NH_2^+CH_2COO^-$. The increase in the frequency of this absorption in the spectra of the metal complexes and the analogy with the N-(p-methoxyphenyl)glycine series indicate the common-type transplanar glycine chelate structure shown in Fig. 1 for the corresponding N-(p-methoxyphenyl)glycino complexes. The nickel and cobalt dihydrated structures would be expected to have the water molecules in transoctahedral positions.

The infrared spectral information indicates that both compounds, N-(p-methoxyphenyl)glycine and N-(p-hydroxyphenyl)glycine, form chelate compounds of similar type for the metal ions studied. Because the hydroxy group renders the hydrogen atoms ortho to it in the substituted benzene ring more active than does the methoxy group in its corresponding compounds, N-(p-hydroxyphenyl)glycine would appear to be the more suitable compound for direct formaldehyde condensation and, therefore, for chelate polymer formation. If, however, stability constant determinations should warrant it, the methoxy polymer could be prepared by some other suitable synthesis. Because of possible condensation at the amine function of N-(p-hydroxyphenyl)glycine, it would be well to include in this study a compound, such as N-methyl-N-(p-hydroxyphenyl)glycine, which has ring positions active to formaldehyde condensation, but which is a tertiary amine and therefore incapable of condensation at the nitrogen function.

Model Compound (III): N-Methyl-N-(p-Hydroxyphenyl)Glycine and Its Metal Complexes

The analysis for the compound is in good agreement with that calculated for its empirical formula. The decomposition point determined was 109°C, compared with the 114°C reported [34], but no analysis was given in the prior report [34] and it is not known whether the decomposition point reported was for the anhydrous compound or for the monohydrate.

Because of OH absorption and because of possible water interaction, no interpretation for possible NH^+ stretching vibration absorption could be made in the 3000 cm^{-1} region of the ligand spectrum. In the metal complexes, NH bonds are not involved, and, therefore, the infrared spectra do not provide suitable means for detecting possible nitrogen-to-metal bonding. Graddon [40], based upon a study of the visible spectrum and the instability of the material in solution, proposed that nitrogen-to-metal bonds are not involved in the copper compound of (N-methyl-N-phenyl)glycine. Basolo and Chen [39], as a result of formation constant studies, conclude that dialkyl glycines have low chelating tendencies. They attribute this to steric hindrance about the nitrogen atom. Thus, N-methyl-N-(p-hydroxyphenyl)glycine might be expected to have even less tendency to coordinate at the nitrogen atom.

The carboxylate antisymmetric stretching vibration absorption in the spectrum of the ligand is strong and broad at about 1610 cm^{-1} with a shoulder at 1590 cm^{-1}. This is a lower frequency than those assigned for this absorption to the other ligands. It is probably due to water interference. The carboxylate antisymmetric stretching vibration frequencies for the copper (II) and zinc compounds of N-methyl-N-(p-hydroxyphenyl)glycine are 1604 and 1590 cm^{-1}, respectively. This lack of change may be taken as an indication of salt formation rather than coordination.

The carboxylate symmetric stretching vibration absorption in the ligand is broad (1395-1370 cm^{-1}) and is probably a composite with CH_3 symmetric deformation absorption, which is reported [42] to occur at 1390-1370 cm^{-1}. The assigned frequencies for the carboxylate symmetric stretching vibration absorptions of the copper (II) and zinc compounds of N-methyl-N-(p-hydroxyphenyl)glycine are 1390 and 1392 cm^{-1}, respectively. No interpretation of these data can be made regarding possible carboxylate coordination.

Several attempts were made to isolate the nickel (II) and cobalt (II) compounds of N-methyl-N-(p-hydroxyphenyl)glycine. In each case a very small suspension formed for a very short time, and then the system became a dark-brown or black solution. This behavior also indicates no appreciable chelating tendencies for N-methyl-N-(p-hydroxyphenyl)glycine.

Even though N-methyl-N-(p-hydroxyphenyl)glycine is a suitable compound for formaldeyde condensation, it is not a chelating agent and does not appear to be worthy of additional consideration.

Model Compound (IV): N-(p-hydroxyphenyl)Iminodiacetic Acid and Its Metal Complexes

Because of the strong chelating tendencies of iminodiacetic acid and related compounds, such as EDTA, it was thought worthwhile to investigate the chelating properties of N-(p-hydroxyphenyl)iminodiacetic acid. Also, because this compound is a tertiary amine and incapable of formaldehyde condensation at the nitrogen atom, it was considered to be a possible model compound for a chelating polymer.

An important step in the synthesis of N-(p-hydroxyphenyl)aminodiacetic acid is that it must be first obtained in the form of its sodium salt. It was found that when less than 6 moles of sodium hydroxide were used per mole of p-aminophenol hydrochloride reacting with chloroacetic acid, the monoacetic acid compound precipitated. The acid is isolated by reacting the sodium salt with concentrated hydrochloric acid and then hydrolyzing the hydrochloride formed. Galatis [43] reported the sodium salt as a by-product in the synthesis of N-(p-hydroxyphenyl)glycine. He also described the conversion of the sodium salt to the acid; the decomposition point was about 160°C. The decomposition point of the product reported in this paper is 148°C. The analysis of both materials is in agreement with the empirical formula for the compound. The difference in the decomposition point might be due to different methods of determination or differently defined decomposition points. No indication was given [43] as to how the measurement was made.

Two procedures were followed in making the metal complexes. Procedure (a) involved a ligand-to-metal ion molar ratio of 1:1 at a pH of 5. Procedure (b) involved a ligand-to-metal ion molar ratio of 2:1 at a pH of 5. The product in either case was, as indicated by the analysis, the 1:1 compound.

The analyses for the copper and zinc compounds formed from the 1:1 molar reactant ratio procedure are in good agreement with those expected for the compounds indicated by the formulas.

$Cu(HOC_6H_4N(CH_2COO)_2)$ and $Zn(HOC_6H_4N(CH_2COO)_2) \cdot 2H_2O$. The analyses for the nickel (II) and cobalt (II) compounds formed from similar reaction procedures are lower than expected for $Ni(HOC_6H_4N(CH_2COO)_2) \cdot 2H_2O$ and $Co(HOC_6H_4N(CH_2COO)_2) \cdot 2H_2O$. The low results reported in the analyses are probably due to metal hydroxide impurities.

The analyses of the copper and zinc compounds formed from the 2:1 molar reactant ratio procedure are in good agreement with the indicated compounds. The analyses of the nickel (II) and cobalt (II) compounds formed from similar reaction procedures are higher than expected for the indicated compounds. This might be due to the presence of a small amoun of unreacted ligand or to chain formation.

The spectrum of the ligand showed a peak at 3295 cm^{-1} (weak). This might be due to NH^+ stretching vibration absorption. This peak did not appear in the spectra of the metal complexes. The infrared specta can offer no evidence supporting or contradicting nitrogen-to-metal bond, but once again the steric hindrance about the trisubstituted nitrogen atom most likely prevents such bonding.

The carboxylate antisymmetric stretching vibration frequency of the ligand is 1650 cm^{-1}. This is high compared with the usual assignment and is most likely due to an inductive effect toward the un-ionized carboxyl group in the iminodiacetic acid function.

The carboxylate antisymmetric stretching vibration frequencies for the metal complexes are:

N-(p-hydroxyphenyl)iminodiacetato-copper (II), 1580 cm^{-1}
N-(p-hydroxyphenyl)iminodiacetato-nickel (II) dihydrate, 1610 cm^{-1}
N-(p-hydroxyphenyl)iminodiacetato-cobalt (II) dihydrate, 1585 cm^{-1}
N-(p-hydroxyphenyl)iminodiacetato-zinc (II) dihydrate, 1580 cm^{-1}

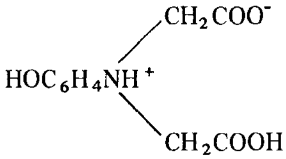
Although these frequencies are lower than the one assigned to this absorption for the spectrum of the ligand, they are in agreement with the values for this assignment in the spectra of other metal complexes, and, therefore, carboxylate-to-metal ion interaction is probable.

The carboxylate symmetric stretching vibration frequency for the ligand is weak and straddling at 1450 cm^{-1}. The carboxylate symmetric stretching vibration frequencies for the metal complexes are:

N-(p-hydroxyphenyl)iminodiacetato-copper (II), 1395 cm^{-1}
N-(p-hydroxyphenyl)iminodiacetato-nickel (II) dihydrate, 1400 cm^{-1}
N-(p-hydroxyphenyl)iminodiacetato-cobalt (II) dihydrate, 1400 cm^{-1}
N-(p-hydroxyphenyl)iminodiacetato-zinc (II) dihydrate, 1380 cm^{-1}

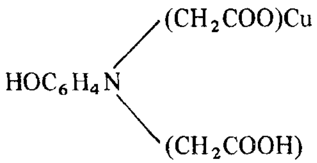
This shift toward lower frequencies is indicative of carboxylate-metal ion interaction.

In the spectrum of the ligand, absorption at 1714 cm^{-1} indicates the presence of an undissociated carboxyl group. This, coupled with the evidence for a carboxylate group in the ligand molecule, suggests a zwitterion of the following structure:

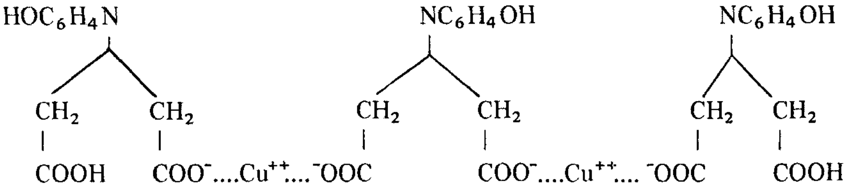


The spectra of the zinc complexes prepared by procedures (a) and (b) were identical and did not show a peak in the 1720 cm^{-1} region. The spectra of the cobalt and nickel complexes prepared by the 1:1 molar reactant ratio procedure did not show this peak, but the spectra of those prepared by the 2:1 molar reactant ratio procedure did show a weak peak at 1720 cm^{-1}. This weak peak at the same frequency as the one in the spectrum of the ligand suggests the possibility of some unreacted ligand, which, as an impurity, would explain the high analysis for these complexes.

The spectra of the copper complexes prepared by either method are identical, and a strong peak appears at about 1735 cm^{-1}. The difference in carboxyl absorption, in addition to the rather consistant analysis of the complexes, suggests an explanation other than unreacted ligand and indicates a possible structure of the type:



Such a structure might be proposed on the basis of copper (II) reduction to Cu(I), or chain formation, such as



but of such length that the extra ligand function beyond the 1:1 ratio does not appreciably affect the analysis.

Graddon [40] proposes for nonnitrogen-coordinated complexes of aryl glycinates an alkanoate-type structure in which both oxygen atoms of the carboxylate group act as coordinators. This proposal applied to the nickel

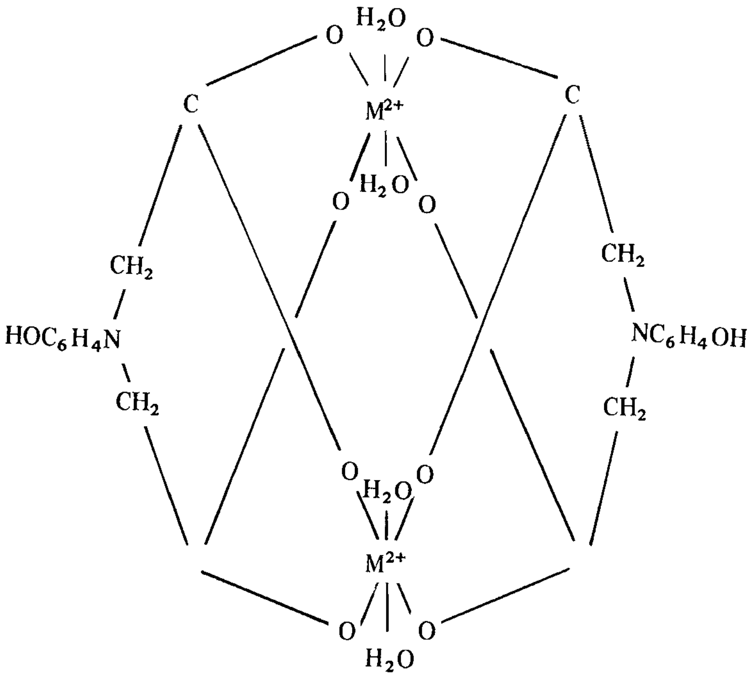


Fig. 2. Structure of complexes of N-(p-hydroxyphenyl)iminodiacetic acid.

(II), cobalt (II), and zinc (II) complexes of N-(p-hydroxyphenyl)iminodiacetic acid implies the structure shown in Fig. 2.

Model Compound (V): N-(p-Hydroxybenzyl)Glycine and Its Metal Complexes

Possible OH absorption and water interaction in the zinc complex make it impossible to draw, from the spectra of the compounds in this series, any conclusions regarding NH stretching vibration absorption and related frequency shifts. However, it might be pointed out that there is in the spectrum of the ligand a profile effect in the 3000-2500 cm^{-1} region, probably due to the NH_2^+ group, which is considerably changed in the spectra of the complexes. It is to be further noted that there are definite peaks at 2680 and 1650 cm^{-1}. An NH_2^+ stretching vibration frequency and an NH_2^+ deformation vibration frequency are reported for these peaks, respectively [44]. These two peaks disappear on chelation. This fact, along with the profile change, indicates some type of nitrogen-to-metal coordination.

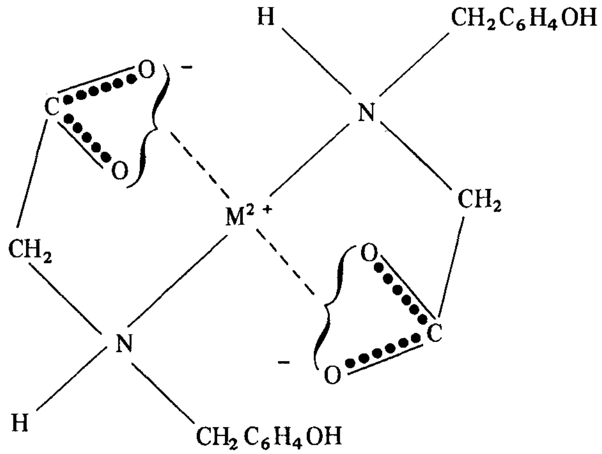


Fig. 3. Structure of complexes of N-(p-hydroxybenzyl)glycine.

The probable carboxylate antisymmetric stretching vibration frequency in the spectrum of N-(p-hydroxybenzyl)glycine is 1581 cm^{-1}.

The carboxylate antisymmetric stretching vibration frequencies for the metal complexes are:

Bis-(N-(p-hydroxybenzyl)glycino)-copper (II), 1615 cm^{-1}
Bis-(N-(p-hydroxybenzyl)glycino)-nickel (II), 1595 cm^{-1}
Bis-(N-(p-hydroxybenzyl)glycino)-cobalt (II), 1585 cm^{-1}
Bis-(N-(p-hydroxybenzyl)glycino)-zinc (II) monohydrate, 1593 cm^{-1}

The shift toward a higher frequency in the spectrum of each metal complex gives evidence for a carboxylate group coordinated to a metal ion.

The carboxylate symmetric stretching vibration frequency assigned to N-(p-hydroxybenzyl)glycine is 1389 cm^{-1}. The corresponding frequencies assigned to the metal complexes are:

Bis-(N-(p-hydroxybenzyl)glycino)-copper (II), 1357 cm^{-1}
Bis-(N-(p-hydroxybenzyl)glycino)-nickel (II), 1363 cm^{-1}
Bis-(N-(p-hydroxybenzyl)glycino)-cobalt (II), 1361 cm^{-1}
Bis-(N-(p-hydroxybenzyl)glycino)-zinc (II) monohydrate, 1367 cm^{-1}

The carboxylate stretching vibration absorptions and the NH_2^+ absorptions in the spectrum of the ligand indicate the zwitterion structure:

$$HOC_6H_4CH_2NH_2^+CH_2COO^-$$

The changes in the spectra of the metal complexes indicate the common type of transplanar glycine chelate structure [42] shown in Fig. 3.

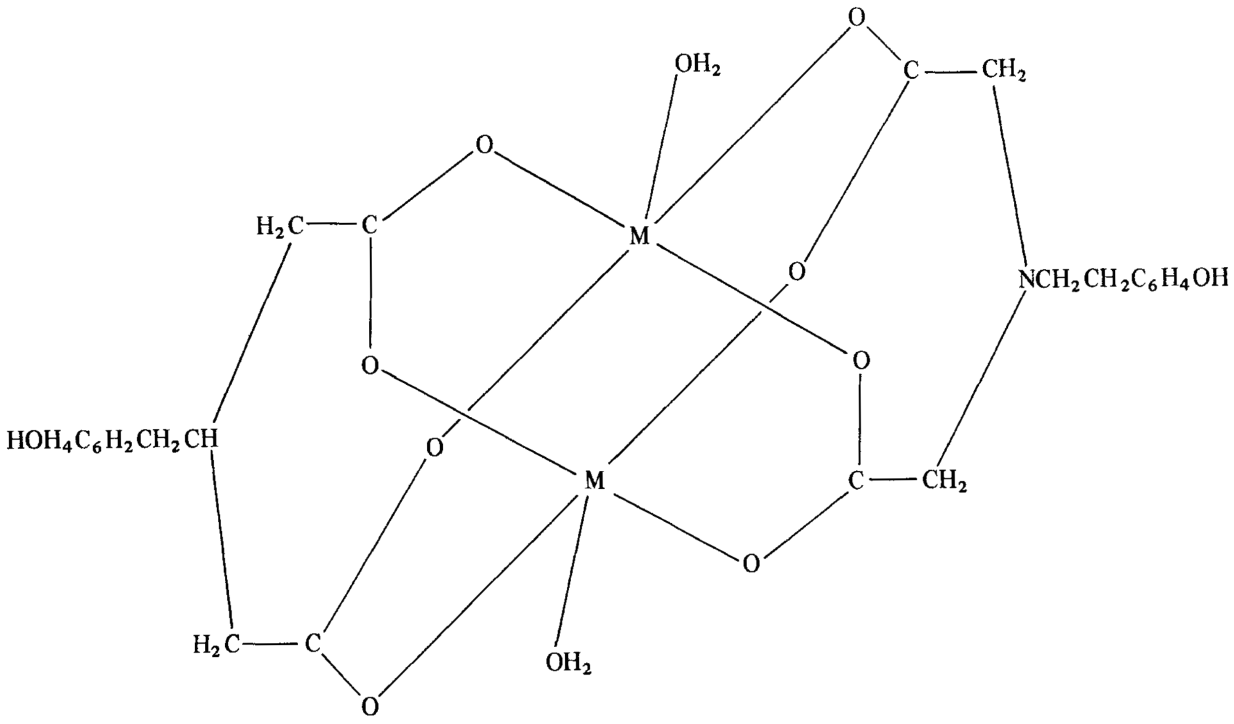


Fig. 4. Structure of complexes of N-(p-hydroxyphenylethyl)iminodiacetic acid.

The separation between carboxylate symmetric and antisymmetric stretching vibration frequencies for the various metal complexes decreases in the following order: Cu(II) > Ni(II) > Zn(II) > Co(II). This order coincides with the order of stabilities for glycine complexes with the above metal (II) ions as determined by Monk [45].

The relative chelating powers of N-(p-hydroxyphenyl)glycine and N-(p-hydroxybenzyl)glycine are not determined by the data studied up to the present time. It should be noted that N-(p-hydroxybenzyl)glycine affords definite measurements of the symmetric and antisymmetric carboxylate stretching vibration frequency shifts, whereas this is not possible with N-(p-hydroxyphenyl)glycine.

Model Compound (VI): N-(p-Hydroxyphenylethyl)Iminodiacetic Acid and Its Metal Complexes

The first step in the synthesis of N-(p-hydroxybenzyl)iminodiacetic acid was to prepare the sodium salt of N-(p-hydroxybenzyl)glycine. This salt was then treated with a solution of sodium chloroacetate. After the system had been refluxed for several hours, two products were isolated. The first product was identified as nitrilotriacetic acid. The second product exhibited all of the physical properties of a Bakelite-type resin. The experiment showed that the chloroacetate ion in all probability attacked the benzyl nitrogen, thus forming a quaternary ammonium compound. The ammonium complex most likely cleaved, giving a resonance-stabilized benzyl carbonium ion and nitrilotriacetic acid. It could then be postulated that the carbonium caused resinification by reacting rapidly with other p-hydroxybenzyl carbonium ion groups. The nitrilotriacetic acid formed in this synthesis was very pure.

Due to the difficulties encountered in the attempted synthesis of N-(p-hydroxybenzyl)iminodiacetic acid, it was decided to prepare N-(p-hydroxyphenylethyl)iminodiacetic acid and to study its chelation properties. The profile of the infrared spectrum of N-(p-hydroxyphenylethyl)iminodiacetic acid showed various peaks and shoulders from 2500 to 3300 cm^{-1}. The NH^+ stretching vibration absorption is expected in this region. On chelation, the profile is changed and peaks are shifted. However, the infrared spectrum cannot be used as evidence either to support or to contradict a nitrogen-to-metal bond since this spectrum does not possess an NH stretching vibration frequency.

The procedure for the preparation of the chelates of N-(p-hydroxyphenylethyl)iminodiacetic acid involved a ligand-to-metal ion molar ratio of 1:1 at pH 6. The product was, as indicated by the analysis, the 1:1

compound. Chelation occurred rapidly with this ligand and neither heating nor prolonged reaction time was necessary.

Graddon [40] proposes for non-nitrogen-coordinated complexes of aryl glycinates an alkanoate-type structure in which both oxygen atoms of the carboxylate group act as coordinators. This proposition, when applied to the metal complexes of N-(p-hydroxyphenylethyl)iminodiacetic acid, implies the structure shown in Fig. 4.

The absorption at 1660 cm^{-1} has been assigned to the carboxylate antisymmetric stretching vibration of the ligand. This is quite high compared with the usual assignment, but a carboxylate antisymmetric stretching vibration frequency at 1650 cm^{-1} was assigned for model compound IV and was attributed to an inductive effect toward the un-ionized carboxyl group in the iminodiacetic acid function.

The carboxylate antisymmetric stretching vibration frequencies of the metal complexes are:

N-(p-hydroxyphenylethyl)iminodiacetato-copper (II) monohydrate,	1585 cm^{-1}
N-(p-hydroxyphenylethyl)iminodiacetato-nickel (II) dihydrate,	1580 cm^{-1}
N-(p-hydroxyphenylethyl)iminodiacetato-cobalt (II) monohydrate,	1585 cm^{-1}
N-(p-hydroxyphenylethyl)iminodiacetato-zinc (II) monohydrate,	1580 cm^{-1}

These frequencies are in agreement with values for this assignment in the spectra of the other metal complexes in this paper, and although this evidence does not definitely establish carboxylate-to-metal ion interaction, it gives probable indication of it. The carboxylate-to-metal ion interaction is established by shifts in the carboxylate symmetric stretching vibration frequencies.

The carboxylate symmetric stretching vibration frequency for the ligand has been assigned as 1410 cm^{-1}. The carboxylate symmetric stretching vibration frequencies for the metal complexes are:

N-(p-hydroxyphenylethyl)iminodiacetato-copper (II) monohydrate,	1385 cm^{-1}
N-(p-hydroxyphenylethyl)iminodiacetato-nickel (II) dihydrate,	1390 cm^{-1}
N-(p-hydroxyphenylethyl)iminodiacetato-cobalt (II) monohydrate,	1398 cm^{-1}
N-(p-hydroxyphenylethyl)iminodiacetato-zinc (II) monohydrate,	1407 cm^{-1}

The shift to the lower frequency indicates carboxylate-to-metal ion interaction.

It has been noted that in complexes of this type [46] the relative separations between symmetric and antisymmetric carboxylate stretching vibration frequencies can be taken to be a measure of relative metal-to-oxygen bond strengths. It has also been found that the order of these bond strengths reflects at least qualitatively the order of stabilities of the complexes formed; thus, the greater the separation between symmetric and antisymmetric carboxylate stretching vibration frequencies, the more stable is the complex.

If one assumes the same correlations valid in this study, then the carboxylate stretching vibration frequency separations indicate an order of stability Cu(II) > Ni(II) > Co(II) > Zn(II) for the complexes of the ligand studied.

Thus, the relative chelating powers of N-(p-hydroxyphenyl)iminodiacetic acid and N-(p-hydroxyphenylethyl)iminodiacetic acid cannot be thoroughly compared by this technique. Again, however, it should be noted that N-(p-hydroxyphenyl)iminoacetic acid gives no order of shifts, as does N-(p-hydroxyphenylethyl)iminodiacetic acid, due to its weak and straddling carboxylate symmetric stretching vibration frequency at 1450 cm^{-1}.

The comparison, however, can be made that the N-(p-hydroxyphenylethyl)iminodiacetic acid chelates more rapidly than N-(p-hydroxyphenyl)-iminodiacetic acid.

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