

Short communication

Unusual formations of superoxo heptaoxomolybdates from peroxy molybdates

Quan-Liang Chen^{a,b}, Zhao-Hui Zhou^{b,*}^a College of Chemistry and Environmental Protection Engineering, Southwest University for Nationalities, Chengdu 610041, China^b College of Chemistry and Chemical Engineering, State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China

ARTICLE INFO

Article history:

Received 15 January 2016

Received in revised form 18 March 2016

Accepted 19 March 2016

Available online 24 March 2016

Keywords:

Molybdate

Superoxo

Peroxo

Hydrogen peroxide

Catalysis

ABSTRACT

Two novel dioxygen heptaoxomolybdates $K_5[Mo_7O_{22}(O_2)(OH)]Cl \cdot 6H_2O$ (**1**) and $K_5[Mo_7O_{22}(O_2)(O_2)] \cdot 8H_2O$ (**2**) were isolated from the solution of peroxy molybdate accidentally. The solids were characterized by IR, EPR and X-ray single crystal analysis. Complex **1** contains a superoxo group with a short bond distance 1.27(1) Å, while **2** is a mixed complex with peroxy and superoxo groups [1.43(1), 1.27(1) Å]. All of the dioxygen groups coordinate to molybdenum atoms in side-on (η^2) fashion. The two complexes are short-lived and will decompose into peroxy molybdates $K_5[Mo_7O_{21}(O_2)_2(OH)] \cdot 6H_2O$ (**3**) and $K_6[Mo_7O_{22}(O_2)_2] \cdot 9H_2O$ (**4**) very quickly.

© 2016 Elsevier B.V. All rights reserved.

Metal-dioxygen complexes attract special interest these years particularly due to their important role in biological and industrial catalytic oxidation process [1–3]. Such metal-dioxygen complexes are usually classified as peroxy and superoxo complexes depending on the O—O bond length and the corresponding O—O stretching frequency [4]. Compared with peroxy metal complexes, superoxo metal species are more difficult to obtain because they are always observed as fleeting intermediates due to their thermodynamic instability [5,6]. To better understand the nature of metal-superoxo species, great efforts have been expended to characterize these metal species using various spectroscopic methods including X-ray crystallography [7]. Apart from superoxo alkali metal complexes, to date, reports of superoxo metal complexes with well characterized structures are most for the first low transition metals, such as chromium, iron, nickel, copper [8–13], while the second or third low transition metals are still rare especially on molybdenum [14]. Because of the importance of dioxygen molybdenum complexes in homogeneous catalysis such as epoxidations of alkene, hydroxylations of benzene and pulp bleaching [15–17], structures and applications of peroxy molybdates have been reviewed [15,18–21]. However, the superoxo molybdates are still mysterious [22–24], despite there were reports on the reactions of molybdenum(V) tetraphenylporphyrins with superoxide [25,26]. No structural data are available for molybdenum superoxo species so far. In this communication, we describe firstly two examples of superoxo oxomolybdates with well characterized structural analyses.

Preparations of **1** and **2** were carried out in aqueous peroxy solution by using high oxidation state molybdate(VI) as the starting material at low temperature, which is different from most reported superoxo metal complexes $M^{n+2}(O_2)^{-1}$ generated by low oxidation state M^{n+1} interaction with O_2 . In the syntheses of superoxo species **1** and **2**, S-lactic acid was used in the reactions (Mo:lact = 4:1 and 1:1). While no lactato molybdate like $K_2[MoO_2(S-lact)_2]$ or peroxy lactato molybdate was isolated in the final product [27–28]. Although the role and the reaction mechanism of S-lactic acid is unclear, we have speculated on the reaction mechanism of S-lactic acid via NMR measurement in our recent report [29]. Like the other polyoxomolybdates or peroxy molybdates, pH value is crucial for the formations of **1** and **2** due to the formations of the other polynuclear peroxy molybdates. The optimal pH values for the syntheses of **1** and **2** are 3.5 and 6.0 respectively. In spite of that, the isolations of **1** and **2** are only successful for several times in hundreds of tests, showing the instability and uncertainty in the preparations of superoxo products. Similar with the other reported superoxo metal species, both complexes are short-lived and unstable in solution and solid state. According to our experiment, **1** and **2** will be converted to more stable peroxy species of $K_5[Mo_7O_{21}(O_2)_2(OH)] \cdot 6H_2O$ (**3**) and $K_6[Mo_7O_{22}(O_2)_2] \cdot 9H_2O$ (**4**) very quickly. The conversions were confirmed by IR and cell parameters from X-ray diffraction. The IR spectra of **3** and **4** are shown in Figure S1. Both structures of **3** and **4** are confirmed as reported [24,29].

The anions of **1** and **2** were characterized by X-ray structural analysis and their perspective views are presented in Fig. 1. Unlike monomeric or dimeric superoxo metal complexes, both anions contain heptanuclear units with superoxo groups. The heptanuclears **1** and **2**

* Corresponding author.

E-mail address: zhzhou@xmu.edu.cn (Z.-H. Zhou).

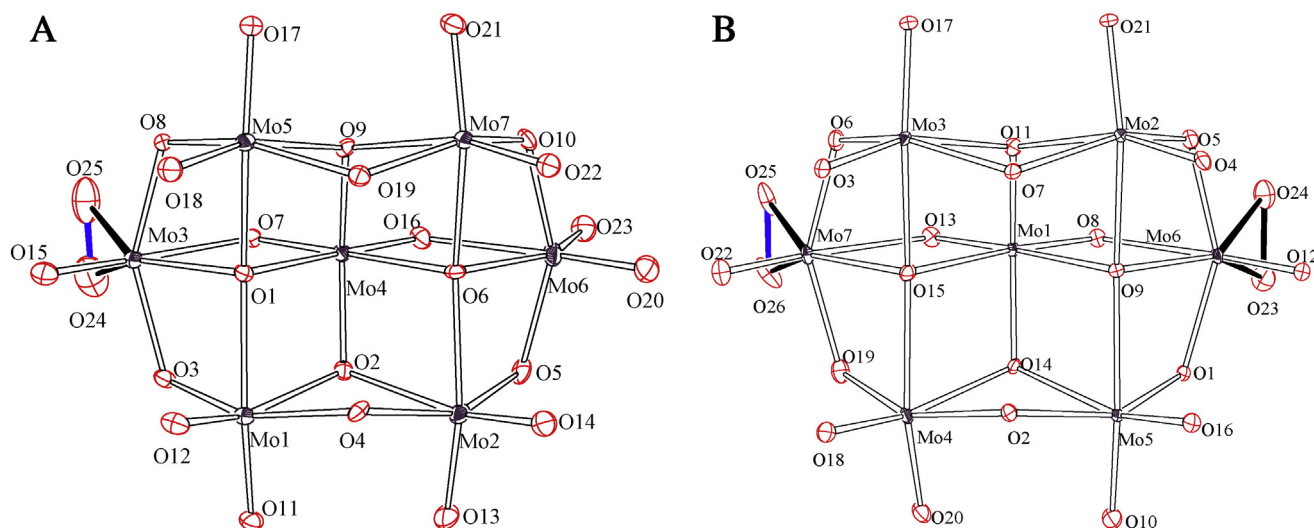


Fig. 1. Perspective views of the anion structures of $K_5[Mo_7O_{22}(O_2)(OH)]Cl \cdot 6H_2O$ (**1**) (left) and $K_5[Mo_7O_{22}(O_2)(O_2)] \cdot 8H_2O$ (**2**) (right).

have the similar heptamolybdate anion $[Mo_7O_{24}]^{6-}$, which was the main species in acidic solution for molybdate. While it is worth noting that the significant difference is the replacement of oxygen atoms of the anion by dioxygen groups.

Comparisons of bond distances (Å) of dioxygen groups in **1** and **2** can be seen in Fig. 2. There is one dioxygen group in **1** [O24—O25, 1.27(1) Å] and two dioxygen groups in **2** [O(23)—O(24), 1.43(1) Å; O25—O26, 1.27(1) Å]. Usually, the dioxygen group can be classified as peroxy and superoxy groups based on their bond distances. The short O—O bond distances [O24—O25, 1.27(1) Å in **1** and O25—O26, 1.27(1) Å in **2**] are in good agreement with the range of superoxy O—O bonds in metal-superoxo complexes (1.2–1.3 Å). The relative long dioxygen group in **2** [O(23)—O(24), 1.43(1) Å] falls in a typical peroxy group for metal-peroxy complexes (1.4–1.5 Å). Accordingly, **1** and **2** are superoxy species based on the definition of superoxy metal complexes depending on dioxygen bond distances. Due to different dioxygen groups in **2**, it can be considered as a mixed molybdenum-dioxygen complex. In both anions of **1** and **2**, all of the dioxygen groups coordinate to molybdenum atoms in side-on (η^2) fashion. Superoxo groups were stabilized by heptameric moiety in **1** and **2** to form superoxy complexes. The molybdenum atoms coordinated to the oxygen ligand are hepta-coordinated, and the pentagonal bipyramidal arrangement of the coordination is also observed in the reported peroxy molybdates [30–32]. By comparing with the other transition metal complexes such as copper, chromium and cobalt superoxy complexes, the bond distances and bond angles of superoxy groups in **1** and **2** show no much difference which can be seen in Table S1. Although there are two kinds of binding modes (end-on or side-on) suggested for superoxy ligands, the present results clearly demonstrate that only side-on fashion found in **1** and **2**. Table S1 also shows that both the metal nature and the coordinating fashion have impact on the bond distances of superoxy groups. The superoxy groups in both heptanuclear clusters are unstable as the other reported superoxy metal complexes, they will react further to replace superoxy groups with peroxy groups in the preparation solution,

and give the corresponding diperoxo complexes as mentioned above. Further studies are needed to elucidate the detailed mechanism for the formation of superoxy molybdate species in peroxy molybdenum solution. In the reported literature, superoxy vanadium species was found by the reaction of high oxidation state metal with hydrogen peroxide [19].

Based on the rule of bond valence sum (BVS), the oxidation states of molybdenum atoms are calculated with a linear correlation [33,34]. The bond valence sums are 5.994, 5.954, 6.490, 6.057, 6.167, 5.916 and 6.088 for Mo1 to Mo7 in **1**, and 5.963, 5.982, 5.985, 6.120, 5.940, 6.348 and 6.493 for Mo1 to Mo7 in **2** respectively. Therefore, the oxidation states are +6 for molybdenum atoms in **1** and **2**. The detail bond distances and angles of **1** and **2** are shown in Tables S3 and S4. Comparisons of their bond distances with the other peroxy molybdates are shown in Table 1. In the heptameric moieties of **1** and **2**, the bond distances of Mo=O (terminal) are between 1.686(7)–1.774(8) Å and 1.681(4)–1.726(3) Å and the bond distances of Mo—O—Mo (bridge) are between 1.732(6)–2.442(6) Å and 1.762(3)–2.444(3) Å in **1** and **2** respectively. The long bond distances [Mo(4)—O(1), 2.274(6); Mo(4)—O(6), 2.283(6) Å and Mo(1)—O(9) 2.271(6), Mo(1)—O(15) 2.269(6) Å] are the results of the *trans* influence of the terminal bonds of Mo4—O16, Mo4—O7 and Mo1—O12, Mo1—O8 in **1** and **2** respectively. The same phenomenon has also been observed in **3** and **4**. However, the average Mo—O bond distances of peroxy groups are much longer than those of superoxy groups [1.908(8)_{av.} Å in **1**, 1.894(9)_{av.} Å in **2**]. This may be caused by the short bonding of O—O superoxy ligand.

The IR spectra of short-lived **1** and **2** in solid state are tested at room temperature as shown in Fig. 3. From the spectra, it still can be seen characteristic superoxy (O—O) vibration peaks (1118 cm^{-1} for **1** and 1114 cm^{-1} for **2**). These peaks are in agreement with other reported superoxy vibration frequencies around 1100 cm^{-1} . However, the superoxy peaks in **1** and **2** are very weak due to the decompositions into diperoxo complexes **3** and **4** respectively. The peaks 845 cm^{-1} and 843 cm^{-1} can be assigned to the own or converted peroxy groups

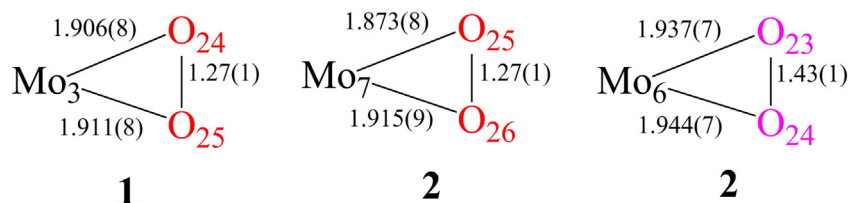


Fig. 2. Comparisons of bond distances (Å) of dioxygen groups in **1** and **2**.

Download English Version:

<https://daneshyari.com/en/article/1303216>

Download Persian Version:

<https://daneshyari.com/article/1303216>

[Daneshyari.com](https://daneshyari.com)