

Determination of Oxidation States in Mn(III,IV) Cluster by a MEM Analysis

Takuya Shiga¹, Hiroshi Sawa², Hiroki Oshio*¹

¹Univ. of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan

²KEK-PF, Tsukuba, Ibaraki 305-0801, Japan

Introduction

Metal oxide clusters exhibit a wealth of organic-inorganic hybrid materials such as photosystem II and as quantum spin systems. It is noted that mixed valence metal ions play important roles in their properties. We prepared an icosanuclear cluster of $[\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4\text{Cu}^{\text{II}}_8\text{O}_{16}(\text{OME})_4(\text{OAc})_4(\text{NO}_3)_2(\text{bemp})_4(\text{H}_2\text{O})_{10}](\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$ (**1**, $\text{H}_3\text{bemp} = 2,6\text{-bis}[N\text{-(2-hydroxyethyl)iminomethyl]-4-methylphenol}$). Oxidation states of metal ions can be assigned using charge considerations, coordination bond lengths, and bond-valence-sum (BVS) calculations. However, determination of the oxidation states of metal ions, which have non-localized valence electrons, is rather difficult. We report here a determination of the oxidation states of manganese ions by using the maximum entropy method (MEM) for X-ray diffraction data. [1]

Experimental

X-ray diffraction data for **1** was obtained with a Weissenberg-type imaging plate detector. MEM analysis was performed with the Enigma program (Tanaka, H.; Tanaka, M.; Nishibori, E.; Kato, K.; Iishi, T.; Sakata, M. *J. Appl. Crystallogr.* **2002**, *35*, 282.) at a resolution of $128 \times 128 \times 128$ pixels, and the *R* factor of the final MEM charge density was 0.046. Electron counting on each manganese ion was performed within the particular compartment of the space (Voronoi cell), which was defined as a region surrounded by perpendicular bisecting planes of bonds between manganese and neighboring oxygen nuclei.

Results and discussions

A dark brown crystal of **1** crystallizes in the tetragonal space group $I4_1/amd$ (Figure 1). A complex cation of **1** contains four dinuclear copper units ($[\text{Cu}^{\text{II}}_2(\text{bemp})]$) capping a penta-cubic core of manganese oxide, $[\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4(\mu_3\text{-O})_8(\mu_5\text{-O})_4]$. The manganese oxide core, which is composed of twelve manganese ions bridged by four $\mu_5\text{-O}^{2-}$ (O5) and eight $\mu_3\text{-O}^{2-}$ (O6) ions, has five face-shared cubes arranged in a cross-shape. Four $[\text{Cu}^{\text{II}}_2(\text{bemp})]$ units cap the oxide core on its top and bottom faces. The average coordination bond length ($d_{\text{av}} = 1.968 \text{ \AA}$) of the Mn1 is shorter than that ($d_{\text{av}} = 2.033 \text{ \AA}$) of the Mn2 ion. BVS calculations yielded values of 3.42 and 3.07 for Mn1 and Mn2, respectively. The structural data suggest that the Mn1 ions have higher oxidation states than the Mn2 ions. It is difficult to precisely count the number of electrons on metal centers, however, the

maximum entropy method (MEM) analysis for the accurate X-ray data appears the most suitable way for this purpose. The X-ray diffraction data were obtained in the Photon Factory at KEK, Japan, and the MEM analysis was applied to assign the oxidation state of the manganese ions. Contour maps of the electron density reproduced from the MEM are depicted in Figure 2. The electrons on the Mn1 and Mn2 ions were computed to be 19.9 and 20.3, and the Mn1 and Mn2 were assigned to be Mn^{IV} and Mn^{III} ions, respectively. It is noted that electron counting analyses are affected by the diffuseness of the outer shells, and the obtained values are sometime less than the ones predicted by the formal oxidation state.

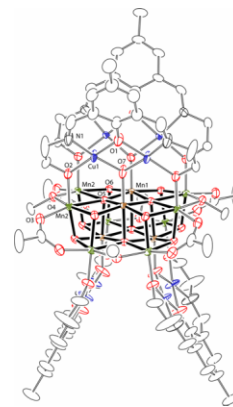


Figure 1. ORTEP diagram of cation **1**

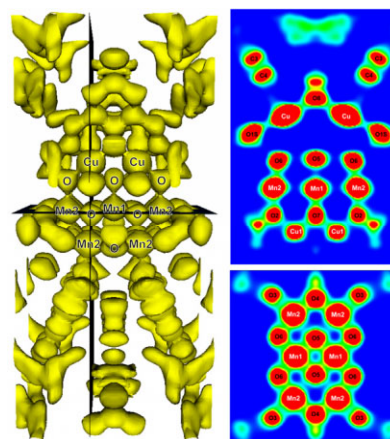


Figure 2. MEM electron-density distribution in the oxide core of **1**: horizontal (right bottom) and vertical (right top) divisions were taken from planes of the whole molecule (left). The contour maps are drawn from 0.001 to 2.0 e \AA^{-3} , and high electron density is colored in red.

References

- [1] H. Oshio et al., *Inorg. Chem.* **46**, 3810 (2007)
* oshio@chem.tsukuba.ac.jp