$[Cu^{I}(im)]_{\infty}$: Is this Air-Stable Copper(I) Imidazolate ($8^{2}10$)-Net Polymer the Species Responsible for the Corrosion-Inhibiting Properties of Imidazole with Copper Metal?

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An air-stable two-dimensional (2D) copper(I) imidazolate polymer, $[Cu^{I}(im)]_{\infty}$ (**1**), with a d^{10}-d^{10} interaction, was synthesized solvothermally and structurally characterized by X-ray crystallography: $a = 8.069(2)$, $b = 8.068(2)$, $c = 13.425(3)$ Å, $\beta = 99.414(3)°$, monoclinic, $C2/c$. This is the first example of an air-stable copper(I) imidazolate polymer that may play a significant role in the corrosion-inhibition mechanism of imidazole (or its derivatives) with copper metal.

Introduction

Imidazolate is an important ligand since it participates in the construction of the active sites of various bioenzymes, such as superoxide dismutase (SOD)[1] and cytochrome c.[2] As an exobidentate ligand, imidazolate can form metal coordination polymers,[3,4] a good example being the cobalt(II) imidazolate polymer,[4] which is a potential metal-organic porous material since its extended polymorphic framework demonstrates not only the necessary relatively high thermal stability but also a zeolitic porous structure. Moreover, according to recent publications,[5] imidazole and its derivatives are of interest as corrosion inhibitors for copper metal and its alloys. Despite extensive studies on the issue, until now it is still questionable which mechanism is adequate to explain the inhibition of copper corrosion by imidazole, in particular what is the substance formed on the surface of the copper metal. It is generally thought that a Cu^{II}-based imidazolate polymer may form a strong anti-corrosion layer[6] since copper(II) imidazolate polymers are known to afford five different polymorphs that show different spectroscopic and structural properties.[3a] However, there are also researchers who regard a Cu^{I}-based imidazolate polymer (or monomer) as the anti-corrosion substance[7] even though an air-stable copper(I) imidazolate polymer was, until now, unknown [Masciocchi et al. have reported a copper(I) imidazolate polymer whose structure, and even its cell parameters, are still not known due to the poor X-ray powder diffraction pattern of the easily oxidizable sample[3b]]. Here we describe an air-stable 2D copper(I) imidazolate polymer, $[Cu(im)]_{\infty}$ (**1**), whose structure should be different from Masciocchi's species since its simulated XRPD pattern from a single crystal (Figure S3) is very different from the XRPD pattern measured by Masciocchi et al.[8]

Results and Discussion

The reaction of $Cu(CH_3COO)_2{\cdot}4H_2O$ (1.0 g, 5 mmol) with imidazole (0.68 g, 10 mmol) in 3-methyl-1-butanol (MB; 30 mL) under solvothermal conditions at 140 °C gave golden transparent single crystals that were suitable for X-ray diffraction. The elemental analysis reveals a copper(I) compound formulated as $C_3H_3N_2Cu$ $\{[Cu(im)]_{\infty}$, **1**$\}$. Although the yield of the substance is very low, its synthesis is reproducible. An EPR measurement on a sample of the compound exposed to air for almost half a year demonstrates that the substance remains unchanged. The formation of a copper(I) compound from a copper(II) precursor may be due to a redox reaction between the precursor and the reductive organic solvent under the solvothermal conditions employed. In order to compare Masciocchi's species with our air-stable compound spectroscopically, it was also prepared in our laboratory. However, we could not charac-

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terize it spectroscopically since the white polymer rapidly turned blue after being formed in acetonitrile, especially upon removal of the solvent.

X-ray crystallography showed that the copper(I) ions in the crystal of **1** are bridged by imidazolates in a *trans* manner[3b] (Cu−N: 1.867 Å) forming infinite 1D chains. The parallel chains run along the [110] direction and intersect with those running along the [1−10] direction in a Cu−Cu (d^{10}-d^{10}) interaction, forming the 2D sheet of a typical (8^{2}10) net (Figures 1 and 2).[9] Within the imidazolate-bridged chains, the distance between adjacent Cu···Cu centers is 5.75 Å, while between the intersected chains the nearest Cu−Cu distance is 2.783 Å, slightly shorter than two times 1.40 Å, which is the van der Waals radius of copper, and 0.23 Å longer than the Cu−Cu distance in Cu metal (2.56 Å). Within the sheet, if the imidazolato ring planes in the chains running along [110] vary in +22.3° and 157.7° dihedral angles alternately with the *ab* plane, those imidazolato rings in the chains along [1−10] should vary in −22.3° and −157.7° dihedral angles alternately with the *ab* plane. In other words, the dihedral angles between adjacent imidazolato ring planes in all the chains are ±44.6°, and imidazolato rings with the same orientation are parallel to each other between the parallel chains.

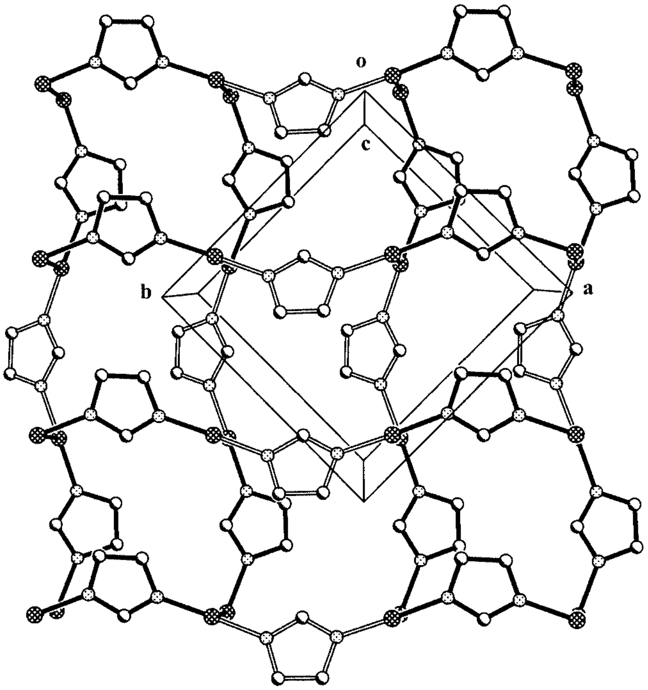


Figure 2. View of [Cu(im)]$_{\infty}$ (**1**) along the [001] direction; the imidazolate rings with solid or open bonds are those in the asymmetric unit

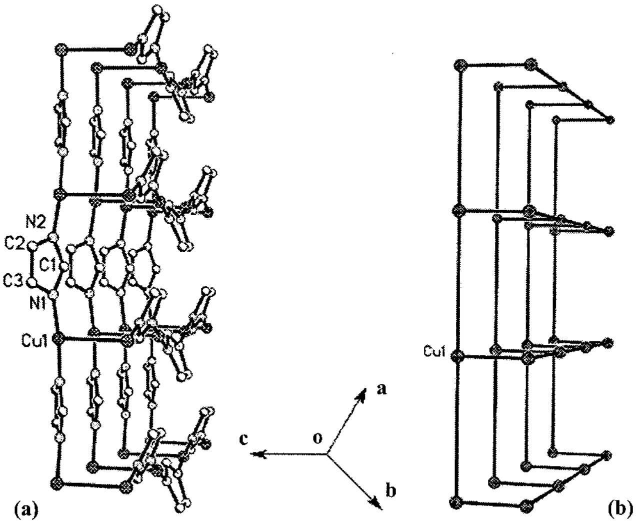


Figure 1. Cu−Cu (d^{10}-d^{10}) interaction forming a 2D sheet: (a) ball-and-stick diagram of [Cu(im)]$_{\infty}$ (**1**) (hydrogen atoms are omitted for clarity); (b) (8^{2}10) net of **1**, the spheres represent Cu atoms and the sticks represent imidazolates

In the crystal, these (8^{2}10) sheets are parallel to the *ab* plane and separated by 1/2*c* along the *c* axis. However, the imidazolato ring planes are not always parallel to each other between the parallel intersheet chains. Therefore, the imidazolato rings in the asymmetric unit of the crystal are statistically disordered, with dihedral angles of +22.3° and +157.7° (or −22.3° and −157.7°) relative to the *ab* plane (Figure 3).This phenomenon is not due to molecular thermal vibration. The layer structure depicted in Figures 1 and 2 is to be expected bearing in mind that copper(I) usually has a linear coordination geometry when it is coordinated to deprotonated imidazole molecules, as is also observed in [CoCu$_2$(im)$_4$]$_{\infty}$,[10] and that molecules in parallel will suffer from the smallest degree of steric interaction (Figure 3).

It has been reported that the geometrical constraints of some ligands can produce Cu^{I} clusters and oligomers with a d^{10}-d^{10} interaction[11] that have an even shorter Cu−Cu distance than the Cu−Cu separation in Cu metal. Nevertheless, extended Hückel MO calculations have shown that the Cu−Cu interactions in these compounds are only weakly attractive.[12] Since imidazolate possesses none of the above-mentioned geometrical constraints, the short Cu−Cu distance in **1** is due only to the weakly attractive Cu−Cu interaction. Therefore, the Cu−Cu d^{10}−d^{10} interaction should be the same as those in the Cu^{I} clusters or oligomers.

Coordination polymers resulting from d^{10}-d^{10} interactions in Au^{I} [13] and Ag^{I} [3b,14] complexes with geometrically unconstrained ligands have already been reported. Of them, polymeric silver(I) imidazolate has a 3D structure constructed from one-dimensional [Ag(im)]$_{\infty}$ chains in a *cis-trans-cis-trans* sequence through these d^{10}-d^{10} interactions.[3b] However, the copper(I) imidazolate polymer reported here is only a 2D structure due to the relatively large dihedral angles between adjacent imidazolato rings in the chains {±44.6° in [Cu(im)]$_{\infty}$ and ±8° in [Ag(im)]$_{\infty}$} that prevent the copper(I) ions between the sheets from bonding to each other to form a 3D structure. Nevertheless, this is the first reported copper(I) coordination polymer resulting from a d^{10}-d^{10} interaction, and it may give a clue as to why imidazole and its N-substituted derivatives are good corrosion inhibitors for copper metal.[6c] We propose that the

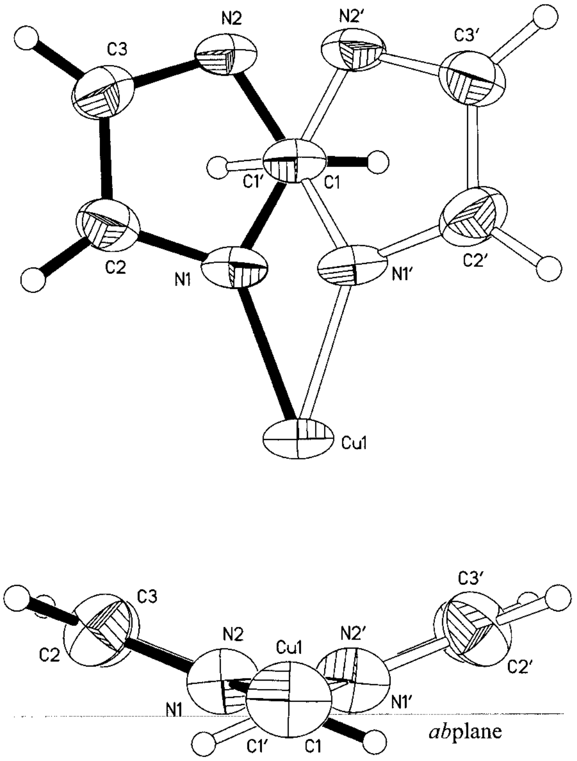


Figure 3. ORTEP drawing of the asymmetric unit of **1** showing the position disorder of the imidazolate rings; thermal ellipsoids are at the 30% probability level; top: view of the molecule along [001]; bottom: view of the molecule along [1−10]; the disordered imidazolate rings each have 30% occupancy

copper(I) imidazolate polymer (or monomer) may form an anti-corrosion layer on the copper metal surface and that the stability of this layer is enhanced by a Cu−Cu (d^{10}-d^{10}) interaction between the copper(I) polymer (or monomer) and the copper surface. Paradies et al. have reported a Cu−Cu distance of 2.85 Å in their EXAFS studies[15] on colloidal copper with adsorbed imidazole. However, although they were surprised by the result they did not give any reasonable explanation. Therefore, the air-stable copper(I) polymer with Cu−Cu bonds, in combination with the EXAFS results of Paradies et al., is good evidence that a copper(I) imidazolate polymer (or monomer) produces the anti-corrosive effect with copper metal[15] (Scheme 1), since Cu−Cu (d^{10}-d^{10}) interactions cannot be formed in a Cu^{II}-based imidazolate polymer. We suppose that if the inhibition were actually based on a Cu^{II}-related polymer layer, the hydrophobic interactions between the polymer (or monomer) and the copper surface should play a key role. However, such a copper(II) imidazolate polymer should not be formed under acidic conditions. Copper(II) *N*-substituted imidazolate monomers also cannot form the anti-corrosion layer since such monomers are water-soluble under acidic conditions. In fact, imidazole inhibits copper corrosion even in 1 M HNO_3 [5] and *N*-substituted imidazoles are even better inhibitors than imidazole itself in acidic solution.[6c] Therefore, it is reasonable for us to propose the copper(I) imidazolate as the anti-corrosion substance. However, the role of the Cu−Cu interactions must be stressed as they not only prevent the Cu^{I} complex from being oxidized to Cu^{II}, but they also bind the Cu^{I} complex polymer (or monomer) tightly to the copper metal surface. Without these Cu−Cu interactions a copper(I) imidazolate polymer may even be air-sensitive and therefore not able to provide the anti-corrosion effect. We propose that Masciocchi's white species may be a copper(I) imidazolate polymer without Cu−Cu interactions.

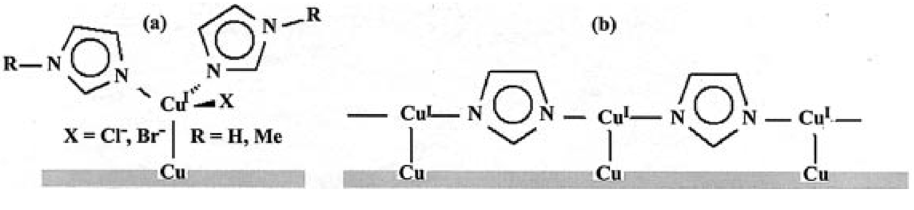
Conclusion

An air-stable copper(I) imidazolate polymer containing (8^{2}10) nets due to Cu−Cu (d^{10}-d^{10}) interactions can be synthesized under solvothermal conditions. This is the first structurally characterized copper(I) imidazolate polymer and is the only structural example supporting the proposal that a copper(I) imidazolate polymer (or monomer) produces the anti-corrosive effect of imidazole with copper metal.

Experimental Section

General Remarks: Imidazole, copper(II) acetate monohydrate and 3-methyl-1-butanol were purchased from commercial sources and used without further purification. Elemental analyses for C, H and N were performed with a Perkin−Elmer 240 analyzer. FT-IR spectra were measured from KBr pellets.

[Cu^{I}(Im)]$_{\infty}$ (1): $Cu(OAc)_2{\cdot}H_2O$ (0.50 g, 5 mmol) and imidazole (0.68 g, 10 mmol) were added to 30 mL of 3-methyl-1-butanol. After stirring at room temperature for 12 h, this heterogeneous mixture was transferred into a Teflon-lined autoclave (34 mL). The autoclave was then sealed and heated at 140 °C for 24 h. After cooling to room temperature, golden crystals of **1** mixed with a large amount of amorphous substance (the XRPD pattern is shown in Figure S3) were collected, washed three times with 15 mL of ethanol and dried in vacuo. About 0.05 g of **1** was separated by



Scheme 1. The proposed layer structure of copper(I) imidazolate polymer or *N*-substituted imidazole monomer adsorbed on the copper surface by Cu−Cu (d^{10}-d^{10}) interactions: (a) the anti-corrosive substance formed by copper(I) and *N*-substituted imidazole or imidazole in acidic condition; (b) the anti-corrosive substance formed by copper(I) and deprotonated imidazole

hand [yield ca. 8% based on the $Cu(Ac)_2{\cdot}H_2O$ used]. $C_3H_3CuN_2$ (130.62): calcd. C 27.58, H 2.30, N 21.45; found C 27.24, H 2.45, N 21.30. IR (KBr pellet): $\tilde{\nu}$ = 3124 cm^{-1} (w), 1574 (s), 1486 (vs, sh), 1313 (m, sh), 1239 (m, sh), 1179 (w, sh), 1089 (vs, sh), 960 (w), 819 (m), 750 (m), 665 (m).

X-ray Crystallographic Study: $C_3H_3CuN_3$ (**1**), M = 130.42, monoclinic, space group $C2/c$, a = 8.069(2), b = 8.068(2), c = 13.425(3) Å, β = 99.414(3)°, V = 862.24(4) $Å^3$, Z = 2, D_c = 2.012 $Mg{\cdot}m^{-3}$, $\mu(\text{Mo-}K_{\alpha})$ = 4.877 mm^{-1}, $F(000)$ = 512, GOF = 1.000. A total of 936 reflections were collected of which 803 were unique (R_{int} = 0.0156). $R1$ and $wR2$ were 0.0229 and 0.0468, respectively, for 92 parameters and 936 reflections [$I > 2\sigma(I)$]. CCDC-220508 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[10] Unpublished crystal data for $[CoCu_2(im)_4]_\infty$: $a = b$ = 10.9513(15), c = 6.3063(13) Å, space group $P42_1c$. For view of crystal structure see Figure S2.

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