

## Heteronuclear copper(II)-molybdenum(VI) oxoperoxo complex containing glycine and imidazole

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**Abstract.** A facile synthesis of the above titled homogeneous mixed ligand complex is reported. The reaction of equimolar mixture of copper (Cu) and molybdic acid ( $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ) powders with an aqueous solution of glycine (Hgly) and imidazole (Him) in excess hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), at ambient conditions results in the formation of novel complex  $[\text{Cu}, \text{Mo}(\text{O})(\text{O}_2^{2-})(\text{gly})_2(\text{Im})_2(\text{H}_2\text{O})_2]$  (1)-Compound **1** was characterised by elemental analysis, IR and electronic spectra, and thermogravimetric analysis both in air and argon. It is interesting to find that ESR spectra of **1** both at 300 K and 77 K gave  $g$  values characteristic of an axially compressed octahedral geometry ( $g_{\perp} > g_{\parallel} > 2.00$ ), around Cu(II) centre in the heteronuclear complex both in solution and solid phase. It is worth mentioning that the corresponding copper(II)-zinc(II) heteronuclear complex of **1** was reported to exhibit an axially elongated octahedral geometry around Cu(II) centre with  $g_{\parallel} > g_{\perp} > 2.00$  values.

**Keywords.** Copper(II)-molybdenum(VI) complexes; mixed ligand complexes; oxoperoxo complexes; heteronuclear complexes; imidazole-glycine complexes.

### 1. Introduction

Free amino acids in addition to providing important sites for binding of metal ions in biosystems, participate in enzyme metabolic reactions. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a metabolic by-product in many living systems. It is well known that  $\text{H}_2\text{O}_2$  functions not only as a coordinating peroxo ligand with various bonding modes but also as a redox agent because, it can be easily cleaved homolethically yielding powerful reactive oxo species like OH free radicals during the course of its reactions with some transition metals<sup>1</sup>. Recently during the course of investigations on interaction of some amino acids with  $\text{H}_2\text{O}_2$  in the presence of some bioactive transition metals and ligands, the present authors observed a profound influence of addition of second transition metal to the above mentioned reaction systems. Thus, it was reported that copper (Cu) and zinc (Zn) metals react individually with glycine (Hgly) in  $\text{H}_2\text{O}_2$  to yield peroxo amino acid complexes, while the same reaction with equimolar mixture of Cu and Zn results in deamination of amino acid to carbonate<sup>2</sup>. Interestingly it was also reported that addition of imidazole (Him) to the same reaction system containing a mixture of Cu and Zn metals, inhibits the deamination of amino acid and instead forms a novel heteronuclear mixed ligand complex<sup>3</sup>. It was reported in the literature that glycine interacts with  $\text{H}_2\text{O}_2$  in the presence of either  $\text{MoO}_3 \cdot \text{H}_2\text{O}$  or Cu to yield corresponding

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peroxo amino acid complexes. However it is not known whether the interaction of glycine with  $H_2O_2$  is affected in the presence of a mixture of  $Cu-MoO_3 \cdot H_2O$ . In view of the above mentioned effect of  $Cu-Zn$  mixture compared to individual reactants on the interaction of glycine with  $H_2O_2$ , it is considered to be of interest to extend the study to the present system of  $Cu, MoO_3 \cdot H_2O$ , glycine and hydrogen peroxide. The results of the extended study would be useful in finding whether the biologically important phenomena of deamination of amino acids is specific only to  $Cu-Zn$  system.

This paper reports the novel effect of a mixture of  $Cu-MoO_3 \cdot H_2O$  on the interaction of glycine with  $H_2O_2$  and also the influence of addition of Him to the above mentioned mixture by isolating the reaction products and characterising them by various physico-chemical methods.

## 2. Experimental

All chemicals were of AR grade and 30% aqueous  $H_2O_2$  solution was used for the reactions. The reactions were carried out in aqueous medium at ambient conditions. IR spectra were recorded with an FTIR cygnus 100 spectrometer using CSI discs with both nujol and fluorolube mulls. Diffuse reflectance spectra of solid complexes were taken on a Shimadzu 210-A spectrophotometer using  $BaSO_4$  as a reflectance standard in the region 200–800 nm. ESR spectra of polycrystalline compound and aqueous solution spectra (flat quartz cells) were recorded both at room temperature (300 K) and liquid nitrogen temperature (77 K), at X-band frequencies on a Bruker ESP300 spectrometer using DPPH as an internal field marker. Thermogravimetric analysis (TGA), both in air and argon streams, were carried out in Shimadzu DT-30 micro TG instrument with the sample weight in the 10 mg range.

Copper and molybdenum were determined by atomic absorption method, C, H, N by microanalysis. Peroxo oxygen atoms ( $O_2^{2-}$ ) were determined by ceric sulphate method<sup>2</sup>.

### 2.1 Preparation of $[Cu, Mo(O)(O_2^{2-})(gly)_2(Im)_2(H_2O)_2]$ (1)

To an equimolar (0.1 mM) mixture of  $Cu$  and  $MoO_3 \cdot H_2O$  powders, an aqueous solution of 0.2 mM glycine and 0.4 mM imidazole and excess  $H_2O_2$  (4 ml) was added and stirred for 30 min at ambient conditions, whereby a clear royal blue solution was obtained without any trace of undissolved  $Cu$  (reddish-brown powder) or  $MoO_3 \cdot H_2O$  (white powder). The stirring was continued for about an hour and the clear solution was filtered and kept over  $P_2O_5$  for drying. A light blue powder thus obtained was washed with alcohol and acetone and recrystallised again from aqueous solution. The vacuum dried royal blue compound melts with decomposition between 156–159°C. It is soluble in water but insoluble in common organic solvents. Conductivity measurements indicated compound **1** is an undissociated neutral molecule.

Analysis found:  $Cu, 12.92, Mo, 18.56, O_2^{2-}, 6.15, C, 23.60, H, 3.40, N, 16.40$ ; Calc. for  $Cu, Mo(O)(O_2^{2-})(gly)_2(Im)_2(H_2O)_2$ ;  $Cu, 12.52, Mo, 18.91, O_2^{2-}, 6.30, C, 23.64, H, 3.50, N, 16.55$ .

TGA found: Weight loss in air, 58.65% (from room temperature to 650°C); Calc. for  $CuMoO_4$  as residue, 57.64% the greenish-yellow residue was identified by XRD; weight loss in argon, 71.00%; Calc. for  $Cu + Mo$  mixture as residue, 69.64% (the lustrous grey residue was identified by XRD). IR absorption bands ( $\nu, cm^{-1}$ ): 3400 (w, br), 3128(s, br), 1641(w), 1602(s, br) 1538(w), 1503(w), 1407(w), 1383(w), 1330(w),

1262(m), 1170(m), 1133(m), 1070(s), 1027(w), 1019(w), 984 (vs), 913(s) 893(s), 869(s), 845(m, br), 760(m, br) 721(s), 694(s), 685(m, br), 620(s), 539(m), 506(w).

### 2.2 Reaction of glycine with an equimolar mixture of $\text{Cu, MoO}_3 \cdot \text{H}_2\text{O}$ in excess $\text{H}_2\text{O}_2$

Glycine (0.2 mM), Cu (0.1 mM),  $\text{MoO}_3 \cdot \text{H}_2\text{O}$  (0.1 mM),  $\text{H}_2\text{O}_2$  (4 ml) were mixed in aqueous solution and stirred for 5 days (at room temperature), whereby slowly the reactants started dissolving giving a brown precipitate. Ammonia gas evolution from the reaction mixture was detected by qualitative tests<sup>2,5</sup>. The brown precipitate was filtered, washed with water and alcohol and characterised by XRD as  $\text{Cu}_2\text{MoO}_5(\text{H}_2\text{O})_2$ . The slightly alkaline (pH 7.5) light yellow filtrate solution was found to contain slight  $\text{MoO}_3$  by XRD on drying the filtrate.

## 3. Results and discussion

The ESR spectrum of 1 exhibits a characteristic signal with  $g_{\perp}$  values of 2.118 at 77 K (2.124 at 300 K)  $> g_{11}$  value of 2.062 at 77 K (2.059 at 300 K) with a  $g_{ave}$  value of 2.102. The shape of ESR spectrum observed for 1 suggests that geometry around the Cu(II) centre could be an axially compressed distorted octahedral ( $dz^2$  ground state),<sup>6</sup>. The aqueous solution ESR spectra of 1 exhibits features due to typical monomeric Cu(II) species with  $g_{ave}$  value of 2.106 (a mobile spectrum with an mI dependent interaction of  $\text{Cu}^{63}$  hyperfine lines). The near identical  $g_{ave}$  value of 1 both in aqueous solution and solid state suggests the similarity of coordination geometry in both the phases. The absence of ESR signals due to Mo(V) ions both in solid and solution states at 300 K and 77 K indicates 1 has Mo in hexavalent state<sup>7</sup>.

The nature of ESR spectrum and  $g$  values clearly rule out 1 being a mixture of corresponding individual components. This is supported by comparing with the nature of ESR spectrum and  $g$  values reported for the corresponding individual Cu(II) complexes, viz. Cu peroxyglycine,<sup>2</sup> Cu peroxy imidazole<sup>8</sup>. Also the reported non-peroxy Cu(II) glycine (both *cis* and *trans* form),<sup>9</sup> has an axial spectrum with  $g_{11} > g_{\perp} > 2.00$  ( $dx^2 - y^2$ , ground state), in contrast to axially compressed spectrum of 1. The homogeneity of 1 is also ascertained from its physical properties like melting point, solubility and molar conductivity. Thus the m.p. of individual components of 1 was reported to be  $> 200^\circ\text{C}$ <sup>2,4,8,11</sup>, compared to  $156\text{--}159^\circ\text{C}$  observed for 1. Molar conductivity measurements also support that 1, is not a mixture but is an undissociated neutral homogeneous compound, due to its nonelectrolyte nature in the aqueous solution.

The diffuse reflectance spectrum of 1, shows a broad absorption peak in the visible region around 680 nm attributable to Cu(II)  $d-d$  transition because of its position and intensity; and a very high intense broad band in the uv region around 300 nm, attributable to charge transfer transitions<sup>2,3,5,8</sup>. The absence of any other absorption bands in the visible region due to Mo(V) or Mo(IV) ions<sup>7,12</sup> suggests that 1 contains Cu in divalent state and Mo in hexavalent state. The nonobservation of ESR signal due to Mo(V) ion also substantiates these results. The aqueous solution absorption spectrum of 1 exhibits an identical spectrum observed for the solid compound with  $\epsilon$  value of 70 at 650 and  $\epsilon > 2000$  at 300 nm. The absence of absorption peaks of 330 nm and 430 nm (even in solution state) also indicates that no neutral imidazole or imidazolate bridging moieties are present in 1<sup>13</sup>. Also the shift to lower energy of  $d-d$  transition band in 1 compared to 650 nm reported for  $\text{CuN}_4$  chromophore

of  $\text{Cu}(\text{HIm})_2^{2+}$  complex<sup>13</sup>, clearly suggests the presence of a different set of coordination atoms around  $\text{Cu}(\text{II})$ .

The IR absorption bands are listed in the experimental section. The complexity of 1 and overlap of imidazole and glycine IR absorption peaks in the region of interest for structural characterisation, precludes any unambiguous assignments. The IR spectrum of 1 exhibits a very strong absorption at  $984\text{ cm}^{-1}$  which is tentatively assigned to  $\text{Mo}=\text{O}$  terminal stretch, because no other strong band due to imidazole<sup>8,13</sup> or glycine<sup>2</sup>, are expected in this region, and the observed peak is in the range reported for  $\nu\text{Mo}=\text{O}$  in many complexes<sup>4,12</sup>. Similarly a medium broad band at  $845\text{ cm}^{-1}$ , was assigned to  $\nu(\text{O}_2^{2-})$  based on the absence of IR absorption bands in this range for the corresponding non peroxo individual  $\text{Cu}(\text{II})$  and  $\text{Mo}(\text{VI})$  complexes<sup>9,10</sup> and also in accordance with the reported assignments for the related peroxo complexes<sup>2,3,4,5,8,11</sup>. Only a single weak broad band at  $3400\text{ cm}^{-1}$  is observed in the region  $3200\text{--}3400\text{ cm}^{-1}$  (lococit). This indicates that both glycine and imidazole act as deprotonated coordinating ligands, because if  $\text{HIm}$  or  $\text{Hgly}$  function as protonated neutral coordinating ligands, additional peaks due to  $\nu\text{NH}$  of  $\text{HIm}$  or  $\nu\text{NH}_3$  of  $\text{Hgly}$  are expected in that region<sup>8,14</sup>. Although no unambiguous identification of glycine/imidazole either as a neutral or deprotonated molecule can be made from IR spectra alone, the stoichiometric analysis and valency considerations of the metal ions in 1 indicates that both  $\text{Hgly}$  and  $\text{HIm}$  are acting as deprotonated coordinating ligands. Accordingly, the other bands observed in the IR spectrum of 1 (lococit) are assigned to coordinated glycine and imidazole moieties in accordance with the reported data for the complexes<sup>2,3,5,8,15,16</sup>.

Thermogravimetric (TG) analysis of 1 was carried out both in air and argon streams. The results are given in the experimental section. The main feature of TGA curves are the continuous gradual decrease in weight loss with initial loss starting beyond  $120^\circ\text{C}$ . The interesting thermal behaviours in air beyond  $680^\circ\text{C}$ , in which a small mass gain of  $\sim 3\%$  on heating up to  $800^\circ\text{C}$  corresponds to the similar reported behaviour of  $\text{CuMoO}_4$  in air<sup>17</sup> corroborating the residue observed at  $680^\circ\text{C}$  for 1, as  $\text{CuMoO}_4$ . The close agreement of expected and observed weight loss in both air and argon (lococit) corroborates the stoichiometric formula and the number of water molecules arrived at from elemental analysis, and from estimation of peroxo oxygen atoms. The beginning of weight loss only at  $120^\circ\text{C}$  suggests the presence of coordinated water molecules instead of lattice water molecules.

Thus the combined evidence from the above discussed physico-chemical results clearly indicate that 1 is a clean homogeneous (not a mixture of individual components) novel compound containing coordinated imidazole, glycine peroxo and water molecules. Hence compound 1 is structurally formulated as  $[\text{Cu}, \text{Mo}(\text{O})(\text{O}_2^{2-})(\text{gly})_2(\text{Im})_2(\text{H}_2\text{O})_2]$ .

It is to be pointed out here that the composition of 1 indicates only 2 moles of imidazole, whereas 4 moles of imidazole were taken for the reaction. It was also observed that the filtrate after isolating the reaction product did not give any solid residue on evaporation. Hence it is interesting to find that the excess imidazole was decomposed to ammonia in accordance with the reported behaviour in corresponding  $\text{Cu}\text{--}\text{Zn}$  complexes<sup>8</sup>. However, it is likely that the added imidazole first forms complexes with  $\text{Cu}(\text{II})$ ,  $\text{Mo}(\text{VI})$  ions which in turn react with glycine resulting in formation of 1, because in absence of  $\text{HIm}$  the  $\text{Cu}, \text{MoO}_3\text{H}_2\text{O}$ , glycine and  $\text{H}_2\text{O}_2$  mixture reacts to give the decomposed  $\text{Cu}_2\text{MoO}_5$  product (lococit). Also it is pertinent

to note that while ESR spectrum of **1** gave  $g$  values corresponding to axially compressed octahedral geometry ( $dz^2$  ground state), the corresponding Cu, Zn heteronuclear complex<sup>3</sup> gave  $g$  values of a typical axially elongated octahedral stereochemistry ( $dx^2-y^2$  ground state). This interesting difference in coordination geometry around one metal ion in related heteronuclear complexes may suggest novel steric effect of replacing small size Zn(II) ion by larger size Mo(VI) ion or due to presence of oxo atom in addition to peroxo group or both.

To conclude, the preceding discussion clearly indicated an interesting and perhaps significant effect of coordination of peroxo ion, amino acid and imidazole to Cu and Mo ions in the formation of novel heteronuclear complex **1**. This work also revealed that decomposition of amino acid in presence of  $H_2O_2$ , is specific not only to Cu, Zn mixture, but also to other systems like the present Cu, Mo mixture, although a subtle difference in the nature of decomposed product is observed, namely to oxide with Cu, Mo mixture and to carbonate with Cu, Zn mixture. Perhaps the most significant outcome from this work is the observation of novel steric influence on coordination stereochemistry of Cu(II) due to change in the nature of second metal ion in the related heteronuclear complexes.

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