MS.61.1

Acta Cryst. (2011) A**67**, C140

Supramolecular assembly based on multinuclear silver(i) ethynide synthons

Thomas C. W. Mak, *Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, (China).* E-mail: tcwmak@cuhk.edu.hk

In the context of supramolecular chemistry, the coordination concept as commonly applied to metal ions has been extended to polyatomic anionic species [1]. In the designed construction of coordination networks, it is of interest to determine the highest ligation number (HLN) of simple inorganic polyatomic anions, namely the largest number of coordination bonds that a particular anion can form with neighboring metal centers in its complexes [2].

In 1998, we embarked on a systematic study on the HLN of small inorganic anions such as the pseudohalides CN^-, SCN^-, N_3^- and $SeCN^-$ using the silver(I) ion as an ideal probe [3]. Such a choice is favored by the tendency of Ag(I) to form multinuclear aggregates through the d^{10}-d^{10} argentophilic interaction [4]. By dissolving each silver(I) pseudohalide in a concentrated aqueous solution containing one or more water-soluble silver(I) salts, a series of new double and triple silver(I) salts were obtained, and their crystal structures were determined by X-ray crystallography.

We subsequently investigated the ligand behavior of the C_2^{2-} dianion (ethynediide, also named acetylenediide,), an isoelectronic structural analog of CN^-, N_2 and NO^+. In a wide variety of novel double, triple and quadruple silver(I) salts, the dumbbell-like $^-C{\equiv}C^-$ species was found to be invariably encapsulated in a polyhedral silver(I) cage of 6-10 vertices, and each C-terminal has significant ionic, covalent σ, π, and mixed (σ, π) interactions with four or five vertices. We then expanded the scope to synthesize silver(I) complexes of the homologous all-carbon $^-C{\equiv}C{-}C{\equiv}C^-$ (1,3-butadiyne-1,4-diide) ligand and related ethynide species $R{-}C{\equiv}C^-$ (R = alkyl, aryl, heteroaryl), thereby establishing the identity and synthetic utility of the multinuclear metal-ligand supramolecular synthons $C_2@Ag_n$ (n = 4,5), $Ag_4{\subset}C{\equiv}C{-}C{\equiv}C{\supset}Ag_4$ and $R{-}C{\equiv}C{\supset}Ag_n$ (n = 4,5) for the construction of discrete molecules and 1D-3D coordination networks. Several factors of influence, including the choice of counter anions, the presence of ancillary spectator molecules, and variation of aromatic ring substituents on the self-assembly of silver-ethynide supramolecular synthons in crystallization have been systematically explored. Our work spanning a decade has been summarized in two 2007 reviews.[5]

Recent advances including our designed construction of large mixed-metal clusters based on the $R{-}C{\equiv}C{\supset}Ag_n$ supramolecular synthon and polyoxometalate building blocks[6] will be presented.

This work is supported by Hong Kong Research Grants Council GRF Ref. No. CUHK 4268/00P, 401704, 402405, 402408 and 402710.

[1] (a) A. Bianchi, K. Bowman-James, E. Garcia-Espańa (eds.), *Supramolecular Chemistry of Anions*, Wiley-VCH, New York, **1996**. (b) P.D. Beer, D.K. Smith, *Prog. Inorg. Chem.* **1997**, *46*, 1-96. [2] G.-C. Guo, T.C.W. Mak, *Chem. Commun.* **1999**, 813-814. [3] G.-C. Guo, T.C.W. Mak, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 3183-3186. [4] (a) P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597-636. (b) P. Pyykkö, *Chem. Soc. Rev.* **2008**, *37*, 1967-1997. (c) J. Muñiz, C. Wang, P. Pyykkö, *Chem. Eur. J.* **2011**, *17*, 368-377. [5] (a) T.C.W. Mak, X.-L. Zhao, Q.-M. Wang, G.-C. Guo, *Coord. Chem. Rev.* **2007**, *251*, 2311-2333. (b) T.C.W. Mak, L. Zhao, *Chem. Asian J.* **2007**, *2*, 456-467. [6] (a) G.-G. Gao, P.-S. Cheng, T.C.W. Mak, *J. Am. Chem. Soc.* **2009**, *131*, 18257-18259. (b) Y.-P. Xie, T.C.W. Mak, *J. Am. Chem. Soc.*, Publication Date (Web): February 24, **2011** (Communication), DOI: 10.1021/ja1112035.

Keywords: argentophilicity, silver, supramolecular synthon

MS.61.2

Acta Cryst. (2011) A**67**, C140-C141

Polycoordinate hydride inside a Cu_7 cluster authenticated by neutron diffraction

Alison J. Edwards,[a] Chen-Wei Liu,[b] Ping-Kuei Liao,[b] Ching-Shiang Fang,[b] [a]*Bragg Institute, Australian Nuclear Science and Technology Organization, Lucas Heights, N.S.W. (Australia).* [b]*Department of Chemistry, National Dong Hwa University, Hualien, (Taiwan). R.O.C.* E-mail: Alison.Edwards@ansto.gov.au

The encapsulation of hydride inside high nuclearity copper (and silver) chalcogenide clusters has been pursued at length to elucidate fundamental aspects of the behaviour of hydride compared to heavier closed shell anions. Recently the Liu group has published a series of hydride centered tetra-capped tetrahedral copper and silver clusters surrounded by six dichalcophosphate ligands $\{E_2P(OR_2)^-$, E = S[1], Se[2]$\}$. Although all the experimental evidence presented including single crystal X-ray diffraction, proton and deuterium NMR, and ESI-mass spectrometry are entirely consistent with incorporation of hydride within (and central to) the cluster, reports of this interpretation of the available data have met resistance in refereeing and publication due to the perceived difficulty in unequivocally assigning the hydride atomic site.

We are now pleased to report that we have successfully collected and analyzed single crystal neutron Laue diffraction data for a $Cu_7(H)(dtc)_6$ [dtc = S_2C(aza-15-crown-5)] cluster compound, which is formed from the reaction of $[Cu_8(H)(dtc)_6]^+$ with BH_4^-, and from this data we can definitively locate the hydride at the centre of the cluster, concordant with the apparent position derived from X-ray crystallographic data as shown in Figure 1 demonstrating the geometry of the cluster deltahedron.

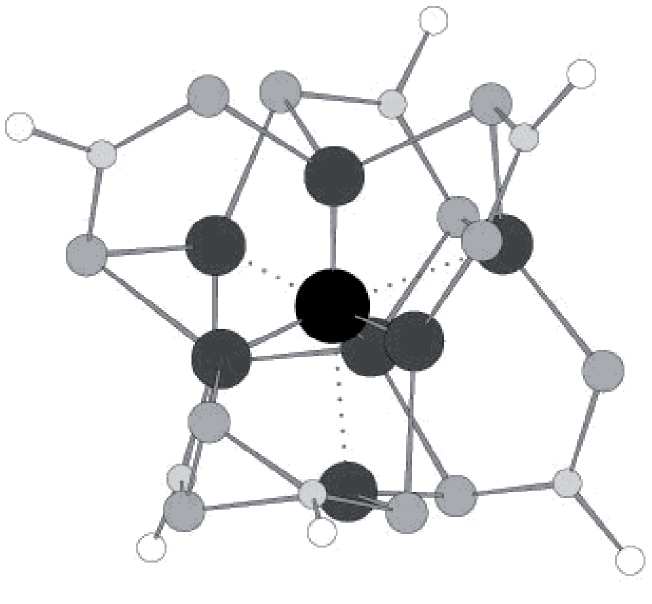

Figure 1: the copper cluster deltahedron: H=black Cu=darkgrey S=midgrey C=lightgrey N=white

Recent advances in neutron diffraction methods – in particular the resurgence of the Laue method has facilitated this study but the size requirement for neutron diffraction studies can still present a formidable obstacle to a chemist possessed of a novel and otherwise thoroughly characterized material. In addition to revealing the detail of this particular structure determination, the question of the adequacy of the apparent hydride position derived from X-ray diffraction studies will be addressed.

[1] (a) P.-K. Liao, B. Sarkar, H.-W Chang, J.C. Liu Wang, C.W. *Inorg. Chem.*