Spectroscopic Studies on the Polymerization of Benzimidazole with Metallic Copper

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The co-ordination polymerization of benzimidazole with metallic copper has been investigated by i.r. and *X*-ray photoelectron spectroscopy. When a chemically cleaned copper disk or powder is immersed in benzimidazole solution, benzimidazole forms ligands to copper to form a complex of benzimidazole-Cu^0, which can be easily oxidized and deprotonated in air. The product formed is bisbenzimidazolatocopper(2+), which covers the surface of copper in the form of a polymeric film.

Benzimidazole (BIMH) is of considerable interest as a ligand toward transition metal ions in a variety of biological molecules including ionheme systems, vitamin B_{12} and its derivatives, and several metalloproteins. A large amount of work has been published on benzimidazole and related ligands and the complexing properties of such compounds, both in the solid state and in solution.[1] The unprotonated benzimidazole usually functions as a ligand in solutions near neutrality *via* the unshared electron pair on nitrogen. In sufficiently basic media the conjugate base of benzimidazole is formed and may also function as a ligand. The tendency then is formation of an 'inner' complex of stoicheiometry $M^{2+}(BIM^-)_2$ or $M^+(BIM^-)$ with dipositive ions. These materials are usually insoluble in organic solvents and are generally considered to be polymeric in nature.[2,3]

Benzimidazole is also of interest as a corrosion inhibitor for metals and alloys. The molecular structure and anticorrosion mechanism have been studied by many authors but are still not well understood.[4–10] The consensus is that benzimidazole can react with surface oxides on metal to form a metal–azole co-ordination film.[11–17] Relatively few reports exist on the direct reaction of benzimidazole with metallic copper or other transition metals. We have investigated the reactions of benzimidazole on a chemically cleaned copper surface. It was found that bisbenzimidazolatocopper(2+) complex was formed when metallic copper was immersed in benzimidazole solution exposed to the air. The intermediate in the reaction, a complex of benzimidazole and copper(0), could be isolated during the reaction.

Experimental

Benzimidazole (Chinese Chemical Co.) (10 g), m.p. 172—174 °C, was dissolved in ethanol (50 ml). Copper powder (1.0 g) was etched in 5% HNO_3 to remove surface oxides and repeatedly washed with ethanol. The chemically cleaned copper powder was immersed in benzimidazole–ethanol solution before coming into direct contact with air. Strong agitation was applied. A white material formed gradually. When the system was exposed to the air, it changed to a red powder. Both white and red material were isolated and purified and their structures analysed by i.r. and *X*-ray photoelectron spectroscopy and elemental analysis.

I.r. spectra were obtained by the use of a Nicolet 170 SX spectrometer from 4 000 to 100 cm^{-1}. Photoelectron (XPS) spectra were measured by means of an ES-300 three-ray spectrometer using Mg $K_{1,2}$ as the exciting source (*h* 1 253.6 eV). The C(1*s*) line (B.E. 284.4 eV) from residual pump-line oil contamination was used as internal standard for spectral calibration. Possible changes in the compounds under *X*-ray action were monitored by repeating scans, but no significant change in the spectra was observed. Measurements of the average of three different values from different samples were considered accurate to ±0.2 eV. A Dupont 310 curve resolver was used for peak deconvolution with a Gaussian fit.

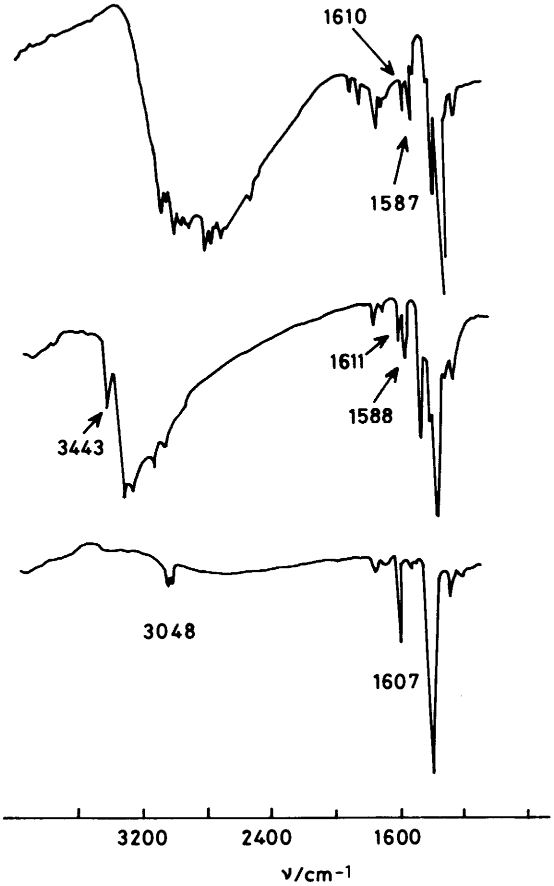


Figure 1. I.r. spectra: upper, solid benzimidazole; middle, intermediate; lower, product

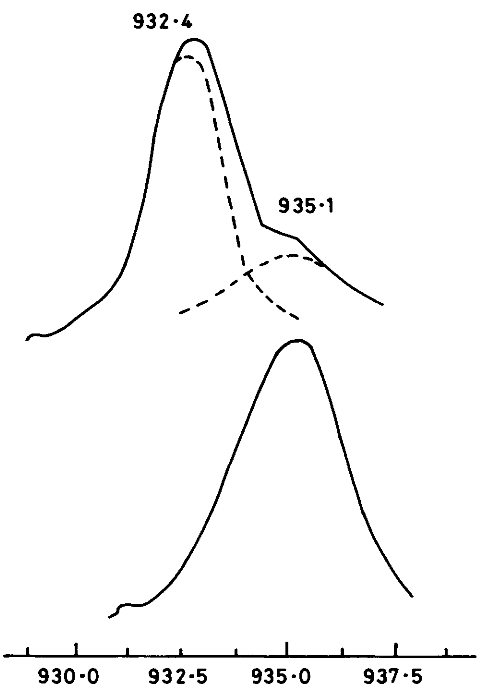


Figure 2. XPS spectra: upper, the intermediate; lower, the product

Results and Discussion

Figure 1 illustrates a comparison of the spectra in the mid-i.r. region recorded from pure benzimidazole, the white material, and the red material. There are obvious differences between these spectra. Benzimidazole has strong intermolecular hydrogen bonding in the solid state, which makes the i.r. spectrum show strong and broad absorption in the region 3 600—2 400 cm^{-1}. The spectrum of the red material, the product, shows only weak absorption near 3 048 cm^{-1} which is probably due to the C–H stretching vibration of the aromatic ring. The complete absence of both N–H stretching frequencies near 3 200 cm^{-1} and the N–H bending frequency at 1 587 cm^{-1} indicates the absence of the imino hydrogen in the product. The spectral features of the white material, which is supposedly an intermediate of the reaction, are specially interesting. The appearance of a strong sharp band at 3 443 cm^{-1} indicates the existence of an unbonded N–H group.

Figure 2 shows photoelectron spectra. The binding energy value of Cu(2*p*) in the product corresponds to Cu^{2+}. While the analysis of Cu(2*p*) spectrum of the intermediate (*i.e.* the white material) shows two binding values, 932.4 and 935.1 eV. The first value coincides with that for Cu^0, and the second for Cu^{2+}.[18]

The i.r. and XPS studies indicate the formation of bisbenzimidazolatocopper(2+), $Cu^{2+}(BIM^-)_2$. The intermediate contains mainly Cu^0 and some Cu^{2+} formed by oxidation during sample transfer.

Figure 3 illustrates the spectra in the far-i.r. region. Benzimidazole spectrum shows a ring torsion vibration near 270 cm^{-1} and lattice vibrations near 150 cm^{-1}. The spectrum of the product shows bands at 328 and 305 cm^{-1} which were assigned as Cu^{2+}–N stretching and N–Cu^{2+}–N bending vibration modes, respectively.[19] The spectrum of the intermediate of the reaction shows a broad band near 180 cm^{-1}. We assigned it as the Cu^0–N stretching mode. A surface-enhanced Raman scattering study found that the nitrogen atom of pyridine could bond to silver and copper atoms, and these bonds show vibration absorption near 200 cm^{-1}. The Ag^+–N bond of imidazolatosilver(1+) shows Raman absorption near 345 cm^{-1} and i.r. absorption at 340 cm^{-1}.[3,20] It seems reasonable to assign the band at 180 cm^{-1} in the spectrum of the intermediate as the Cu^0–N vibration and the 328 cm^{-1} band in the spectrum of the product as the Cu^{2+}–N stretching mode (Figure 3). It has been long considered that copper could react with azole compounds only when it was covered with copper(I) oxide.[11–17] But our experiments show evidence for the direct reaction of metallic copper whose surface oxides had been removed by etching. The difference in the reactivity between metallic copper and copper(I) oxide with benzimidazole is illustrated by the spectra shown in Figure 4. The spectrum for the copper sample, which had been immersed in benzimidazole–ethanol solution (5% concentration) for 5 min at room temperature before the spectrum was taken, shows clearly an N(1*s*) binding energy value at 400 eV but no O(1*s*) band near 533 eV. The photoline for the oxide sample, which had been treated in the same way, shows a small band for N(1*s*). The spectral comparison shown in Figure 4 indicates that metallic copper can react with benzimidazole at a more rapid rate than copper(I) oxide.

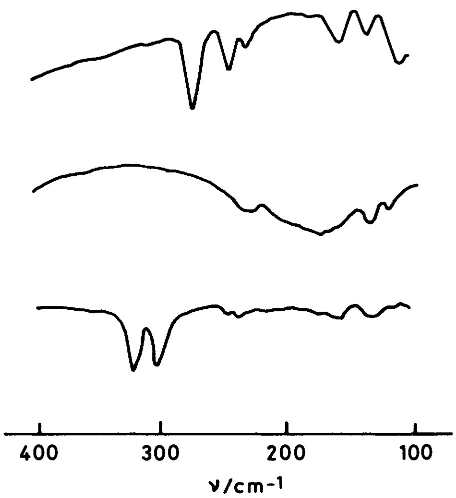
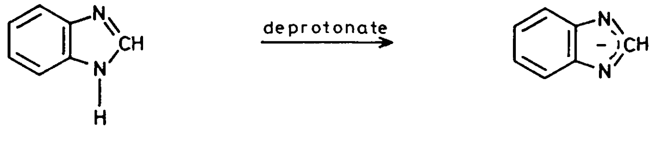


Figure 3. Far-i.r. spectra: upper, solid benzimidazole; middle, intermediate; lower, product

A study in the expanded N(1*s*) spectral region for the product of metallic copper with benzimidazole showed that there is only one band at 399.6 eV. Benzimidazole contains two nitrogen atoms, one the so-called pyrrole nitrogen and the other the pyridine nitrogen. The two nitrogen atoms have different electromagnetic surroundings. The XPS spectrum of benzimidazole is expected to show two binding energy values for N(1*s*).[18] Deprotonation at the imino group results in the formation of anionic benzimidazole, which is also aromatic.



The two nitrogen atoms in benzimidazolate anion are indistinguishable. The spectrum for the reaction product shows only one binding energy value for N(1*s*), indicating the existence of benzimidazolate anion. The chemical composition of the intermediate and product has been determined by elemental analysis. The data are in the Table. In the intermediate, the white material, the ratio of atoms C:H:N is the same as for benzimidazole. But the ratio changed to 7:5:2 after the reaction,

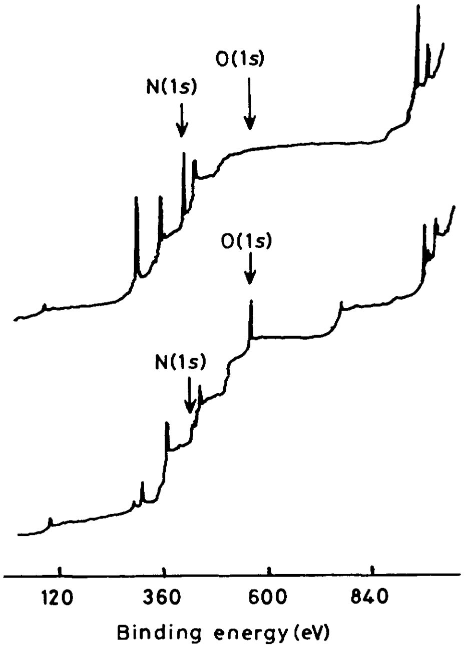


Figure 4. XPS spectra: upper, metallic copper treated with benzimidazole; lower, copper(I) oxide treated with benzimidazole

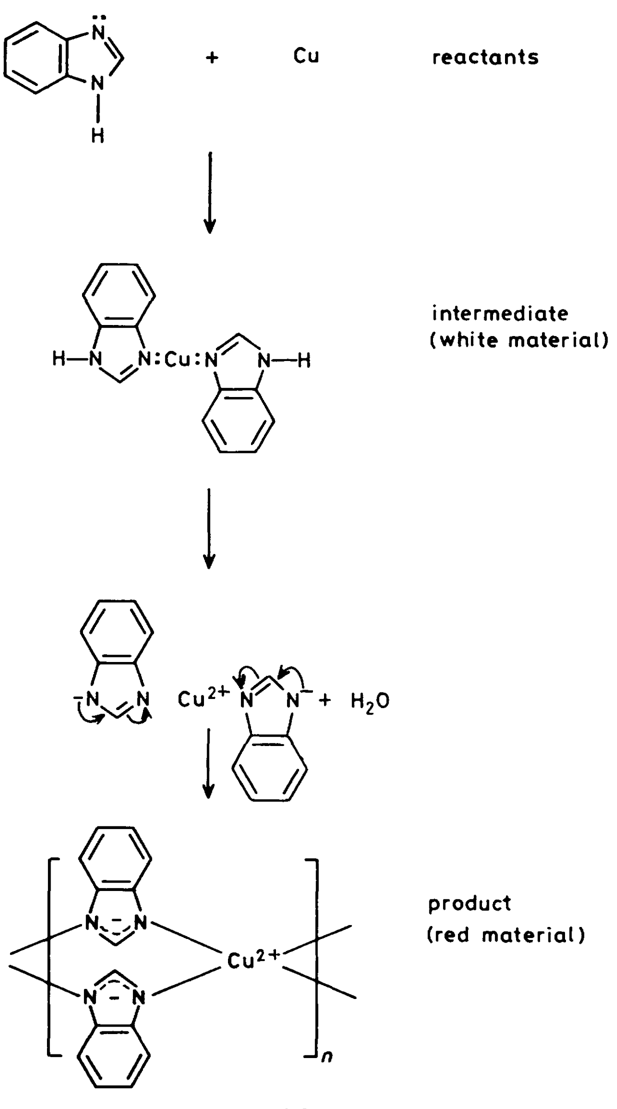
Table. Elemental analysis of benzimidazole, intermediate, and product

Benzimidazole ($C_7H_6N_2$)			
Calculated (%)	C, 71.2	H, 5.1	N, 23.7
Found (%)	C, 71.1	H, 5.2	N, 23.8
Benzimidazolecopper(0) complex ($C_{14}H_{12}N_4Cu$)			
Calculated (%)	C, 56.0	H, 4.0	N, 18.7
Found (%)	C, 55.9	H, 4.15	N, 18.9
Bisbenzimidazolatocopper(2+) ($C_{14}H_{10}N_4Cu$)			
Calculated (%)	C, 56.5	H, 3.4	N, 18.82
Found (%)	C, 56.7	H, 3.55	N, 18.45

indicating deprotonation. Elemental analysis gave data supporting the structures proposed from the i.r. and XPS studies.

Benzimidazole possesses the properties of basicity, intermediate between that of saturated amines such as NH_3 and aromatic amines such as pyridine. In addition to its basic properties, benzimidazole is also a weak acid. But copper has not been considered to be active enough to substitute for the pyrrole proton in benzimidazole–ethanol solution. Metal benzimidazolates are usually prepared by boiling sufficiently basic solutions of benzimidazole and metal ions.[21] The formation of bisbenzimidazolatocopper(2+) from benzimidazole and metallic copper in neutral solution at room temperature seems to follow a new mechanism. We found that this reaction may take place in many kinds of solvents such as water, alcohols, ethers, and acetone. When a predried solvent was used, a minute quantity of water was detected after the reaction. As oxygen was removed from the solution by bubbling with prepurified nitrogen, the reaction could not go to the end. Based on the reaction conditions and the structure of the product, we proposed the Scheme.

In solutions near neutrality unprotonated benzimidazole usually functions as a ligand by means of the unshared pair of electrons on the pyridine nitrogen. So it seems reasonable to propose the formation of a complex composed of benzimidazole and copper as the first step of the reaction. This complex was isolated and its structure determined by i.r. and XPS spectra as shown in Figures 1—3. Since the pyridine nitrogen was bonded to copper in the intermediate, it is reasonable to predict the formation of a free N–H bond. The i.r. spectrum is different from benzimidazole in the region 3 600—2 400 cm^{-1}. The intermediate complex is not stable, and can dissociate to metallic copper and benzimidazole in an acidic medium. The product, bisbenzimidazolatocopper(2+), dissociates to copper cation in a medium with pH <4. The copper atom and benzimidazole become more reactive after they are co-ordinated together. Deprotonation and oxidation take place as the medium is exposed to air, resulting in the formation of bisbenzimidazolatocopper(2+).



Scheme.

Attempts have been made to prepare a model compound $Cu^+(BIM)^-$ by reaction of a copper(I) compound with benzimidazole in basic solution. But the product is so unstable that it was oxidized to $Cu^{2+}(BIM)^-$ immediately. We thus excluded the possibility of the presence of Cu^+ in the product from copper and benzimidazole.

The two nitrogen atoms in the benzimidazole anion are not distinguishable as shown by the XPS study. The benzimidazole anion possesses two equivalent sites for co-ordination. Each copper cation can co-ordinate with four nitrogen ligands. It is reasonable to suppose the structure of bisbenzimidazolatocopper(2+) to be that of an infinite polymeric network with the benzimidazole anions acting as bridging ligands. In fact, it has been reported that imidazolatocopper(1+) was a polymeric material.[22]

Acknowledgements

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