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Structure Determination of a Silver-Ethynide and Polyoxometalate Composite Cluster

Sho Tamari,[1] Kosuke Ono,[2] Masato Hashimoto,[3] and Tomoji Ozeki[4*]
[1]Department of Chemistry and Materials Science, Tokyo Institute of Technology,
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551, Japan
[2] Department of Chemistry, Faculty of Science, Tokyo University of Science,
1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601
[3] Department of Material Science and Chemistry, Faculty of Systems Engineering,
Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan
[4] Department of Chemistry, College of Humanities and Sciences, Nihon University,
3-25-40 Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan

We have been successful in selecting the binding site of a polyoxometalate to the silver alkynide cluster by tuning the surface charge of the precursor polyoxometalate. A novel polyoxometalate—silver ethynide composite cluster, $[Ag_{42}(CO_3)\{C{\equiv}CC(CH_3)_3\}_{27}(\alpha\text{-A-}SiW_9Nb_3O_{40})_2]^-$ (**1**), has been prepared and its crystal structure has been determined by single crystal synchrotron X-ray diffraction at the AR-NW2A beamline. Multidimensional and multinuclear NMR spectra revealed that **1** maintains its precise atomic connectivity in the solution.

1 Introduction

Polyoxometalates is attracting increasing interest due to various applications based on versatile structures. Polyoxometalate—silver alkynide composite clusters can potentially exhibit much wider structural variety. We are interested in rationally designing such composite clusters. We recently reported that triply Nb-substituted Dawson polyoxotungstate, $[P_2W_{15}Nb_3O_{62}]^{9-}$, selectively bind to silver alkynide cluster at its Nb-substituted hemisphere.[1] This result implies that silver alkynide prefers less negatively charged surface of polyoxometalate. To demonstrate this tendency, we reacted Nb-substituted Keggin polyoxotungstate, $[\alpha\text{-A-}SiW_9Nb_3O_{40}]^{7-}$, with silver alkynide and obtained a novel polyoxometalate—silver alkynide composite cluster, $[Ag_{42}(CO_3)(C{\equiv}C^tBu)_{27}(SiW_9Nb_3O_{40})_2]^-$ (**1**) [^{t}Bu = $C(CH_3)_3$]. In **1**, the Keggin polyoxometalate is bonded to the silver alkynide cluster moiety in the proximity of the Nb atoms where the surface is less negative compared with the remaining part.[2]

2 Experiment

Synchrotron X-ray diffraction data for **1** were collected on a Rigaku Mercury CCD diffractometer at the NW2A beamline of the Advanced Ring in the Photon Factory (PF-AR). Crystal data for $[(C_4H_9)_4N][Ag_{42}(CO_3)(C{\equiv}C^tBu)_{27}(SiW_9Nb_3O_{40})_2]{\cdot}5CH_3CN$: $C_{189}H_{294}Ag_{42}N_6Nb_6O_{83}Si_2W_{18}$, M = 12431.8, triclinic, space group $P\bar{1}$, a = 21.172(1) Å, b = 24.383(1) Å, c = 31.630(1) Å, α = 90.138(1) °, β = 95.802(2) °, γ = 93.545(1) °, V = 16213.2(11) Å^3, Z = 2, T = 123 K, μ(synchrotron, λ = 0.6890 Å) = 8.306 mm^{-1}. 168053 reflections measured, of which 59080 independent (R_{int} = 0.0996). The final $R1(F)$ = 0.0823 (40942 reflections with $I > 2\sigma(I)$) and $wR(F^2)$ = 0.2425 (all data).

3 Results and Discussion

Figure 1 illustrates the structure of **1**, which unambiguously demonstrate that the less negative part (Nb-substituted part) of the Keggin polyoxometalate bind to the silver ethynide moiety. ^{183}W, ^{29}Si, ^{13}C and ^{1}H NMR spectra indicate that this structure remains intact in the solution.

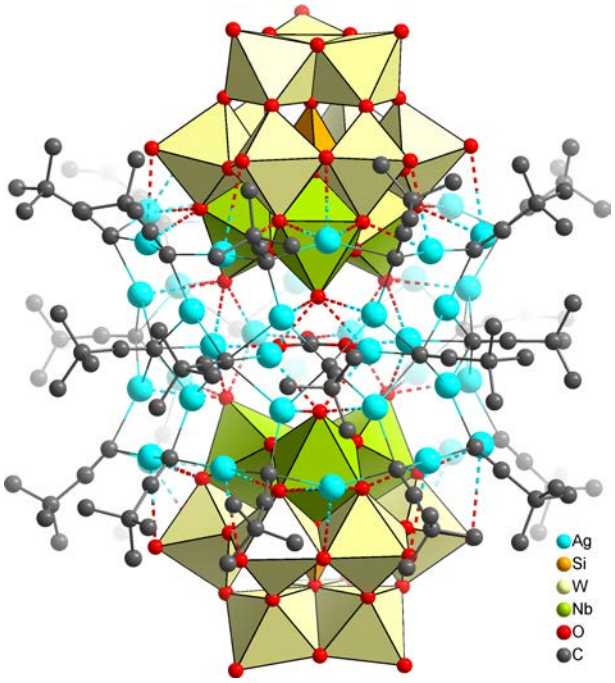

Fig. 1: Structure of $[Ag_{42}(CO_3)\{C{\equiv}CC(CH_3)_3\}_{27}(\alpha\text{-A-}SiW_9Nb_3O_{40})_2]^-$ (**1**).

References

[1] M. Kurasawa, F. Arisaka and T. Ozeki, *Inorg. Chem.*, **54**, 1650-1654 (2015).
[2] S. Tamari, K. Ono, M. Hashimoto and T. Ozeki, *Dalton Trans.*, **44**, 19056-19058 (2015).

* ozeki@chs.nihon-u.ac.jp