nuclear $^4J_{113CdH^a}$ coupling (Table I).

Experimental Section

Rat liver [^{113}Cd$_7$]–MT2 was prepared as described previously.[14] For the NMR measurements, ca. 0.01 M solutions of the protein in ^{2}H$_2$O containing 0.02 M [^{2}H$_{11}$]Tris/^{2}HCl at p^{2}H 7.0 and 0.05 M KCl were used. The labile protons had been exchanged with deuterium by twice freeze-drying and redissolving the material in ^{2}H$_2$O. The sample was kept under argon.

For the ^{1}H COSY spectrum with ^{113}Cd-filter, 224 scans were collected per t_1 value, with a relaxation delay of 1.6 s, including the acquisition time. The complete eight-step phase cycle of Table II was combined with CYCLOPS,[15] so that the total phase-cycling scheme consisted of 32 steps. For both spectra in Figure 3, the digital resolution before zero-filling was 3.2 Hz along ω_2 and 5.1 Hz along ω_1.

For the ^{1}H COSY spectra with a 2X-filter or a 2X(ω_2)-half-filter, 384 scans were acquired per t_1 value. The relaxation delay was 1.8 s, including the acquisition time. For the 2X(ω_2)-half-filter, a tuned delay of τ = 20 ms (Figure 1B) was used, which corresponds to a J_{HX} value of 12.5 Hz. A 128-step phase cycle was used for both experiments, corresponding to the combination of the complete 32-step phase cycling

scheme of Table III with CYCLOPS.[15] Before zero-filling, the digital resolution was 4.3 Hz along ω_2 and 8.6 Hz along ω_1.

All experiments were recorded with time-proportional phase incrementation (TPPI) of the first pulse[16] on a Bruker AM 360 spectrometer equipped with an ASPECT 3000 computer and modified to allow ^{1}H observation and ^{113}Cd pulsing. The temperature was 25 °C. For all the spectra displayed in Figures 3–5, fourfold zero-filling was applied in both dimensions. Prior to the phase-sensitive Fourier transformation, the time domain data were multipled in both dimensions with sine-bell windows.[20]

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Chemical Reactions of Imidazole with Metallic Silver Studied by the Use of SERS and XPS Techniques

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Abstract: Chemical reactions of imidazole with metallic silver have been studied by surface-enhanced Raman scattering (SERS), infrared (IR), and X-ray photoelectron spectroscopy (XPS) techniques. We found that imidazole can react with metallic silver directly in the presence of oxygen. The product formed is (imidazolato)silver(I), which covers the surface of metal as a monolayer. The reaction scheme and the structural features of the product are discussed.

Imidazole (ImH) is of considerable interest as a ligand in that its presence in many biological systems provides a potential binding site for metal ions. A large amount of work has been published on imidazole and related ligands and the complexing properties of such compounds, both in the solid state and in solution.[1] The unprotonated imidazole usually functions as a ligand in solutions near neutrality via the unshared pair of electrons on nitrogen. Complexes including Ag(ImH)Cl, Cu(ImH)$_4$Cl$_2$, Co(ImH)$_2$Cl$_2$, Ni(ImH)$_2$Cl$_2$, etc., have been studied extensively.[2–6] In sufficiently basic media the conjugate base of imidazole, Im$^-$, is formed and may function as a ligand too. The tendency then is for formation of an "inner" complex of stoichiometry M^{2+} (Im$^-$)$_2$ or M$^+$(Im$^-$) with dipositive metal ions. These materials are usually insoluble and generally are considered to be polymeric in nature. Examples reported include bis(imidazolato)copper(II) and (imidazolato)silver (I).[7–11]

The complexes of Im$^-$ are usually prepared from the metal ion and imidazole in basic solution.[11] In this work we report our finding about the formation of (imidazolato)silver(I) by direct reaction of metallic silver and ImH.

Imidazole and its derivatives are also of interest as corrosion inhibitors for metals and alloys. The molecular structure and anticorrosion mechanism have been studied by many authors but are still not well understood.[12–15] The consensus is that imidazole can react with surface oxides on metal to form a metal–azole coordination film.[16–19] Relatively few reports exist in the literature concerning the direct reaction of imidazole with metallic copper or silver.

The observation on enormously enhanced cross sections (factors up to 10^6) for Raman scattering from molecules adsorbed on metal surface is one of the most important discoveries in the field of surface science in the last few years.[20–22] We have taken advantage of this sensitivity of SERS to study the molecular structure of the imidazole residue on silver colloids, resulting in the discovery

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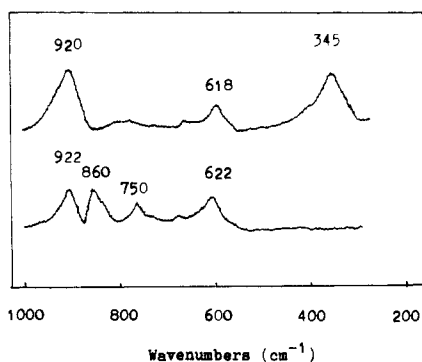
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Figure 1. Raman spectra of imidazole: (A) surface-enhanced Raman scattering of imidazole (0.008 M) on silver colloids, (B) normal Raman spectrum of imidazole (6.25 M).

of a chemisorbed monolayer on silver surface. An IR study confirmed the deprotonation of imidazole in its reaction with silver powder. X-ray photoelectron spectroscopy of the molecular structure of chemisorbed imidazole on a metallic silver disk shows that a monolayer of (imidazolato)silver(I) formed on the surface.

Experimental Section

SERS Study. Imidazole, from the Chinese Chemical Co. (mp 88–90 °C), was dissolved in distilled water. A concentrated solution (6.25 M) was prepared for normal Raman study. Aqueous silver solution were prepared by reducing silver nitrate with sodium borohydride according to the method outlined by Creighton et al.[23] A dilute aqueous solution of imidazole (0.008 M) with silver colloids (2.5 × 10^{-4} M) was prepared for a SERS study. Raman spectra were recorded in the normal way for liquid samples, with a GDM-1000 spectrometer. A backscattering geometry with an angle of incidence near 90° and a monochromator slit width of 1 mm was used. The incident laser excitation was with the 5145-Å line from an argon ion laser, and the incident power was 31.6 mW.

IR Study. A total of 3 g of molecular silver powder prepared by reducing silver salt was immersed in 20 mL of imidazole–ethanol solution (5% in concentration) at 35 °C with vigorous agitation for 15 days. The solution was exposed to the air. After separation, 0.3 g of gray product was obtained. An IR spectrum was obtained by the use of a Nicolet 170 SX spectrometer. The spectrum was recorded from 4000 to 100 cm⁻¹.

XPS Study. A piece of silver disk was etched in 10% HNO_3 to remove silver oxide, repeatedly washed by distilled water, and dried in vacuo. The cleaned silver disk was then immersed in imidazole–ethanol solution (5% in concentration) at room temperature without agitation. This solution was exposed to air for 1 day. After the silver disk was withdrawn, it was washed with ethanol to remove the physisorbed imidazole.

Photoelectron spectra were obtained by means of an ES-300 3-ray spectrometer with Mg $K_{1,2}$ as the exciting source (hv = 1253.6 eV). The C_{1s} line (BE = 285.0) from residual pump-line oil contamination was used as the internal standard for spectral calibration. Possible changes in the compounds under X-ray action were monitored by repeating scans, but no significant changes in the spectra were observed. Measurements of the average of three different values from different samples have been considered accurate to ±0.2 eV. A Du Pont 310 curve resolver was used for peak deconvolution with a Gaussian fit.

Results and Discussion

Figure 1 illustrates the comparison of SERS and normal Raman spectra of imidazole in the 1000–200-cm⁻¹ region. Both spectra show adsorption bands near 920 cm⁻¹, which were assigned to the ring-bending vibration.[24,25] The surface enhancement factor for this band, the ratio of the Raman intensity for a single surface molecule with SERS to the intensity for a single molecule in solution, is estimated to be 2 × 10⁶. It should be kept in mind that more than one mechanism may be responsible for the enhancement and that the observed enhancement factor may result from a combination of several contributions.[26,27] The absence

Table I. Principal IR Absorption Frequencies (cm⁻¹)[a]

imidazole $(C_3N_2H_4)$	reaction product $[Ag(C_3N_2H_3)]$	assgnt
	3130 (m)	CH str
3124–2540 (b, vs)		NH–N str
1543 (m)		NH bend
1448 (s)	1462 (s)	ring str
1328 (m)	1300 (m)	CH bend
1263 (m)	1240 (m)	ring breathing
1148 (m)		NH bend
1055 (vs)	1088 (vs)	CH bend
841 (m)	830 (m)	ring bend
757 (s)	777 (m)	CH out-of-plane bend
658 (s)	663 (s)	torsion
	340 (m)	Ag-N str
141 (m)		lattice vibrn
133 (m)	103 (m)	lattice vibrn

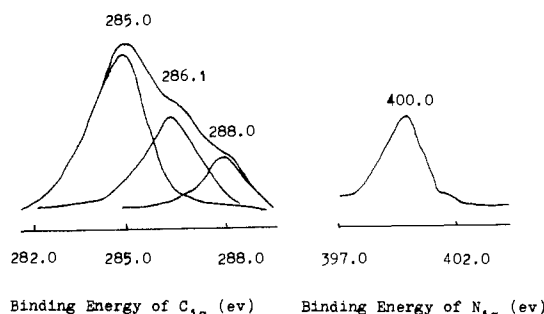[a] Key: s, strong; m, medium; b, broad; v, very; vs, very strong.

Figure 2. XPS spectra of imidazole residue adsorbed on silver surface. Note: The C_{1s} band at 285.0 eV from residual pump-line oil contamination was used as the internal standard for spectral calibration.
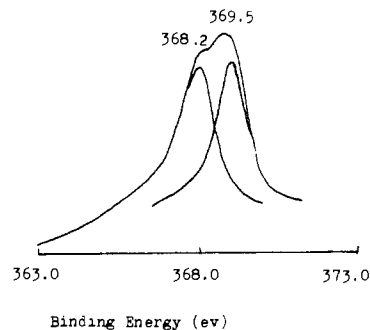

Figure 3. XPS spectrum of Ag_{3d} for imidazole-treated silver.

of the N–H vibration absorption bands at 860 and 750 cm⁻¹ in the SERS spectrum indicates deprotonation of imidazole in the chemisorbed material. A new band at 345 cm⁻¹ appeared in the SERS spectrum. Walter and Cordes calculated and observed the metal–nitrogen stretching and bending vibration absorption in the region 320–380 cm⁻¹ for Cu–N, Ni–N, and Co–N bonds.[28,29] Miles reported that Ag–N stretching shows absorption at 370 cm⁻¹ in the Raman spectrum of $Ag(NH_3)_2NO_3$ aqueous solution.[30] Tian et al.[31] observed the SERS spectrum of NH_3 + NH_4Cl on a silver electrode surface with a Ag–NH_3 stretching vibration absorption at 322 cm⁻¹. We may therefore assign the band at 345 cm⁻¹ in the SERS spectrum to be due to the Ag–N vibration. The differences between SERS and normal Raman spectra of imidazole show the deprotonation and the formation of the Ag–N bond, but the hydrogen vibrations in SERS are generally less

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Table II. Binding Energy Values of Imidazole and Imidazole Residue on Silver

samples	binding energy values, eV	
	C_{1s}	N_{1s}
imidazole	287.2 (2)	402.3 (1)
	285.7 (4)	
	286.5 (5)	400.7 (3)
chemisorbed imidazole	286.1 (4 & 5)	400.0 (1 & 3)
	288.0 (2)	

enhanced than the ring modes. It is necessary to get further evidence for the deprotonation. IR absorption frequencies in the middle- and far-infrared regions are shown in Table I. The disappearance of the N–H stretching bands in the region $3124-2540$ cm^{-1} and the appearance of a new band at 340 cm^{-1} indicate the formation of a Ag–N bond and the deprotonation of a N–H bond. The IR spectral changes strongly support the conclusion from the SERS study.

Figures 2 and 3 show photoelectron spectra of the chemisorbed material on a silver disk. Table II gives the binding energy of C_{1s} and N_{1s} for imidazole and the chemisorbed imidazole moieties. The two nitrogen atoms in the imidazole molecule (N-1, "pyrrole"; N-2, "pyridine") have different electromagnetic surroundings. The XPS spectrum of imidazole is expected to show two binding energy values for N_{1s} and three for C_{1s}.[32] Deprotonation at N-1 results in the formation of anionic imidazole, which is also aromatic. The two nitrogen atoms in imidazole anion are indistinguishable.[33,34] The XPS analysis for the chemisorbed material on silver surface shows only one value of binding energy for N_{1s} and two for C_{1s}, indicating the formation of an imidazole anion on silver surface. The analysis of the Ag$_{3d}$ spectrum in Figure 3 shows two binding energy values: 368.2 and 369.5 eV. The first value coincides with the value of Ag(0) and the second with Ag(1+). The XPS results give evidence for Ag$^+$(C$_3$H$_3$N$_2$)$^-$ formation on the surface of the silver disk. This result coincides with the Raman and IR studies mentioned above.

The XPS measurement gives the binding energy values for Ag$_{3d}$ in both absorbate (369.5 eV) and adsorbent (368.2 eV). Since the mean free paths of the photoemitted electron in the energy range of interest are only of a few to a few tenths of angstrons, XPS analysis indicates that a very thin layer or even just a monolayer of chemisorbed material exists on the surface of silver. The SERS study also provides information on the molecular structure of the monolayer adsorbed on silver colloids.

Imidazole possesses the property of basicity, intermediate between that of saturated amines such as NH$_3$ and aromatic amines such as pyridine. In addition to its basic property, imidazole is also a weak acid.
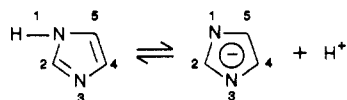
The pK for this reaction has been estimated as 14.2. Silver has not been considered to be active enough to substitute for the pyrrole proton from the imidazole–ethanol solution. Metal imidazolates are usually prepared by boiling sufficiently basic solutions of imidazole and metal ions.[11] The formation of silver imidazolate (i.e. (imidazolato)silver) by imidazole and metallic silver in neutral solution at room temperature seems to follow a new reaction

scheme. We found that this reaction may take place in many kinds of solvents such as water, alcohols, ethers, acetone, or dimethylformamide. When predried benzyl methyl ether, imidazole, and molecular silver were used, a minute quantity of water was detected after the reaction. As the system was warmed to 60 °C or the oxygen was removed from the solution by bubbling with prepurified nitrogen, the reaction ceased. On the basis of the reaction conditions and the structural properties of the product, we proposed the reaction scheme as follows:
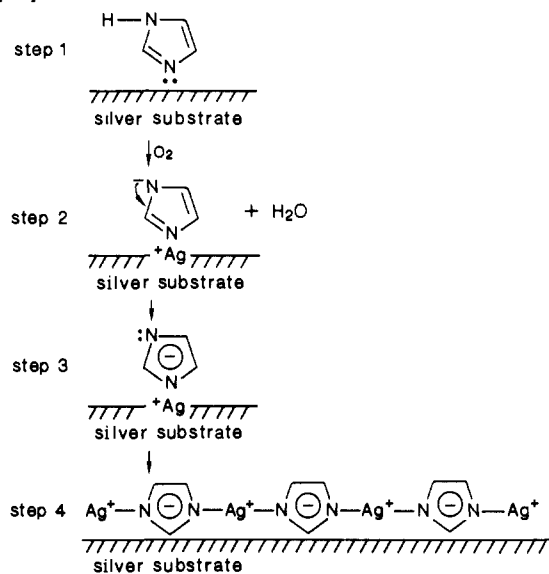
The first step of the reaction seems to be the formation of an argentous complex by ligation of N-3 of imidazole with metallic silver. This can be evident by SERS study for pyridine adsorbed on silver electrode or on silver colloids.[36-38] Pyridine has a nitrogen atom that has large electronegativity and functions as a ligand site toward transition-metal ions. It was found from SERS studies that an argentous complex formed through the connection of nitrogen and silver atoms.[39,40] Imidazole contains two nitrogen atoms: one is the so-called pyrrole nitrogen (N-1), and the other is the pyridine nitrogen (N-3). In solutions near neutrality the unprotonated imidazole molecule usually functions as a ligand via the unshared pair of electrons on N-3. So it seems reasonable to propose the formation of an argentous complex to be the first step of the reaction. In the argentous complex the silver atom and imino group became more reactive. When the solution was exposed to the air, the silver atom would be oxidized and imidazole would be deprotonated, resulting in the formation of (imidazolato)silver(I) and water. The two nitrogen atoms in the anionic imidazole are not distinguishable as evident by the XPS spectrum in Figure 2 and Table II. The anionic imidazole possesses two equivalent sites for coordination. Each silver cation can coordinate with two nitrogen ligands. It is reasonable to suppose the structure of (imidazolato)silver(I) to be that of an infinite polymer with the imidazole anions acting as bridging ligands. In fact, it was reported that (imidazolato)copper(I) was a polymeric material.[9,11] These polymeric complexes are not soluble in normal solvents and form a thin layer on the surface of metals.

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