Contribution from the Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 160, Japan

Raman Spectra of Copper(II)-Histamine (1:2) and Nickel(II)-Histamine (1:2) Aqueous Solutions

MASAO ITABASHI, KAZUO SHOJI, and KOICHI ITOH*

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The pH dependence of Raman spectra was analyzed for Cu(II)-histamine (1:2) and Ni(II)-histamine (1:2) aqueous solutions. The spectra clearly indicate two types of coordination of the imidazolyl groups in these systems, i.e., the coordination through the N(3) atom and that through the N(1) atom. On coordination through the N(3) atom, the Raman band due to one of the imidazole ring vibrations is observed at 1592 cm^{-1} for the Cu(II)-histamine solutions and at 1580 cm^{-1} for the Ni(II)-histamine solutions. On the other hand, on coordination through the N(1) atom, the Cu(II)- and Ni(II)-histamine solutions give the corresponding Raman bands at 1608 and 1600 cm^{-1}, respectively. The existence of the protonated species such as CuA_2H^{3+}, $CuAH^{3+}$, NiA_3H^{3+}, NiA_2H^{3+}, and $NiAH^{3+}$ is strongly suggested for the acidic solutions of these systems, the $CuAH^{3+}$ and $NiAH^{3+}$ species being dominant below the pH values of 3.3 and 4.8, respectively. It was concluded that the protonated ligand in these species is coordinated to the central metal ions through the N(1) atom with the NH_3^+ form of the amino group.

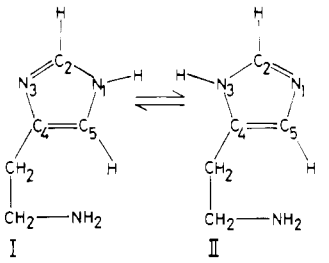
Introduction

The imidazolyl groups of histidine residues are of considerable interest in their role as ligands for transition-metal ions in metalloproteins.[1,2] In the past few decades there have been a number of studies on the interaction mechanism between metal ions and the imidazolyl groups.[3-5] In the previous papers[6,7] we reported the Raman spectra of hexakis(4-methylimidazole)cobalt(II), bis(L-histidinato)zinc(II) dihydrate, and bis(L-histidinato)nickel(II) hydrate in the solid state and those of Cu(II)-L-histidine (1:2) complexes in aqueous solutions. From the analysis of the spectra we concluded that Raman spectroscopy can be used successfully to elucidate the coordination sites of the imidazolyl group to the central metal ions. In this paper we analyze the pH dependence of the Raman spectra of Cu(II)-histamine (1:2) and Ni(II)-histamine (1:2) aqueous solutions.

The complex-forming properties of histamine molecules with transition metals have also been studied by many authors.[8,12] The pH-titration studies give information about the pH-dependent distribution of ionic species formed in the above systems. There are, however, some discrepancies concerning the proposed ionic species. Some of the authors[8,11] assumed only CuA^{2+} and CuA_2^{2+} for the Cu(II)-histamine aqueous solutions while others[9,10] suggested a binuclear diolated complex, $Cu_2A_2(OH)_2$, as the major species in neutral and alkaline solutions of Cu(II) and histamine (1:1). In addition to these ionic species, Gergely and Sóvágó[12] proposed also a protonated species CuA_2H^{3+} for the acidic solutions of Cu(II) and histamine with the metal to ligand ratio larger than 1:2.

The coordination structure of each ionic species in the Cu(II)-histamine system has been studied by using NMR spectroscopy.[13-15] This method, however, is confined to the system with the ligand to metal ion ratio greater than 10^3 because the long electron spin relaxation time of the Cu(II) ion causes line broadening of ligand resonances too large to permit their observation at stoichiometric concentration ratios.[2] As shown in Scheme I, there are two coordination sites in the imidazolyl group, i.e., the N(1) and the N(3) atoms. In the presence of increasing amounts of Cu(II) the resonances of the protons on the C(2) and C(5) atoms (Scheme I) show the same extent of line broadening.[13-15] Therefore, we cannot specify the coordination site from NMR spectra.

Scheme I



The ESR spectra of the Cu(II)-histamine system were also measured by Gergely and Sóvágó.[12] With regards to the coordination structure of the species CuA_2^{2+}, they suggested only the participation of the imidazole nitrogen atom in the coordination on the basis of the superhyperfine splitting from the ^{14}N atom.

We obtained information not only about the species distribution in acidic and neutral solutions of the Cu(II)-histamine and Ni(II)-histamine complexes but also about the coordination structure of the species. Detailed discussions are presented later in the text.

Experimental Section

Materials. Histamine dihydrochloride was obtained from Eastman Kodak Co. and purified by recrystallization from an ethanol-water mixture. $CuCl_2 \cdot H_2O$ and $NiCl_2 \cdot 6H_2O$ of a reagent grade were purchased from Kanto Chemical Co. and used without further purification.

pH Measurements. A TOA Electronics Model HM-6A pH meter with a semimicro combination electrode was used. The pH meter was standardized with monopotassium phosphate-disodium phosphate buffer, pH 6.86 at 25 °C, and potassium hydrogen phthalate-sodium hydroxide buffer, pH 4.01 at 25 °C. Carbonate-free sodium hydroxide (1-5 N) was used to adjust the pHs of the sample solutions. No buffer solution was used for adjusting the pH values.

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Measurements of Raman Spectra. The measurements of Raman spectra were performed on the solutions of histamine (0.4 M) and those containing histamine (0.4 M) and copper(II) (0.2 M) or nickel(II) ion (0.2 M) at room temperature. All the spectra were recorded with a JEOL 400D Raman spectrophotometer equipped with a Spectra-Physics Model 164 Ar ion laser. The spectral slit width was about 7 cm^{-1}. Peak frequencies were calibrated with the spectrum of indene and are believed to be accurate to ± 1 cm^{-1} for well-resolved bands. A spinning cell was used for the measurements of the Raman spectra of the Cu(II)–histamine and Ni(II)–histamine solutions. No sample decomposition was observed after several hours of laser irradiation.

Results and Discussion

A histamine molecule is potentially a bidentate ligand in aqueous solution. As the pH of the solution increases, the imidazole nitrogen (pK_a = 6.1) and the amino nitrogen (pK_a = 9.9) become available for the coordination to metal ions.[16] The neutral imidazolyl group of histamine, as well as of histidine, exists in a tautomeric equilibrium between the N(1)-protonated form and the N(3)-protonated one (Scheme I). Either one of the unprotonated imidazole nitrogens of these tautomers can participate in the coordination to metal ions.

Species Distribution of the Cu(II)–Histamine (1:2) System. As discussed in the preceding section, the pH-titration studies have not given any consistent conclusions about the species distribution in the Cu(II)–histamine (1:2) system. Therefore, to analyze the Raman spectra of Cu(II)–histamine (1:2) aqueous solutions, we used the following most plausible assumptions based on the data given about the distribution. (i) CuA^{2+}, CuA_2^{2+}, $CuAH^{3+}$, and CuA_2H^{3+} are the only species present in significant quantities over the pH region investigated (2.5–10.5).[12,17] (ii) In the pH region from 7 to 10, the species CuA_2^{2+} exists exclusively.[17] (iii) The CuA^{2+} species becomes dominant near pH 5.[12] (iv) When the pH is below 4, the histamine ligands coordinated to the Cu(II) ion exist as the protonated species, CuA_2H^{3+} and $CuAH^{3+}$.

Raman Spectra of Histamine and Cu(II)–Histamine (1:2) Complexes in H_2O. Figure 1 shows the Raman spectra of histamine in H_2O at pH 11.85 (A), 8.52 (B), and 4.30 (C). From the pK_a's of the imidazolyl and amino groups of histamine, it is clear that these groups of the sample that gives the spectrum in Figure 1A are in the neutral form and that the imidazolyl and amino groups in the sample of Figure 1B are in the neutral and cationic forms, respectively. We have already made a detailed normal-coordinate treatment on the ring vibrations of the imidazolyl group.[18] On the basis of this result, we can assign the Raman bands at 1574, 1278, and 990 cm^{-1} in Figure 1B to the ring vibrations of the neutral imidazolyl group. The C=C stretching and C—H in-plane bending vibrations mainly contribute to the 1574- and 990-cm^{-1} bands, respectively. The 1278-cm^{-1} band is due to the ring breathing mode. The Raman bands at 1634, 1269, and 994 cm^{-1} in Figure 1C can be assigned to the corresponding modes of the protonated imidazolyl group. We reported also that the tautomeric equilibrium of the neutral imidazolyl group gives rise to doublet bands for these vibrational modes of 4-methylimidazole[6] and histidine.[7] In the case of histidine, the 1570-, 1285-, and 988-cm^{-1} components of the imidazole ring vibrations were ascribed to the tautomer I (the N(1)-protonated form, cf. Scheme I) and the 1585-, 1262-, and 1004-cm^{-1} components to the tautomer II (the N(3)-protonated form). From the same reasoning as that given for assigning the Raman spectra of 4-methylimidazole and histidine, the 1574-, 1278-, and 990-cm^{-1} bands in Figure 1B are ascribed to the tautomer I and the shoulder around 1590 cm^{-1}

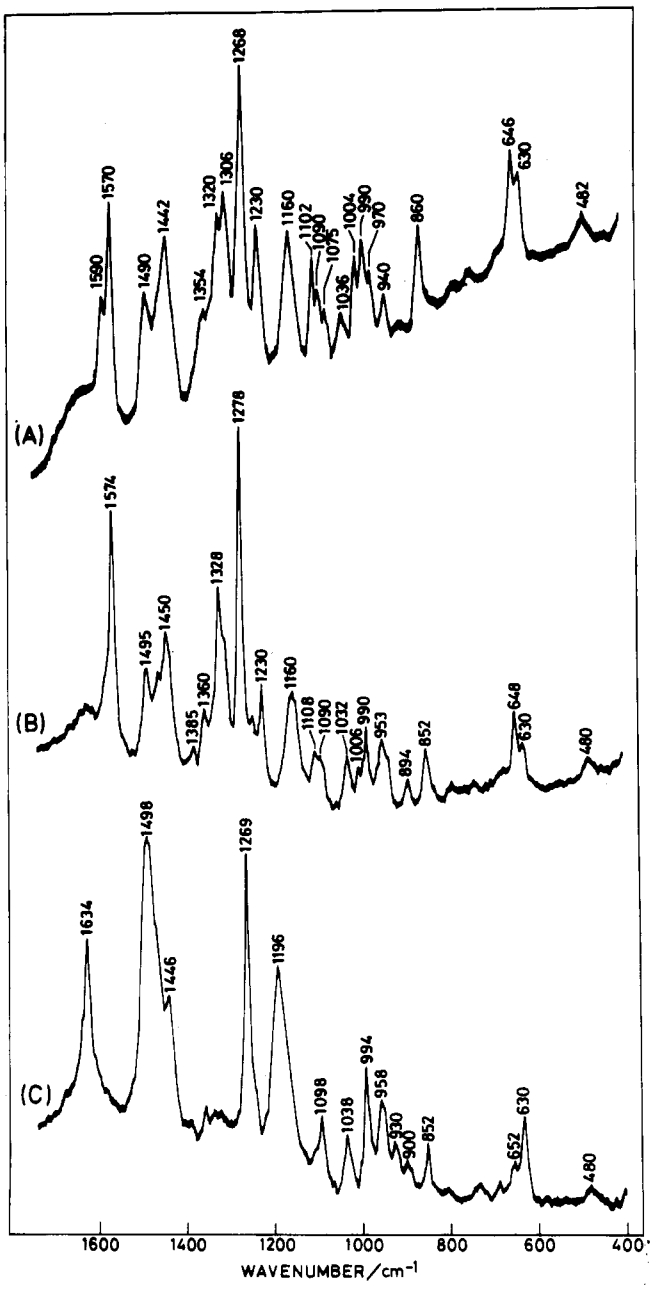

Figure 1. Raman spectra of histamine in aqueous solutions (ca. 10 wt %) at room temperature at pH (A) 11.85, (B) 8.52, and (C) 4.30, with excitation at 488.0 nm. Conditions: laser power (p), 300 mW; slit width (σ), 230 μm; time constant (τ), 3.2 s; scan speed (s), 0.42 cm^{-1}/s.

and the 1006-cm^{-1} band in Figure 1B to the tautomer II. From a detailed pH-titration study Ganellin[19] reported that the existence ratio of the tautomer I to II is about 8:2, which is consistent with the above mentioned result. In Figure 1A, the Raman bands ascribable to the tautomer II (the 1590- and 1004-cm^{-1} bands) increase their intensities, indicating that the existence ratio (II:I) increases on the deprotonation of the amino group from the NH_3^+ form to the NH_2 one. Similar results are observed also for aqueous histidine solutions.[18,20] Unlike the Raman spectrum of histidine, however, the spectrum in Figure 1A does not show any doublet in the region of the breathing vibration. The prominent bands at 1570 and 990 cm^{-1} in Figure 1A tell that the tautomer I is still dominant

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at pH 11.85, and the 1268-cm^{-1} band in Figure 1A is assigned to the breathing vibration of the imidazolyl group with the tautomeric form I. Therefore, this vibrational mode depends on whether the amino group has the NH_3^+ form or the NH_2 form. Presumably in Figure 1A the tautomer II of histamine gives the breathing mode at a frequency close to the one observed for tautomer I.

Figure 2 shows Raman spectra of the copper(II)–histamine (1:2) aqueous solutions with various pH values. When the pH value is raised higher than 10.5, precipitation immediately occurred due to the formation of hydrolyzed species. This prevented us from measuring Raman spectra of the copper(II)–histamine aqueous solutions at higher pH values.

The Raman spectrum at pH 10.36 (Figure 2A) is quite similar to that observed at pH 7.24 (Figure 2B). From the absorption spectrum[21] and the pH-titration data[17] it is known that almost 100% of the Cu(II) ion exists as CuA_2^{2+} at these pH values. In general, the Cu(II) ion prefers a square-planar or a grossly distorted octahedral coordination geometry.[22] According to the X-ray analysis of $Cu^{II}(histamino)_2(ClO_4)_2$,[23] the Cu(II) ion is surrounded by an elongated octahedron, four nitrogen donors making a coordination plane with two imidazole N(3) atoms in the trans position and two perchlorates in the axial sites. Therefore, we can expect that in the species CuA_2^{2+} in aqueous solutions the imidazole N(3) and the amino nitrogen atoms form a six-membered chelate ring with the Cu(II) ion. The bands observed at 1592 and 1277 cm^{-1} in Figure 2B can be assigned to the imidazole ring vibrations of the ligand coordinated to the Cu(II) ion through the N(3) and amino nitrogens. On coordination the imidazole ring vibrations shift to higher frequency sides by 22 and 9 cm^{-1}, respectively. (As shown in Figure 1A, the free histamine ligand gives these modes at 1570 and 1268 cm^{-1}.) These shifts are due to the increase in the bond order of the imidazole ring, which can probably be ascribed to the formation of π bonds between the d orbitals of the metal ion and the π orbitals of this aromatic ring.[24]

A strong and sharp band observed at 420 cm^{-1} in Figure 2A,B can be assigned to one of the Cu(II)–ligand modes because a free histamine molecule with a neutral imidazolyl group does not show any band in this region (Figure 1A,B). This band moves down to 402 cm^{-1} in D_2O, suggesting that its vibrational mode is the Cu–N symmetric stretching of the amino groups in the trans position. The corresponding band is observed at 448 cm^{-1} for the Cu(II)–L-histidine complexes.[7] It is of interest that the ratio of the intensity of the 420-cm^{-1} band to those of the other ligand modes (Figure 2A,B) is remarkably larger than that of the corresponding mode observed for the Cu(II)–L-histidine (1:2) system.[7] The absorption spectrum of the Cu(II)–L-histidine (1:2) system shows a d–d transition at 640 nm near pH 7 while that of the Cu(II)–histamine (1:2) system exhibits the transition at 601 nm.[21] This result suggests that a preresonance effect contributes to the intensity difference mentioned above. In order to confirm the preresonance effect, however, it is necessary to take the Raman spectra by excitation in the 600-nm region. This is now in progress in our laboratory and will be published elsewhere.

As has been discussed already, the dominant species near pH 5 is CuA^{2+}. The Raman spectrum of this species especially in the region of ligand vibrations is considered to be similar to that of CuA_2^{2+}. This presumption is confirmed by the spectrum observed at pH 4.55, which is almost identical with the one shown in Figure 2B except that the former spectrum gives rise to a band at 1634 cm^{-1} and shoulder bands near 1490 and 1190 cm^{-1}. These bands can be ascribed to the free protonated imidazolyl group (see Figure 1C).

As the pH value is reduced further (Figure 2C,D), the intensity of the 1592-cm^{-1} band decreases while the intensity of the 1634-cm^{-1} band increases. In addition, a new band

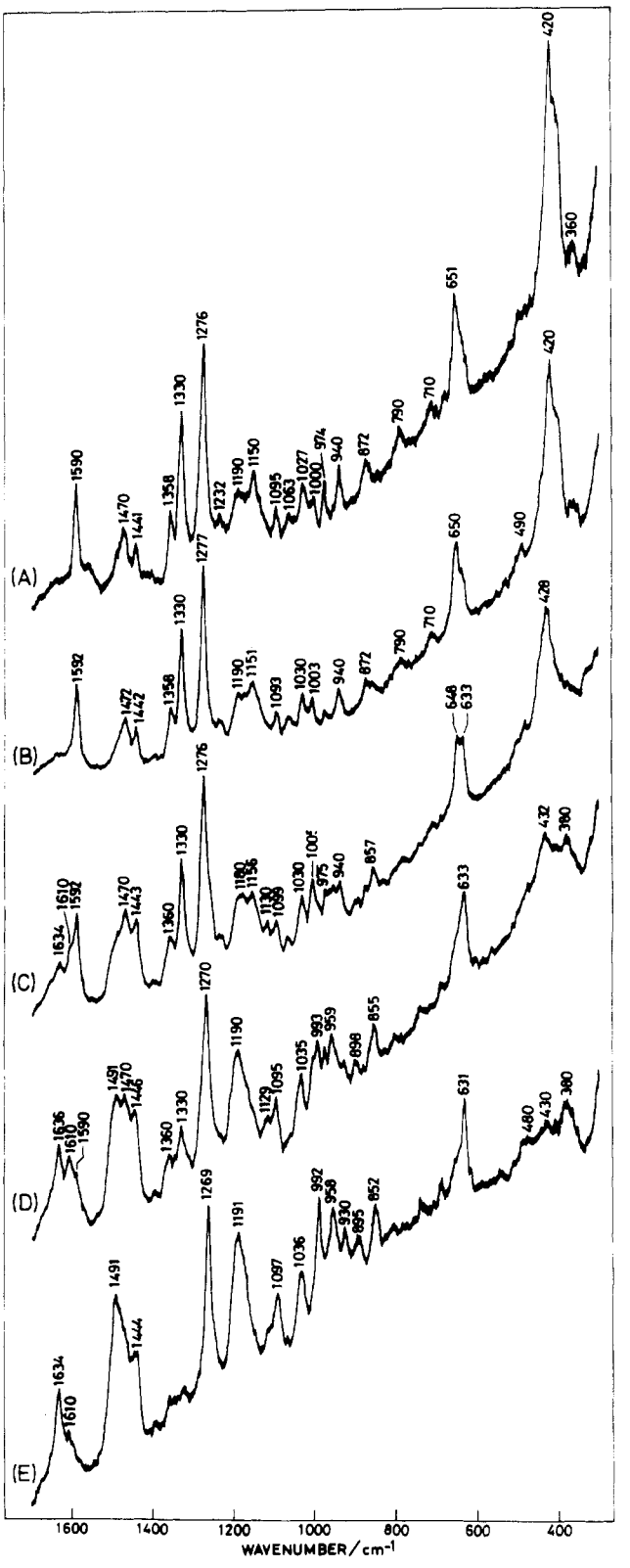

Figure 2. Raman spectra of the Cu(II)–histamine (1:2) system in aqueous solutions (0.2 M) at room temperature at pH (A) 10.36, (B) 7.24, (C) 4.55, (D) 3.44, and (E) 2.50, with excitation at 488.0 nm. Conditions: p, 400 mW; σ, 280 μm; τ, 2.0 s; s, 0.84 cm^{-1}/s.

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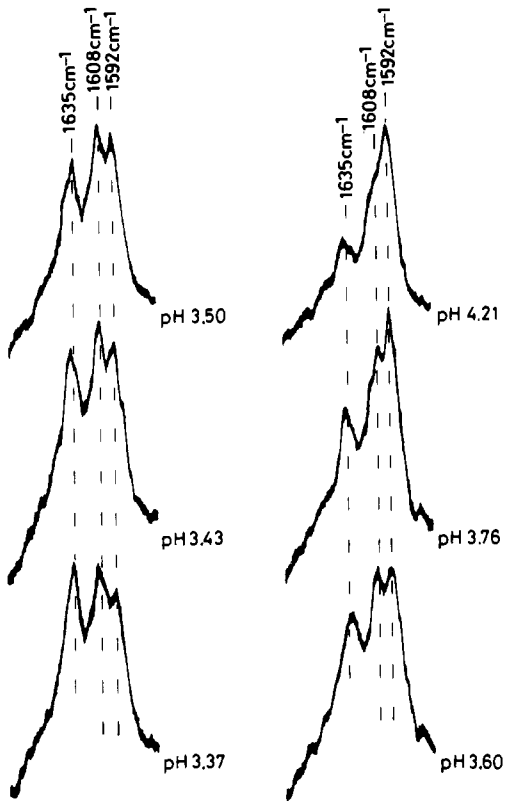

Figure 3. pH dependence of Raman spectra of Cu(II)-histamine (1:2) aqueous solutions (0.2 M) in the 1700–1550-cm^{-1} region, with excitation at 488.0 nm. Conditions: p, 500 mW; σ, 300 μm; τ, 4.0 s; s, 0.42 cm^{-1}/s.

appears at 1610 cm^{-1} (Figure 2C) and gains considerable intensity at pH 3.44 (Figure 2D). Detailed pH-titration measurements of Raman spectra were performed in the pH region from 4.21 to 3.37. The result is summarized in Figure 3. The 1608-cm^{-1} band in Figure 3 can be observed neither for the histamine solutions (Figure 1) nor for the basic and acidic Cu(II)–histamine solutions (Figure 2A,E). This result indicates that the 1608-cm^{-1} band cannot be assigned to one of the deformation vibrations of the NH_3^+ and NH_2 groups (both in the free and in the bound states) of the ligand. As Figure 1A shows, the free histamine molecule with the tautomeric form II gives rise to the Raman band at 1590 cm^{-1}. On coordination of this tautomer to the Cu(II) ion (the N(1) coordination), this band is expected to be observed near 1610 cm^{-1} if the frequency shift due to the N(1) coordination is similar to the shift due to the N(3) coordination ($\Delta\nu$ = 22 cm^{-1}). Therefore, we assigned the 1610-cm^{-1} band in Figure 2C,D and the 1608-cm^{-1} bands in Figure 3 to the ring vibration of the imidazolyl group coordinated to the Cu(II) ion through the N(1) atom. It is sterically impossible for a histamine molecule to make a chelate ring with the Cu(II) ion through the N(1) atom and the amino nitrogen. This means that the ligand coordinated through its imidazole N(1) atom has the free NH_3^+ form. Gergely and Sóvágó[12] assumed only the protonated species CuA_2H^{3+} in the acidic solutions of the Cu(II)–histamine (1:2) system to explain the pH-titration and calorimetric data. They concluded that in this species one histamine ligand forms a six-membered chelate ring with the Cu(II) ion and the other coordinates to the ion through the amino nitrogen with the unbound protonated imidazolyl group. The coordination structure of the latter ligand is not compatible with the result obtained from the Raman spectra. The 1608- and 1592-cm^{-1} bands for CuA_2H^{3+} have the same intensity provided that the Raman scattering tensors of these bands are equal to each other. Figure 3 shows that, as the pH value is

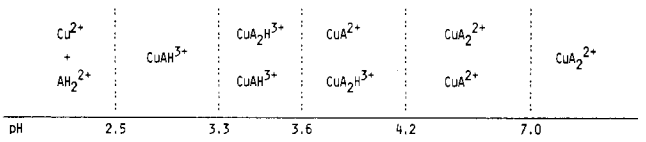

Figure 4. Schematic representation of pH-dependent species distribution in the Cu(II)–histamine (1:2) system.

descreased to 3.37, the intensity of the 1608-cm^{-1} band becomes much stronger than that of the 1592-cm^{-1} band. This result strongly suggests the existence of the species $CuAH^{3+}$ in this pH region because this species gives only the scattering band at 1608 cm^{-1}. As Figure 2D shows, the sample with pH 3.44 gives rise to the Raman bands at 1446, 1129, and 898 cm^{-1}, which are observed only near this pH region and are considered to be characteristic of the N(1)-coordinated species.

The spectrum observed at pH 2.50 (Figure 2E) shows prominent bands at 1634, 1491, 1269, 1191, 992, and 631 cm^{-1} and is quite similar to that of the free ligand containing a protonated imidazolyl group (Figure 1C). The Raman spectrum indicates that no copper(II)–histamine complex is formed around pH 2.5, which is consistent with earlier pH-titration studies.[12,25]

Figure 4 summarizes the pH dependence of the ionic species distribution, which is deduced from the Raman spectra.

Raman Spectra of Ni(II)–Histamine (1:2) Complexes in H_2O. For the Ni(II)–histamine systems, the species NiA^{2+}, NiA_2^{2+}, and NiA_3^{2+} have been considered as major species in the 1:2 solutions.[12,17] In the acidic solutions, a protonated species $NiAH^{3+}$ was also considered to be involved in appreciable amount.[12]

There is a marked tendency for a Ni(II) ion to prefer an octahedral arrangement with ligands containing nitrogen donor atoms (i.e., NH_3, en, or NCS^-).[26] So it is reasonable to expect that the species NiA_3^{2+} has an octahedral coordination geometry.

Figure 5 shows the Raman spectra of Ni(II)–histamine (1:2) aqueous solutions measured at various pH values.

The spectrum observed at pH 8.82 (Figure 5A), where the species NiA_3^{2+} is predominant, shows Raman bands at 1580, 1356, 1326, 1277, 1224, 1014, and 934 cm^{-1}. These bands are from the neutral histamine ligand, which is bound to the Ni(II) ion through the imidazole N(3) atom and the amino nitrogen. The 1580-, 1277-, and 1014-cm^{-1} bands can be assigned to the ring vibrations of the imidazolyl group.

The band at 390 cm^{-1} in Figure 5A can be ascribed to the Ni(II)–N stretching mode of the bound amino group because the neutral free histamine molecule does not give any Raman band near 390 cm^{-1}. As we have already discussed, the corresponding mode is observed at 420 cm^{-1} for the Cu(II)–histamine system. These results reflect the difference in coordination geometries and coordination strength between the Cu(II)–histamine and Ni(II)–histamine systems.

At pH 6.3 (Figure 5B), new bands appear at 1600, 1365, 1258, 1112, 1005, and 950 cm^{-1}, while the bands observed at 1580, 1356, 1326, 1277, 1224, 1014, and 934 cm^{-1} in Figure 5A decrease in intensity. The intensities of the former set of Raman bands continue to increase with the further reduction of the pH values (Figure 5C,D). On the other hand, the latter set of bands almost disappears at pH 4.80 (Figure 5D). The detailed pH dependence of the Raman spectra in the region from 1700 to 1550 cm^{-1} is shown in Figure 6. The 1600-cm^{-1} band observed in the pH region 6.30–3.70 cannot be observed for the aqueous histamine solutions at any pH values (Figure 1) and for the Ni(II)–histamine (1:2) solutions at pH values

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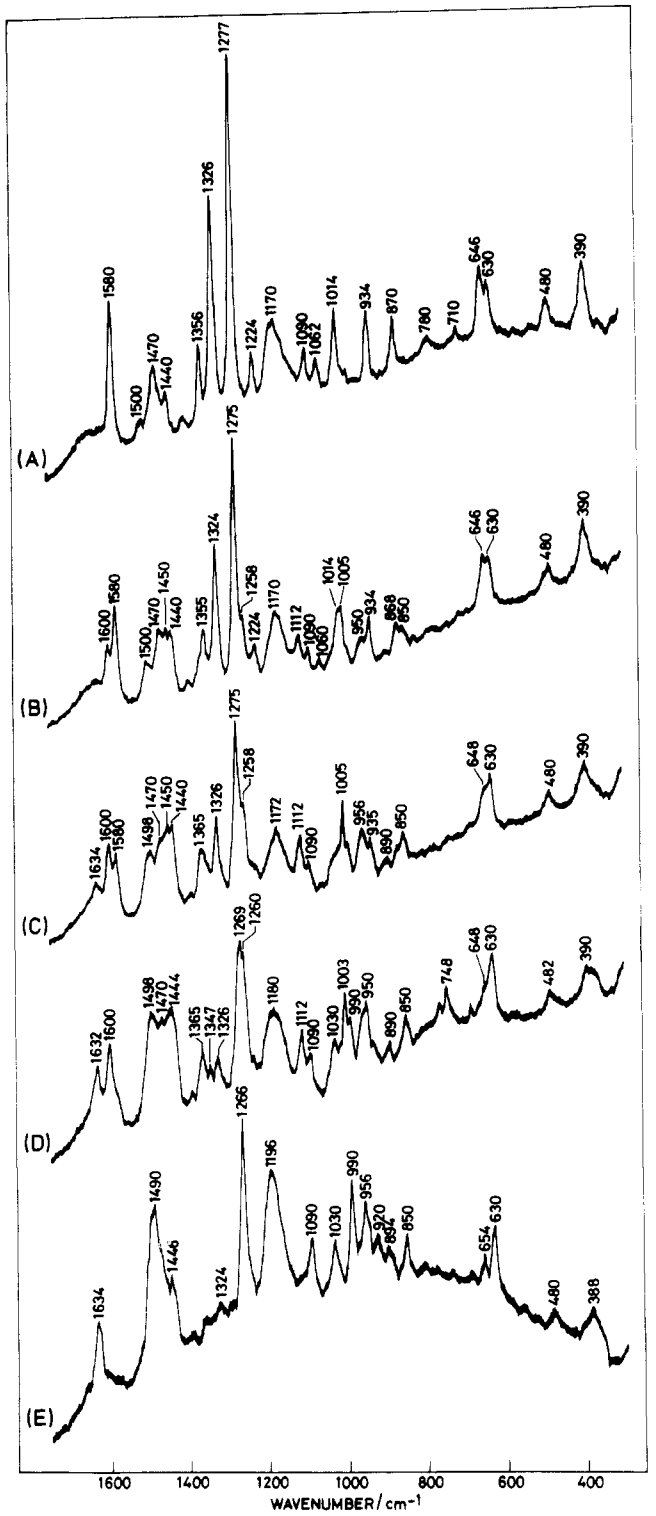


Figure 5. Raman spectra of Ni(II)–histamine (1:2) aqueous solutions (0.2 M) at room temperature at pH (A) 8.82, (B) 6.30, (C) 5.50, (D) 4.80, and (E) 2.30, with excitation at 488.0 nm. Conditions: p, 300 mW; σ, 270 μm; τ, 2.0 s; s, 0.84 cm^{-1}/s.

larger than 7 and smaller than 3 (Figure 5A,E). Therefore, from the same reasoning given to the assignment of the Raman band observed at 1608 cm^{-1} in Figure 3, the 1600-cm^{-1} band can be assigned to one of the ring vibrations of the imidazolyl group coordinated to the Ni(II) ion through the N(1) atom. The frequency shift of this mode due to the N(1) coordination ($\Delta\nu$ = 10 cm^{-1}) is identical with the one observed for the N(3) coordination ($\Delta\nu$ = 10 cm^{-1}). These shifts are considerably smaller than those for the Cu(II)–histamine (1:2) system. (The shift due to the N(3) coordination is 20 cm^{-1} while the

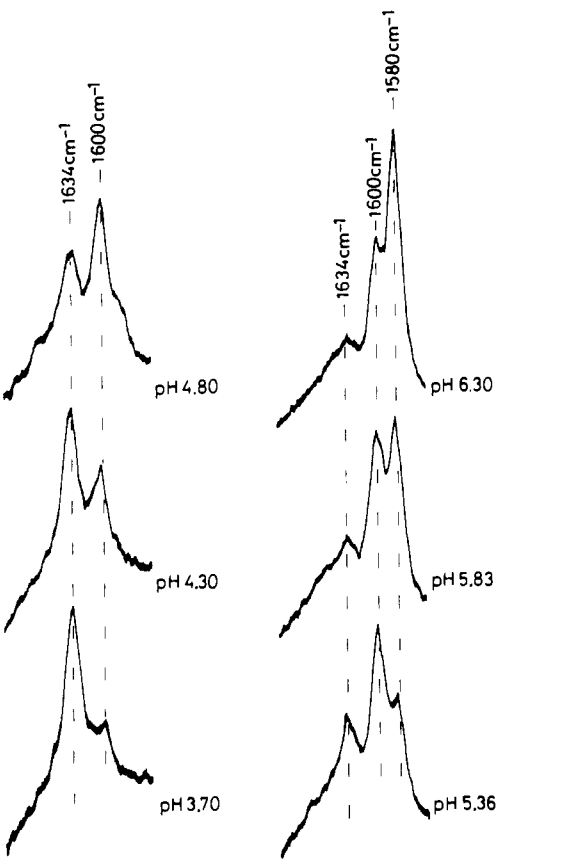


Figure 6. pH dependence of Raman spectra of Ni(II)–histamine (1:2) aqueous solutions (0.2 M) in the 1700–1550-cm^{-1} region, with excitation at 488.0 nm. Conditions: τ, 4.0 s; s, 0.42 cm^{-1}/s; other conditions as in Figure 5.

shift due to the N(1) coordination is 18 cm^{-1}.) Presumably the difference in the frequency shift between the Cu(II)–histamine system and the Ni(II)–histamine system is ascribed to the difference in the coordination geometry and/or strength. The 1365-, 1258-, 1112-, 1005-, and 950-cm^{-1} bands, which show the same pH dependence as the 1600-cm^{-1} band, are also from the ligand bound to the Ni(II) ion via the N(1) atom. The amino group of this ligand cannot form a chelate ring with the Ni(II) ion because of steric reasons and exists in the free and NH_3^+ state. The set of Raman bands mentioned above are then ascribed to the ionic species such as NiA_3H^{3+}, NiA_2H^{3+}, and $NiAH^{3+}$. (Species with a positive charge number larger than 3 are also possible. Their contribution, however, is almost negligible because of their larger electrostatic energy.) Although the relative abundances of these species cannot be determined only from the Raman spectra, it is clear, from Figure 6, that, in the pH region (6.30–5.36) where both the 1600- and the 1580-cm^{-1} bands are observed, the three species are possible candidates for the protonated species while, in the pH region (4.80–3.70) where the 1600-cm^{-1} band is solely observed, the protonated species $NiAH^{3+}$ is only possible.

At pH 2.30 (Figure 5E) the Ni(II)–histamine solution gives Raman bands at 1634, 1490, 1266, 1196, and 990 cm^{-1}, all of which are from the histamine dication. Therefore, any Ni(II)–histamine complex cannot be formed in this acidic solution.

Conclusions

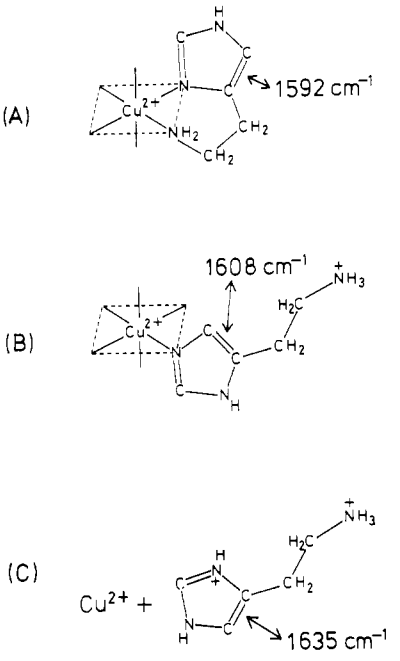
The frequencies and tentative assignments of the Raman bands observed for histamine, Cu(II)–histamine (1:2), and Ni(II)–histamine (1:2) aqueous solutions are listed in Table I. It is obvious from this table that Raman spectra provide us with more direct information about the coordination

Table I. Observed Raman Frequencies (cm^{-1}) of Histamine and Cu(II)- and Ni(II)-Histamine (1:2) Systems[a]

histamine monomer			Cu(II) system		Ni(II) system		
A, pH 11.85	AH^+, pH 8.52	AH_2^{2+}, pH 4.30	CuA_2^{2+}, pH 7.24	$CuAH^{3+}$, pH 3.44	NiA_3^{2+}, pH 8.82	$NiAH^{3+}$, pH 4.80	assignments
1590 (sh)[b]		1634 (s)		1610 (m)		1600 (m)	R[d]
1570 (s)[c]	1574 (s)		1592 (s)		1580 (s)		
1490 (m)	1495 (m)	1498 (vs)	1472 (m)		1470 (m)		R[e]
1442 (m)	1450 (m)	1446 (m)	1442 (m)	1446 (m)	1440 (w)	1444 (m)	$\delta(CH_2)$
1354 (sh)			1358 (m)		1356 (m)	1365 (w)	R + $\delta(CH_2)$
1320 (m)	1328 (m)		1330 (s)		1326 (s)	1347 (w)	
1268 (s)	1278 (vs)	1269 (vs)	1277 (vs)	1270 (s)	1277 (vs)	1260 (s)	R (ring breathing)
1230 (m)	1230 (m)		1232 (vw)		1224 (w)		R
1160 (m)	1160 (m)	1196 (s)	1151 (m)		1170 (m)	1180 (m)	R
1102 (m)	1108 (w)			1129 (sh)		1112 (w)	
1090 (sh)	1090 (w)	1098 (w)	1093 (w)	1095 (w)	1090 (w)		R[f]
1036 (w)	1032 (w)	1038 (w)	1030 (w)		1062 (w)		$\nu(C_\alpha\text{-}N)$
1004 (sh)[b]	1006 (sh)[b]		1003 (w)		1014 (m)		R[f]
990 (m)[c]	990 (m)[c]	994 (m)		993 (m)		1003 (m)	
940 (w)	953 (m)	958 (w)	940 (w)		934 (m)	950 (m)	r(CH_2)
	894 (w)			898 (vw)			
860 (m)	852 (w)	852 (w)	872 (w)	855 (w)	870 (m)	850 (w)	ν(C-C)
			790 (w)		780 (vw)	748 (w)	
646 (m)	648 (m)	652 (sh)	650 (s)		646 (sh)	648 (sh)	R[g] + ν(C-C)
630 (sh)	630 (sh)	630 (m)		633 (m)	630 (sh)	630 (m)	
482 (w)	480 (w)	480 (vw)	490 (vw)		480 (w)	482 (w)	
			420 (vw)		390 (m)		$\nu(M\text{-}NH_2)$

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; R, ring vibration of imidazole ring; ν, stretching; δ, bending; r, rocking. [b] Assigned to tautomer II. [c] Assigned to tautomer I. [d] Mainly due to C=C stretching of the imidazole ring. [e] Mainly due to N-H in-plane bending. [f] Mainly due to C-H in-plane bending. [g] Mainly due to ring deformation.

Chart I



structures of the species taken by the Cu(II)–histamine and Ni(II)–histamine systems as compared with any other techniques, e.g., absorption spectroscopy and NMR and ESR spectroscopies. Especially the ring vibrations of the bound imidazolyl groups observed near 1600 and 1270 cm^{-1} and the metal–N stretching vibrations of the bound amino groups can be used to determine the coordination sites of the species.

Chart I summarizes the dependence of the ring vibration near 1600 cm^{-1} on the coordination geometries of the Cu(II)–histamine system. The following conclusions are made.

(i) The species CuA_2^{2+}, which is present almost to the extent of 100% at neutral pH, has a square-planar structure where two amino and two imidazole N(3) atoms are coordinated in trans positions to the central Cu(II) ion.

(ii) As summarized in Figure 4, the protonated species CuA_2H^{3+} and $CuAH^{3+}$ are formed in the pH region from 4.2 to 3.3. The distribution frequency of the latter species is increased with the reduction of the pH value. The Raman spectra clearly indicate that the protonated ligand in $CuAH^{3+}$ and CuA_2H^{3+} coordinates to the central ion through the N(1) atom of the imidazolyl group with the amino group in the free and NH_3^+ form.

(iii) Two sets of Raman bands from the bound imidazolyl groups are observed for the Ni(II)–histamine (1:2) solution in the pH region from 6.30 to 4.80. One set of Raman bands can be ascribed to the group coordinated to the Ni(II) ion through the N(3) atom and the other set to the one coordinated through the N(1) atom.

(iv) From the pH dependence of the relative intensities of the Raman bands observed at 1600 cm^{-1} (due to the N(1)-coordinated form) and at 1580 cm^{-1} (due to the N(3)-coordinated form), it is known that the protonated species NiA_3H^{3+}, NiA_2H^{3+}, and $NiAH^{3+}$ appear near pH 6.30 and the last species becomes dominant below pH 4.80. In these species the protonated ligand is coordinated to the metal ion through the N(1) atom.

Registry No. CuA_2^{2+}, 18346-87-7; NiA_2^{2+}, 82469-50-9; CuA_2H^{3+}, 82469-51-0; $CuAH^{3+}$, 82469-52-1; NiA_3H^{3+}, 82469-53-2; NiA_2H^{3+}, 82469-54-3; $NiAH^{3+}$, 82469-55-4; NiA_3^{2+}, 82469-56-5.