

Mixed metal zinc (II)–molybdenum (VI) peroxo complexes containing some amino acids and acetic acid

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Abstract. A facile synthesis of the title complexes which involve glycylglycine (Gg) glycine (Gly) and acetic acid (HAc) as ligands is reported. Reaction of equimolar mixtures of zinc and molybdic acid ($\text{MoO}_3 \cdot \text{H}_2\text{O}$) with Gg, or Gly or Ac, in excess hydrogen peroxide (H_2O_2) at ambient conditions, results in the formation of novel mixed metal complexes having the general formula, $[\text{Zn}, \text{Mo}(\text{O})_2(\text{O}_2^{2-})(\text{L})_2(\text{H}_2\text{O})_2]$, ($\text{L} = \text{Gg}^-$ or Gly^- or Ac^-). These new complexes have been characterised by elemental and thermogravimetric analyses, IR and electronic spectra. It is of interest to note that while heteronuclear peroxo complexes are quickly formed, the corresponding homonuclear Zn complexes could not be obtained.

Keywords. Peroxoamino acid complexes; zinc (II)–molybdenum (VI) heteronuclear complexes; peroxo acetic acid complexes; hydrogen peroxide–amino acid interactions.

1. Introduction

Apart from forming coordinated complexes with transition metal ions, hydrogen peroxide (H_2O_2) in its reactions with various metal ions may simultaneously liberate powerful oxidative species, including molecular dioxygen, which play a significant role in metallo–enzyme chemical reactions. Such reactions are also of interest in understanding the effect of secondary metal ions, which among other things may lead to the formation of novel hetero–nuclear peroxo complexes. Recently, we reported the profound mutual influence of some bioactive transition metals and ligands on the interactions of amino acids with H_2O_2 , in which it was observed that copper (Cu)–zinc (Zn) and Cu–silver (Ag) mixtures decompose some amino acids to carbonate (Sastry *et al* 1992, 1994a; Sastry and Gupta 1996c). Cu–nickel (Ni) and Cu–molybdic acid ($\text{MoO}_3 \cdot \text{H}_2\text{O}$) mixtures completely dissociate them, by deamination at ambient conditions (Sastry and Gupta 1996b, c), in contrast to the formation of simple peroxo amino acid complexes with the corresponding individual metal ions (Sastry *et al* 1992, 1994a; Djordjevic *et al* 1985). In order to study this varied novel mutual influence of metals on the interaction of amino acids with H_2O_2 investigations were carried out on zinc and molybdic acid mixture with the amino acids, glycylglycine (Gg), glycine (Gly) and the corresponding carboxylic acid, acetic acid (HAc) with hydrogen peroxide. This paper discusses some very interesting behaviour of Zn(II)–Mo(VI) mixtures studied by

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isolating the reaction products and characterising them by various physicochemical methods.

2. Experimental

All chemicals were of AR grade, 30% aqueous H_2O_2 solution was used for the reactions. IR spectra were recorded on a FTIR cygnus 100 spectrometer using CsI discs with both nujol and fluorolube mulls. Diffuse reflectance spectra of solid complexes were recorded in the 200–800 nm region on a Shimadzu model 210 A spectrophotometer, using BaSO_4 as reference standard. Thermogravimetric analyses (TGA) were carried out in air and argon on a Shimadzu DT-30 micro TG instrument with the sample weighing around 10 mg.

Copper and Zn were analysed by the atomic absorption method and peroxo oxygen atoms by the ceric sulphate method; C, H, N were estimated by micro analysis (Sastry *et al* 1992). The end products of TGA were identified from X-ray diffraction data (XRD).

2.1 Preparation of the complexes

In general, the mixed metal compounds, $[\text{Zn}, \text{Mo}(\text{O})_2(\text{O}_2^{2-})(\text{Gg}^-)_2(\text{H}_2\text{O})_2]$, $[\text{Zn}, \text{Mo}(\text{O})_2(\text{O}_2^{2-})(\text{Gly}^-)_2(\text{H}_2\text{O})_2]$ and $[\text{Zn}, \text{Mo}(\text{O})_2(\text{O}_2^{2-})(\text{Ac}^-)_2(\text{H}_2\text{O})_2]$, designated as compounds **1**, **2** and **3** respectively, are prepared by adding about 5 ml of 30% H_2O_2 solution to the aqueous mixture (1 mMol + 1 mMol) of zinc and $\text{MoO}_3\cdot\text{H}_2\text{O}$ and 2 mMol aqueous solution of any one of the ligands (H_2Gg or HGly or HAc). The reaction mixture was stirred continuously at room temperature in an argon atmosphere. In the case of compounds **1** and **2**, during the dissolution of reactants, an initial red-coloured solution was formed which after complete dissolution of reactants (usually about 4 h) became a clear yellow solution. A hygroscopic yellow powder was obtained after evaporating the solution under vacuum over P_2O_5 . In the case of **3**, the only difference was the absence of any red colour in solution during the early stages of reaction; a pale yellow compound was obtained after evaporation of the clear light-yellow solution. The compounds were purified by recrystallisation from aqueous solutions.

Compound 1: Analysis. Found: Zn, 12.94, Mo, 18.90, C, 18.10, N, 10.10, H, 3.50, O_2^{2-} , 7.00%. Calc. for $[\text{Zn}, \text{Mo}(\text{O})_2(\text{O}_2^{2-})(\text{Gg}^-)_2(\text{H}_2\text{O})_2]$; Zn, 12.48; Mo, 18.39; C, 18.34, N, 10.30, H, 3.43, O_2^{2-} , 6.11%.

Thermogravimetric analysis. Found: 60.10% loss in air, residue ($\text{ZnO} + \text{MoO}_3$) mixture, Calc. loss 56.93%. Found, 71.00% in argon, residue ($\text{Zn} + \text{Mo}$) mixture, Calc. loss, 69.16%.

IR absorption bands (ν , cm^{-1}): 3390 (s, br), 3200 (s, br), 1680 (s, br), 1600 (vs, br), 1440 (vs, br), 1300 (w), 1280 (w), 1120 (m), 1050, 1040 (m), 945 (s, sh), 890 (vs, br), 830 (m, br), 640 (m), 560 (w), 480 (w, br), 400 (m), 370 (s), 350 (s).

Compound 2: Analysis. Found: Zn, 16.15, Mo, 23.90, O_2^{2-} , 7.70, C, 11.20, N, 6.70, H, 2.90%, Calc. for $[\text{Zn}, \text{Mo}(\text{O})_2(\text{O}_2^{2-})(\text{Gly}^-)_2(\text{H}_2\text{O})_2]$; Zn, 15.96, Mo, 23.45, O_2^{2-} , 7.81, C, 11.72, N, 6.83, H, 2.93%.

TGA. Found: loss in air, 47.5%, residue ($\text{ZnO} + \text{MoO}_3$) mixture, Calc. loss, 44.95%.

IR absorption bands (ν , cm^{-1}): 3460 (s, br), 3200 (w, br), 1670 (s, br), 1600 (vs, br), 1495 (s), 1310 (w) 1130 (s), 1050 (wm, br), 935 (s), 900 (s) 860 (m), 700 (s), 640 (s), 560 (s), 380 (m, br).

Compound 3: Analysis. Found: Zn, 17.25, Mo, 25.49, O_2^{2-} , 8.50, C, 12.70, H, 2.70%; Calc.

for Zn, Mo(O)₂((O₂²⁻)(Ac⁻)₂(H₂O)₂ Zn, 17·14, Mo, 25·17, O₂²⁻, 8·39, C, 12·58, H, 2·62%.

TGA. Found: loss in air, 42·50%, residue (ZnO + MoO₃) mixture calc. loss, 40·90%. IR absorption bands (ν , cm⁻¹): 3400 (s, br), 1562 (s, br), 1430 (s), 1297 (w), 1146 (w), 1020 (w), 936 (s, br), 897 (s, br), 844 (m, br), 788 (w), 699 (w), 623 (w, split), 571 (w, br), 470 (w, br).

3. Results and discussion

Compounds 1–3 are stable at room temperature, sparingly soluble in water, insoluble in common organic solvents, and decompose above 170° C.

The IR spectra are given in the experimental section. The broad medium absorption band at 830, 860 and 845 cm⁻¹ for 1, 2, 3 respectively have been tentatively assigned to O–O intra-stretching vibrations of the coordinated peroxo group (ν O₂²⁻), because bands due to free or coordinated ligand bands are not expected in this region but are observable in the region reported for many transition metal peroxo complexes (Sastry *et al* 1992, 1994). The IR spectra also exhibit very strong broad absorption bands at 945, 890; 935, 900; and 935, 895 cm⁻¹ for 1, 2, 3 respectively, characteristic of ν (*cis* Mo(O)₂ moiety) (Sastry and Kulshreshtha 1989, 1991). The ‘intra-stretching’ (O–O) vibrations for the superoxide ion and several different binding modes of the peroxo group to metal ions are observed in the 1000–1300 cm⁻¹ region, which are conspicuously absent in the IR spectra of 1–3 (Nakamoto 1990). This indicates that the peroxo group may be functioning as a “side-on” bidentate chelating ligand. A similar type of coordination mode for peroxo group was reported for the corresponding terpyridine complexes (Sastry *et al* 1994b). The coordination of amino acid and acetic acid ligands is indicated by the shift in the stretching vibrations ν (COO⁻) and ν (NH/NH₂) compared to free amino acid/acetic acid (Sastry *et al* 1994a). The chemical analysis of peroxo oxygen atoms, and valency considerations also suggests that amino acids function as deprotonated univalent anions and the observed IR bands are in accordance with those reported for the corresponding glycylglycinates (Boas *et al* 1969), glycinates (Tomita 1961; Butcher *et al* 1976) and acetates (Ei-ichiro Ochia 1973). The coordination of water molecule is identified by ν (H₂O) bands at 3390, 3460 and 3400 cm⁻¹ for 1–3 respectively. TGA results also suggest coordinated water molecules in these complexes (*vide infra*).

Both diffuse reflectance spectra and aqueous solution spectra of 1–3 indicate only rising absorption in the 350–200 cm⁻¹ region. Hence, no unambiguous assignments for charge transfer bands of the type (O) → Mo(VI) or (O₂²⁻) → Mo(VI) could be made (Dziewielewski and Hasa 1994). No absorption maximum could be observed in the visible region (350–800 nm) in accordance with the presence of Zn(II) and Mo(VI) ions in compounds 1–3.

Thermogravimetric analysis (TGA) both in air and argon have been carried out and the end products are identified by XRD patterns and the results are given in the experimental section. The main features of TGA curves are the continuous gradual decrease in weight loss up to 600° C with an initial loss starting beyond 120° C. Negligible weight loss was observed beyond 650° C. The close agreement of expected and observed weight loss for 1–3 (Dziewielewski and Hasa 1994) corroborates the stoichiometric formulae and the number of water molecules arrived at from elemental analysis. The beginning of weight loss only after 120° C suggests the coordination of water molecules in 1–3.

From the combined evidence discussed above, compounds 1–3 are formulated as $[\text{Zn}, \text{Mo}(\text{O})_2(\text{O}_2^{2-})(\text{L})_2(\text{H}_2\text{O})_2]$, (where L = Gly or glycylglycine or acetate). It is of interest to note the ready formation of heteronuclear compounds 1–3 at ambient conditions, while the corresponding homonuclear zinc peroxo complexes could not be obtained due to nonreactivity of zinc. It is also pertinent to point out here the unique behaviour of the Zn-Mo-glycine- H_2O_2 system in which the amino acid is not decomposed but forms a novel compound 1, in contrast to corresponding Cu-Zn, Cu-Ni, Ni-Zn and MoO_3 -Ni systems (Sastry *et al* 1992, 1994a; Sastry and Gupta 1996b, c) in which the amino acid is decomposed. Acetic acid, the corresponding carboxylic acid of glycine, was taken to determine the influence (if any) of the amino group of glycine on the Zn- MoO_3 system, like the one observed in the case of Cu-Zn system (Sastry *et al* 1992, 1994a), where the amino acid is decomposed to carbonate, but not the corresponding carboxylic acid.

To summarise, the above discussion clearly indicates the varied influence of some bioactive transition metals and ligands on the interaction of amino acids and hydrogen peroxide.

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