Microsymposia

MS.61.1  
Supramolecular assembly based on multinuclear silver(i) ethynide synthons  
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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 ligatation 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, N3, 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 dπ-dπ 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 C2− dianion (ethynediide, also named acetyleneidide, ) an iso-electronic structural analog of CN, N3, and NO. In a wide variety of novel double, triple, and quadruple silver(I) salts, the dumbbell-like C≡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 (α, π) interactions with four or five vertices. We then expanded the scope to synthesize silver(I) complexes of the homologous all-carbon analog of CN, the C≡C−(1,3-butadiyne-1,4-diide) ligand and related ethynide species R−C≡C−R′ (R = alkyl, aryl, heteroaryl), thereby establishing the identity and synthetic utility of the multinuclear metal-ligand supramolecular synthons C≡C−Agn (n = 4, 5), Ag−C≡C−C≡C−Ag, and R−C≡C−Ag (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≡C−Ag 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, 404205, 404208 and 402710.


Keywords: argentophilicity, silver, supramolecular synthon

MS.61.2  
Polycoordinate hydride inside a Cu cluster authenticated by neutron diffraction  
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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 dichalcogenophosphate ligands [E2P(OR)3, 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 Cu2(H)(dttc), [dttc = S2C(aza-15-crown-5)] cluster compound, which is formed from the reaction of Cu2(H)(dttc)n with BH3, and from this data we can definitively locate the hydride at the centre of the cluster, concurrent 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.

Microsymposia

MS.61.3

Germynes: high resolution X-ray data for unambiguous ligand identification
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Despite the long-term chemical interest in low-valent germanium compounds, they are difficult to synthesize and even more difficult to crystallize. Roeky et al. successfully prepared a series of germynes, LGeX (X = OH (1), NH (2), H (3), L = CH(CHMe)(2)-Pr (C6H5)N(3)) [1-3] and studied their fascinating reactivity. Group 14 carbene analogues are known to activate chemically inert entities and therefore represent potent catalysts. [3-5] Single crystals of the entire germylene series were successfully obtained and their structure determination gave first insights into the bonding of the Ge(II) entity. For a deeper understanding of the catalytic properties it is inevitably important to clarify the nature of the bonding interactions, together with the non-bonding ones, could easily explain the observed facts, although large basis sets and different hybrid functionals were used [5]. However, further QTAIM studies on the same model, well as on [(CO)4Mn{(PPPh3)2CH-S-S-CH(PPPh3)2}Mn(CO)4] [1] and [(CO)4Mn{(PPPh3)2CH-Se-Se-CH(PPPh3)2}Mn(CO)4] [2], theoretical electron density calculations have been performed in order to explain the interesting and anomalous features observed in the NMR spectra of such compounds, as compared with their mono- and poly-(S,Se)-bridged counterparts.

The most recent QTAIM calculations, performed on the theoretically optimized geometries of [(CO)4Mn{(PPPh3)2CH-S-S-CH(PPPh3)2}Mn(CO)4] [5], [(CO)4Mn{(PPPh3)2CH-Se-Se-CH(PPPh3)2}Mn(CO)4] [5], and [(CO)4Mn{(PPPh3)2CH-Se-Se-CH(PPPh3)2}Mn(CO)4] [5] show the existence of non-bonding interactions involving CH-X-X-C, as evidenced from their delocalization indexes and other topological parameters [2].

The more thorough investigation involved the most powerful rotating anode generator with confocal multilayer optics. The final high resolution data set revealed crystallographic details which are the key to understand some of the chemical features inherent to compounds.

Keywords: germylene, single crystal x-ray data comparison, high resolution data


Keywords: topological_analysis, theoretical electron_density, organometallic_compounds.

MS.61.4

Theoretical QTAIM study on S- and Se-bridged polynuclear Mn complexes
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Starting from the standard X-ray diffraction experimental geometries of [(CO)4Mn{(PPPh3)2CH-S-S-CH(PPPh3)2}Mn(CO)4] [1] and [(CO)4Mn{(PPPh3)2CH-Se-Se-CH(PPPh3)2}Mn(CO)4] [2], theoretical electron density calculations have been performed in order to explain the interesting and anomalous features observed in the NMR spectra of such compounds, as compared with their mono- and poly-(S,Se)-bridged counterparts.

Preliminary DFT calculations on the simplified cation model [(CO)4Mn{(PPPh3)2CH-S-S-CH(PPPh3)2}Mn(CO)4] [1] could not fully explain the observed facts, although large basis sets and different hybrid functionals were used [3]. However, further QTAIM studies on the same model as well as on [(CO)4Mn{(PPPh3)2CH-Se-Se-CH(PPPh3)2}Mn(CO)4] [2] showed the existence of non-bonding interactions involving CH-X-X-C (X = S, Se) central groups, as evidenced from their delocalization indexes and other topological parameters [2].

The most recent QTAIM calculations, performed on the theoretically optimized geometries of [(CO)4Mn{(PPPh3)2CH-S-S-CH(PPPh3)2}Mn(CO)4] [5] and [(CO)4Mn{(PPPh3)2CH-Se-Se-CH(PPPh3)2}Mn(CO)4] [5] show the presence of additional small interactions between CH groups and phenyl hydrogen atoms, as reflected in the bond critical points and bond paths detected (see Figure). Such bonding interactions, together with the non-bonding ones, could easily explain the anomalous 1H-NMR displacements observed for the CH groups.

Keywords: topological_analysis, theoretical electron_density, organometallic_compounds.