

CHEMISORPTION OF GLYCINATE ON CUPROUS OXIDE DETERMINED BY INFRARED INTERNAL REFLECTION SPECTROMETRY

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Summary : Thin film of copper metal was vacuum deposited on KRS-5 internal reflection prism. Infrared Internal Reflection Spectrometry was employed to observe the chemical reaction taking place at the resulting metal surface with 10^{-6} M glycine solution of 8.2 pH. The investigation shows that the formation of Cu(I) glycinate chelate was formed at the surface of a film of cuprous oxide.

The formation of coordination compounds between transition metals and organic ligands leads to both water-soluble and water-insoluble complexes. Corrosion Engineers employ organic ligands which form water-insoluble coordination compounds to inhibit the corrosion of metals used in construction, including copper, zinc, iron, nickel, etc. in sea water. Smith et al. (1) have demonstrated that the presence of 2×10^{-6} M citrate in artificial sea water nearly doubled the rate of corrosion for copper metal, and that 3×10^{-4} M glycinate increased corrosion rate of copper by about 2.5 times. Niki and Hackerman (2) found that EDTA could both enhance and inhibit the corrosion rate of copper, depending on pH and dominant EDTA species present (H_2Y^{2-} would inhibit, while Y^{4-} enhanced the rate of corrosion).

The evidence for coordination complex formation at a metal surface has only been through induction, based upon measurements of weight loss, corrosion products in solution, etc. It was our intention to examine the initial formation of a metal ligand complex at the surface of a solid metal or properly metal oxide in aqueous solution of pH 8.2, i.e., of sea water. In this work we present evidence, based on internal reflection spectra, for the formation of a Cu(I) glycinate complex at the surface of a film of cuprous oxide.

This investigation used the technique (3) of vacuum depositing a thin film of metal on the reflecting faces of an internal reflection prism, and then recording the infrared internal reflection spectrum of complexes formed, or species absorbed at the exposed metal or metal oxide surface. For this study a 50 Å film of copper was vacuum-deposited on a KRS-5 internal reflection prism. From comparison with the spectra published by Poling (4) Figure 1 shows that the original 50 Å copper film has oxidized in air to Cu_2O , becoming approximately 85 Å thick (assuming complete conversion from bulk Cu to Cu_2O). In Figure 1 the absorption band at 620 cm^{-1} is

due to Cu_2O . As additional evidence that the entire film is oxidized to Cu_2O , we prepared at various times, copper films of 5, 10, 20 and 50 Å thickness, and the absorbance of the Cu_2O band was found to increase proportionally. This oxidation is not instantaneous, and in fact we found it necessary to expose the film to the atmosphere for several hours before complete conversion takes place.

The infra-red spectra were obtained using a Perkin-Elmer Model 180 Infrared Spectrophotometer and a Perkin-Elmer "FMIR" internal reflection accessory. The KRS-5 element was a conventional 25-reflection, 45° angle of incidence, trapezoidal prism. Unpolarized infrared radiation was used, and the instrument was continually purged with dry air at 100 liters/min. The reference spectrum of cis-bis-Cu(II) (glycinate)₂ was obtained in a KBr pellet, in Wilks "Mini Press". Cu(II) (glycinate)₂ was prepared in a aqueous solution at pH 8.2 (adjusted with NaOH), and was heated in a vacuum oven at 140° for 24 hours to prepare the nearly anhydrous form.

To obtain the internal reflection spectrum of the chemisorbed glycinate, a 10^{-6} M solution of twice recrystallized glycine was prepared in triply distilled water, using glassware that had been freshly washed with dichromate cleaning solution and acetone. The pH of the 10^{-6} M glycine aqueous solution was adjusted to 8.2 with NaOH. The cuprous oxide-clad prism was immersed in the solution for ten seconds, with drawn, rinsed with reagent grade acetone in order to remove the water droplets clinging to the surface, then dried with a stream of dry nitrogen.

Figure 1 gives the spectrum of the chemisorbed glycinate, showing only three visually distinct bands, at 3460 , 1560 and 450 cm^{-1} . These bands will be examined in the light of the spectrum of cis-bis-Cu(II) (glycinate)₂. The bands can be assigned by comparison with the results of Condrate and Nakamoto (5).

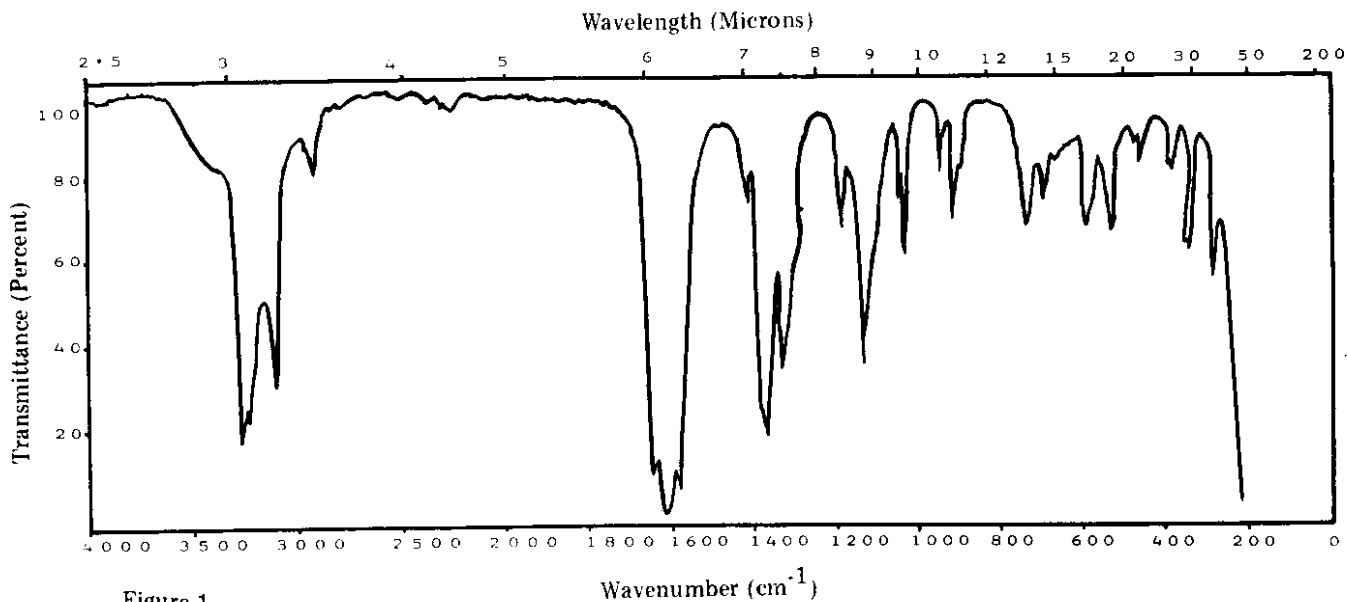


Figure-1.

Infrared Internal Reflection Spectrum of glycinate chemisorbed on 85A Cu_2O film on KRS-5 (25 reflection, 45°). Top spectrum — base line before immersion. Bottom spectrum — after 10 sec. immersion in 10^{-6}M glycine solution, p.H. adjusted to 8.2 with NaOH. Expanded scale spectra — 5x expansion of peaks from chemisorbed glycinate.

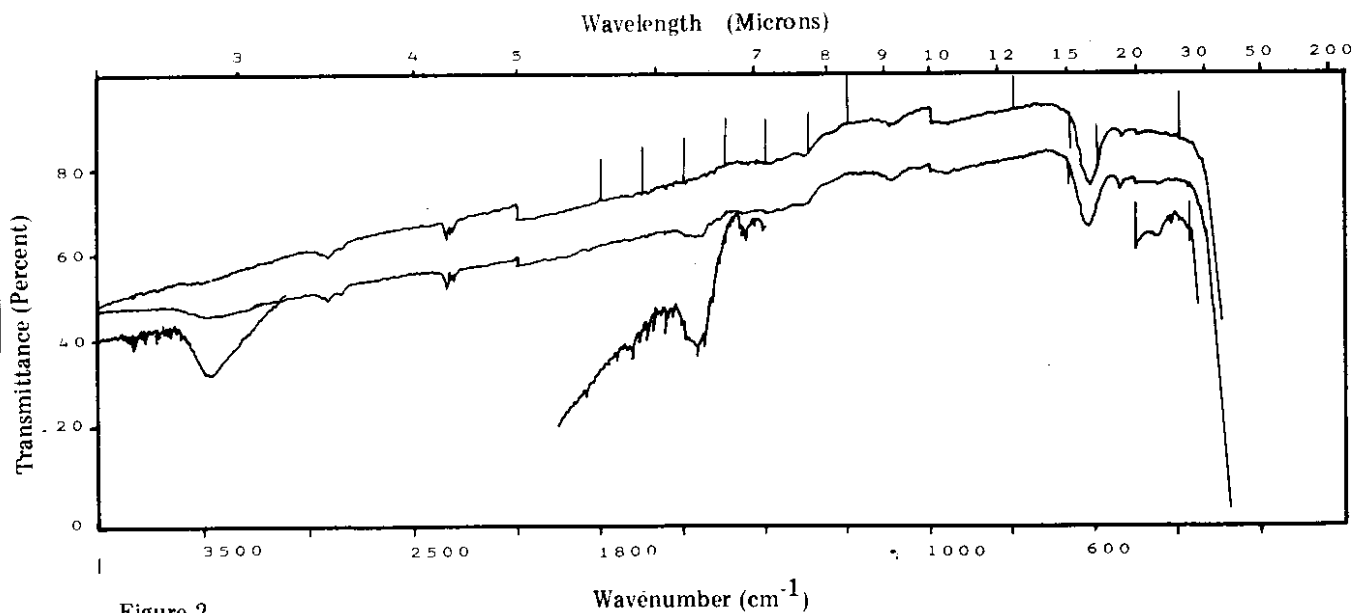
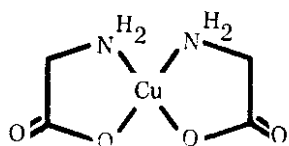
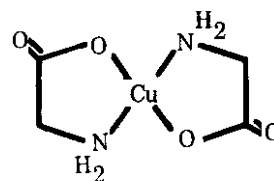


Figure 2.

Transmission (KBr pellet) infrared spectrum of cis-bis - $\text{Cu}(\text{II})(\text{glycinate})_2$ in near anhydrous form. Top spectrum — base line before immersion. Bottom spectrum — after 10 sec. immersion in 10^{-6}M glycine solution, p.H. adjusted to 8.2 with NaOH. Expanded scale spectra — 5x expansions of peaks from chemisorbed glycinate.

cis-bis-Cu(II)(gly)₂

(I)

trans-bis-Cu(II)(gly)₂

(II)

TABLE I — Band Assignments for $\text{Cu(II)-(Glycine)}_2$

IRSHAD & MATTSON cis-bis-Cu(II) (gly) ₂ cm ⁻¹	CONDRATE & NAKAMOTO ⁵ cis-bis-Cu(II) (gly) ₂ ·H ₂ O cm ⁻¹	BAND ASSIGNMENT
3350 b	(broad)	H ₂ O
3270 vs	3360	asym. NH ₂ stretch
3240 sh	obscured	overtone; 2.(1615 cm ⁻¹ .)
3120 s	3260	sym. NH ₂ stretch
2960 w	2965	asym. CH ₂ stretch
2920 m	2935	sym. CH ₂ stretch
2780, 2500	too weak	overtones &
2260 (w)		combinations
1646 sh	1667	H ₂ O
1615 vs	1606	C-N stretch
1580 m	1595	C=O stretch
1420 m	1425	CH ₂ scissors
1385 sh	obscured	??
1370 s	1389	C-O stretch
1332 s	1320	CH ₂ wag
1308 sh	too weak	??
1192 m	1179	CH ₂ twist
obscured	1167	C-N stretch
1139s,b	1120	NH ₂ twist
1050 m	1058	??
1036 m	1035	NH ₂ wag
950 m	955	C-C stretch
918 m	930	CH ₂ rock
900 m	missing	??
740 s	740	C=O in-plane bend
700 m	669	NH ₂ rock
590 m	576	C=O out-of-plane bend
530 m	558	ring deformation
479 w	480	??
462 m	460	Cu-N stretch (cis)
386 m	382	ring deformation
343 m	335	Cu-O stretch (cis)
285 m	285	Cu-O stretch (cis)

v, w, m, s, b, sh: very, weak, medium, strong, broad, shoulder

The assignment for the cis complex are given in Table I.

According to the X-rays analysis of the bis-Cu(II) (gly)₂ complex, the two glycinate anions coordinate to the copper by forming either a trans or a cis square planar structure having two chelate rings (6). The structures are shown in Fig-2.

In the case of chemisorption on a thin metal film, we expect a 1:1 (metal:ligand) structure, rather than the 1:2 structure obtained with Cu(II) in solution. The 1:2 complex is highly water-soluble and if it were formed, would be expected to diffuse rapidly into solution. Evidence that this takes place, is apparent in the fact that, when we use glycinate solutions of 10⁻⁴ M greater, the copper film is rapidly dissolved from the KRS-5. This can be observed by monitoring the disappearance of the 620 cm⁻¹ Cu₂O peak.

In Fig. 1 a broad band appears at 3460 cm⁻¹. This band is not due to liquid water, which would absorb at 3350 cm⁻¹; nor it is due to the NH₂ vibration of the ligand (see Table I). A band at 3400 cm⁻¹ is observed in protein spectra (3) but this assignment would imply polypeptide formation at the Cu₂O surface. This most likely assignment of the 3460 cm⁻¹ band is H-bonded OH. It is also possible that some Cu(II) (OH)₂ may be formed at the surface during its brief immersion in water.

The relatively strong band at 1615 cm⁻¹ in Fig. 1 is a combination of the C-N and C-O bands given in Table-1. The lack of any extended crystalline nature for the surface complex would lead one to expect much less splitting of the C-N and C-O vibrational bands than observed in crystalline Cu(II) (gly)₂.

The 1:1 metal-ligand complex expected would differ from the 1:2 complex in that the metal atom of the 1:1 complex is also bonded to two oxygen atoms of cuprous oxide within the film. The copper atom in cuprous oxide may use sp hybrid orbitals while oxygen may be in the sp³ tetrahedral configuration. The reacted copper atom probably remains monovalent and tetrahedrally (sp³) coordinated and also paramagnetic in character due to unpaired electron. The likely structure of the complex is shown in Fig.3.

There is no reason to expect that any of the ligand vibrations other than Cu-N and Cu-O would be affected by a difference in coordination number, as there is almost no coupling across the central metal atom expect at low frequencies (5). In Fig. 1 only the Cu-N band region is completely free from interference by the KRS-5 transmission cut off.

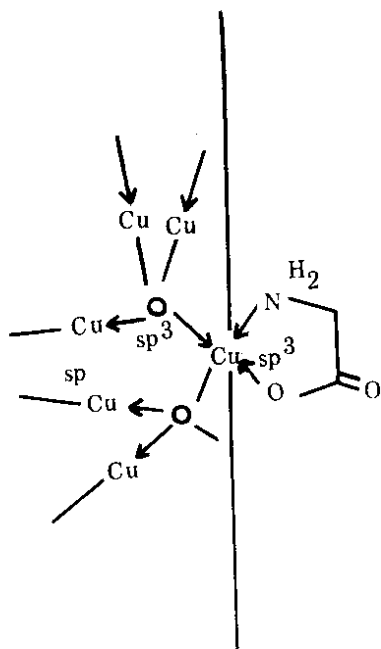


Figure-3.
Molecular model of the 1:1 Cu(II)glycinate linked with the coated film of cuprous oxide.

The absorption band at 450 cm^{-1} , if it can be attributed to the Cu-N vibration, is displaced approximately 10 cm^{-1} to lower frequency from that observed in the cis crystal in Table-1. For the trans form, the Cu-N vibration shifts to a considerably higher frequency (5). In Condrate and Nakamoto's (5) normal coordinate of the Cu(II) (gly)₂ complex, they assumed a 1:1 metal:ligand ratio for ease of computation, and the calculated Cu-N frequency was 458 cm^{-1} 4 cm^{-1} lower than they observed in the cis complex, and 2 cm^{-1} lower in our observation. Since the 450 cm^{-1} band in Fig. 1 is only 8 cm^{-1} lower than the position computed (5) for a 1:1 complex and our Cu-N frequency should be somewhat perturbed by the oxygen atoms on the opposite side of the reacted copper atom, the assignment to Cu-N seems reasonable.

References

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