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Synthesis and Properties of Peroxo α-Amino Acid Complexes of Molybdenum(VI). The Structures of $MoO(O_2)_2(HAA)(H_2O)$, HAA = Glycine, Proline

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Peroxo heteroligand transition metal complexes are an important class of reactive intermediates in catalytic oxidations, and they very likely play a substantial role as active centers in biological processes involving dioxygen species [1–4]. Some more recent review articles on the dioxygen and the peroxo metal complexes [5–8], and on the molybdenum complexes [9–12] summarized the current research and existing knowledge in these areas.

We recently reported the preparation and structure of several heteroligand peroxo vanadates(V) and molybdates(VI) [13, 14]. These results prompted us to investigate whether vanadium or molybdenum might form analogous complexes with α-amino acids. We report here the synthesis, properties and the structure of such complexes of Mo(VI), which represent a novel type of peroxo compounds, and which we could not obtain with V(V). Corresponding to the formula $MoO(O_2)_2(HAA)(H_2O)$, where HAA = glycine, α-alanine, valine, proline, serine and leucine, respectively, these complexes form in aqueous hydrogen peroxide solutions containing MoO_3 and corresponding α-amino-acid in a (1/1) molar ratio. The yellow crystals of the glycine and the proline complex were obtained from such acid solutions by standing at room temperature.

All $MoO(O_2)_2(HAA)(H_2O)$ complexes** are soluble in water, where the peroxo charge transfer bands cannot be resolved, occurring at higher energy [16] in the UV. Their IR spectra revealed the presence of a coordinated carboxylato group [17–22] (CO stretchings occur at about 1660 cm^{-1}, shifted by 65 cm^{-1} towards higher frequencies with respect to the spectra of corresponding amino acids), and the coordinated water molecule (well resolved OH stretchings in the vicinity of 3400 cm^{-1}). The two most characteristic frequencies in the IR spectra of these compounds appear between 978–970 cm^{-1} and 880–870 cm^{-1}, assigned to the Mo=O and the (O–O) stretchings, respectively [8, 18, 22]. Although they overlap sometimes with the vibrational modes of amino acids, these two bands can be clearly distinguished by their high intensities. In the aqueous solutions these complexes display typical cyclic voltammograms, with three distinct irreversible cathodic and an irreversible anodic peak. There is very little difference in the behavior from one HAA complex to another, and further studies of their electrochemistry are in progress.

The peroxo amino acid molybdenum complexes contain three biologically important components: peroxo group, α-amino acid, and Mo(VI). Consequently, they are of interest in biochemistry, and they may also possess catalytic properties, similar to some other molybdenum peroxides [1, 3]. We therefore tried to prepare adequate crystals to be able to determine the structure of the peroxo glycine and the peroxo proline derivative. More important structural features in these compounds are the mode of coordination of the peroxo groups and the amino acid, the coordination polyhedron around Mo(VI), and some selected bond lengths. No structural data exist on even simple amino acid complexes of molybdenum [18, 23], however the structure of a number of divalent metal amino acid complexes is known [21, 24–30]. The structures of $MoO(O_2)_2(HAA)(H_2O)$ (HAA = glycine, proline) were solved by standard Patterson and Fourier procedures and full-matrix least square refinement was carried out as previously described [31, 32]. Crystal data† for $MoO(O_2)_2(Gly)(H_2O)$: space group $P2_1/c$, $Z = 4$, $a = 8.517(1)$ Å, $b = 8.360(1)$ Å; $c = 10.460(2)$ Å; $\beta = 99.84°$, 1793 reflections. $R = 0.022$ and $R_w = 0.026$.

Figure 1 shows the stereoview of the complex, while Fig. 2 shows the molecular packing in the unit cell. Crystal data for $MoO(O_2)_2(Pro)(H_2O)$: space group $P2_12_12_1$, $Z = 4$, $a = 6.788(3)$ Å; $b = 8.738(2)$ Å; $c = 16.508(7)$ Å; 1307 reflections. $R = 0.027$ and $R_w = 0.032$. In both structures the molybdenum polyhedron can best be viewed as a distorted penta-

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**All the compounds were analyzed for C, H, N, and peroxides. Analyses agree well with the formula, for example $MoO(O_2)_2Ala(H_2O)$ requires: C, 12.8; H, 3.2; N, 4.9; O_2^{2-}, 22.6. Found: C, 12.8; H, 3.2; N, 4.9; O_2^{2-}, 22.6%. Peroxide determination with thiosulfate is useless, probably because of molybdenum presence. We found the potentiometric determination with Ce(IV) to be the most reliable method [15].

†Further experimental details are available upon request from the authors.

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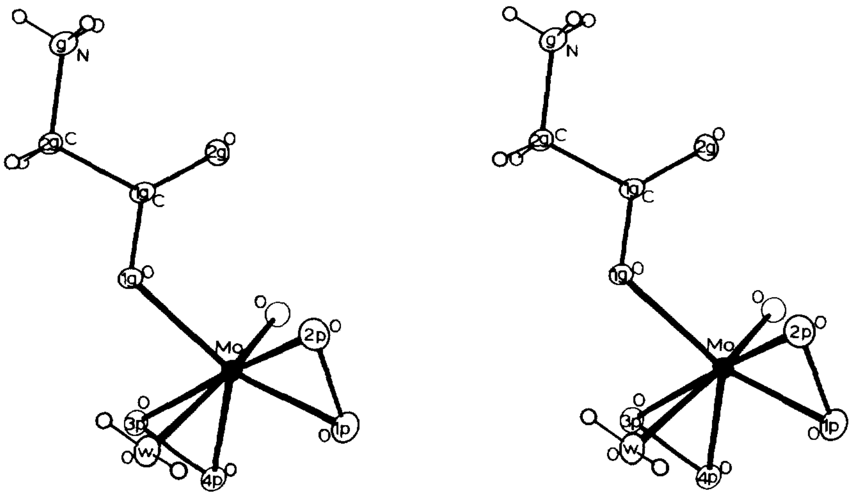

Fig. 1. $MoO(O_2)_2(Gly)(H_2O)$ molecules. Principal bond distances (Å): O1p–O2p, 1.481(1); O3p–O4p, 1.464(1); Mo–O1p, 1.947(1); Mo–O2p, 1.962(1); Mo–O3p, 1.943(1); Mo–O4p, 1.932(1); Mo–O, 1.680(1); Mo–Ow, 2.346(1). Selected bond angles (deg): O1p–Mo–O2p, 44.54(3); Mo–O1p–O2p, 68.28(3); Mo–O2p–O1p, 67.18(4); O3p–Mo–O4p, 44.39(3); Mo–O3p–O4p, 67.39(3); Mo–O4p–O3p, 68.22(3); O–Mo–Ow, 174.53(3).

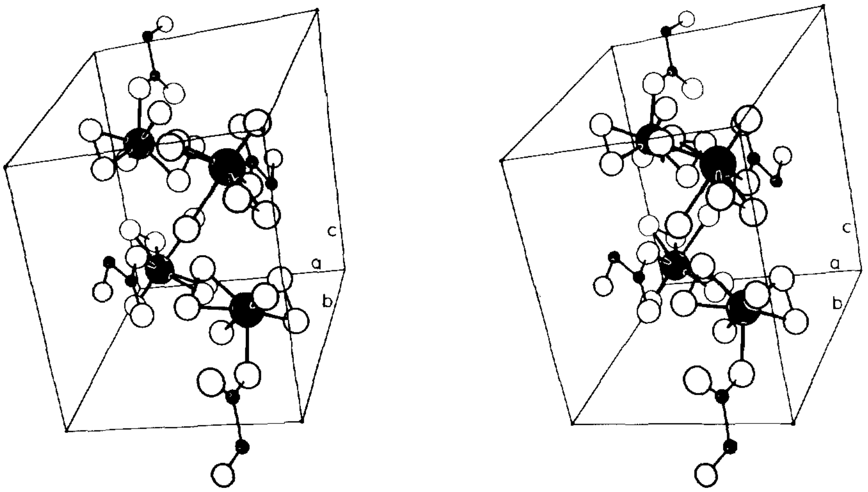

Fig. 2. Molecular packing of $MoO(O_2)_2(Gly)(H_2O)$ in the unit cell. Structural units are linked together by intermolecular hydrogen bonds to form an infinite polymeric network.

gonal bipyramid (found previously in most Mo(VI) [1, 19, 22, 33–36] and V(V) [8, 14] peroxides), with Mo=O and Mo–OH_2 at the apical positions. The two peroxo groups occupy equatorial positions forming the pentagonal ring along with the oxygen (carboxyl) from the amino acid. The molybdenum atom is 0.36 Å above the ring plane, pulled towards the oxo group. The longest (M–O) bond is Mo–O-(H_2O) (2.346(1) Å for glycine, and 2.353(2) Å for proline derivative). The Mo=O bond length falls in the expected range: 1.673(1) Å (Pro), and 1.680 Å (Gly). The O=Mo–OH_2 angle of 174.5° is not very far from the ideal 180°, similar again to some heteroligand peroxo vanadates(V) [14]. Two equatorial peroxo groups in the glycine and one in the proline complex are only slightly unsymmetrical, with the Mo–O (peroxo) bond lengths ranging from 1.923(2) Å to 1.962(2) Å, and differing within one group by 0.011(2) Å to 0.015(2) Å only. The second equatorial peroxo group in the proline complex is significantly unsymmetrical, with two Mo–O (peroxo) distances of 1.974(2) Å and 1.929(2) Å. The Mo–O–O bond angles in this group differ by 3°, whereas the difference of 1° only is found in the other three peroxo groups. The perturbation of the symmetrical bidentate coordination of a peroxo group in various ligand spheres should be studied further, particularly in relation to the charge transfer bands [16, 37] in the UV, and the reactivity [38] of the peroxo group. The (O–O) bond length in these complexes ranges from 1.464(3) Å to 1.481(1) Å, and does not depend upon the Mo–O–O bond angles. It is definitely longer than the (O–O) bond length of 1.44 ± 0.01 Å found in the six V(V) peroxo heteroligand complexes [14]. With the molybdenum atom about 0.36 Å above the equatorial plane, all the O=Mo–O(equatorial plane) angles ranging from 97° to 103°, and the $(H_2O)O$–Mo–O(equatorial plane) angles ranging from 78° to 83°, the coordinated water molecule seems to be caged in an umbrella-like enclosing of the distorted pentagonal ring. This 'pocket', occupied by the oxygen of the water molecule, and farthest away from central molybdenum ion, is an interesting feature in the stereochemistry of these molybdenum complexes. Observed Mo–$O(H_2O)$ distances (2.346(1) Å in the glycine, and 2.353(2) Å in the proline complex) lay within the expected range. In both complexes the structural units $MoO(O_2)_2(HAA)(H_2O)$ are linked together by intermolecular hydrogen bonds to form infinite polymeric networks, as shown in Fig. 2.

The bonding of the glycine and the proline via oxygen, and their coordination as zwitterions, is an interesting structural feature in these complexes. Nonchelating metal–OOCR interactions are not common nor thermodynamically favored [24]. The relative bond orders of the two C–O bonds from the coordinated carboxyl group can be deduced from the respective bond lengths. In these compounds the C–O (coordinated) distance is 1.296(1) Å in the glycine, and 1.305(4) Å in the proline complex. The adjacent C=O bond is significantly shorter: 1.221(4) Å in both compounds. The bond orders of the two bonds are thus significantly different, approaching the limits quoted before [24]. Such unusual bonding via terminal carboxylato oxygen must occur in these complexes because of the character of the oxodiperoxomolybdenum(VI) moiety, which seems to be very stable, and therefore directs the selection and the orientation of additional heteroligands attached to Mo(VI), displaying preference for oxygen over nitrogen. Steric requirements probably prevent the chelation. Investigations of peroxo complexes with the other amino acids are in progress.

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