Preparation, Identification, and *X*-Ray Structure of a Novel High-nuclearity Heterometallic Anionic Ag_6Cu_7 Cluster

Omar M. Abu-Salah[a], **M. Sakhawat Hussain,***[b] **and Elmer O. Schlemper**[c]

Departments of Chemistry, [a] *College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia*
[b] *King Fahd University of Petroleum and Minerals, P.O. Box 1830, Dhahran 31261, Saudi Arabia*
[c] *University of Missouri, Columbia, 65211 Missouri, U.S.A.*

A novel silver–copper anionic cluster $[Ag_6Cu_7(C_2Ph)_{14}]^-$ has been synthesized from the reaction of $[PhC_2AgC_2Ph]^-$ and a mixture of $[AgC_2Ph]_n$ and $[CuC_2Ph]_n$; Its structure constitutes a central linearly co-ordinated copper atom linked through Cu–Ag interactions to three tetranuclear $[Ag_2Cu_2(C_2Ph)_4]$ subclusters, and within each unit of the sub-cluster, copper and silver atoms are bonded through metal–metal interactions and *via* bridged phenylethynyl ligands.

We have reported recently the syntheses and structures of $[Au_3Cu_2(C_2Ph)_6]^-$ and $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$ as representatives of two classes of clusters between Group 1B metal arylacetylides.[1,2] We now report the synthesis and *X*-ray structure† of a novel heterometallic cluster anion in $[(Ph_3P)_2N][Ag_6Cu_7(C_2Ph)_{14}]$. Bis(phenylethynyl)copper(I), which was found recently[3] to be a useful ethynylating agent for some gold(I) and platinum(II) complexes, serves as a nucleus in building up the cluster when treated with a mixture of phenylethynylsilver and phenylethynylcopper. Thus stirring $[PhC_2AgC_2Ph]^-$ with a mixture of $[AgC_2Ph]_n$ and $[CuC_2Ph]_n$ (1:4:4 mol ratio) in dichloromethane at room temperature resulted in an immediate orange-red colouration, and a clear solution was obtained within 20 minutes. Filtration and addition of pentane effected the formation of orange-red crystals of $[(Ph_3P)_2N][Ag_6Cu_7(C_2Ph)_{14}]$ in high yield (65%).

Elemental analysis and the ^1H n.m.r. spectrum are in agreement with the above formula. The latter indicated two types of aromatic protons having distinct chemical shifts in the ratio 3:7 with the phenylacetylide protons being at higher field. The i.r. spectrum revealed a broad $\nu(C{\equiv}C)$ band at *ca.* 2045 cm^{-1} characteristic of π-complexed acetylides.

Single crystal *X*-ray structure determination revealed the arrangement of metal atoms in the anionic Ag_6Cu_7 cluster as shown in Figure 1. Two each of silver and copper atoms are bonded alternately in a rectangular (or nearly square)

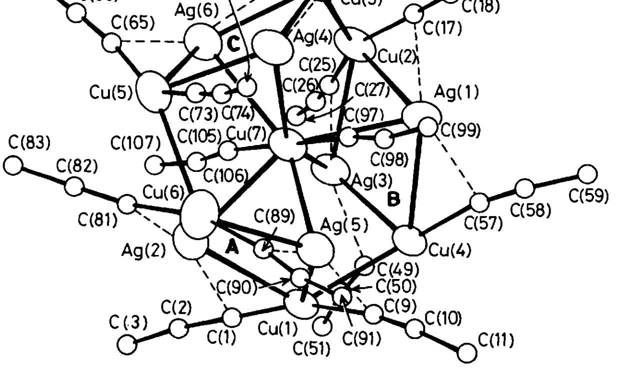

Figure 1. The molecular structure of $[Ag_6Cu_7(C_2Ph)_{14}]^-$ anion. Only one carbon atom of the phenyl groups is shown. The carbon–silver bridges are shown as dotted lines and the three sub-clusters are labelled as A, B and C. Atoms in the $[(Ph_3P)_2N]^+$ cation are well beyond the bonding distance.

---

† *Crystal data:* $[(Ph_3P)_2N][Ag_6Cu_7(C_2Ph)_{14}]$; $M = 3091$, monoclinic, space group $P2_1/n$, $a = 13.950(3)$, $b = 34.787(8)$, $c = 25.681(4)$ Å, $\beta = 99.03(4)°$, $U = 12308(1)$ Å^3, $Z = 4$, $D_c = 1.67$ g/cm^3, $\mu(\text{Mo-}K_\alpha) = 21.7$ cm^{-1}. Data were collected with Mo-K_α radiation on a CAD4-SDP82 diffractometer system. A total of 9667 unique reflections were measured; 4607 with $I > 2\sigma(I)$ were used for structure solution by direct method (MULTAN82). Data were corrected for Lorentz and polarization effects and for absorptions. Only copper, silver, and phosphorus atoms were refined anisotropically whereas carbon and hydrogen atoms were isotropic. The agreement factor at the present stage of refinement is 0.092. Full details will be published elsewhere. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

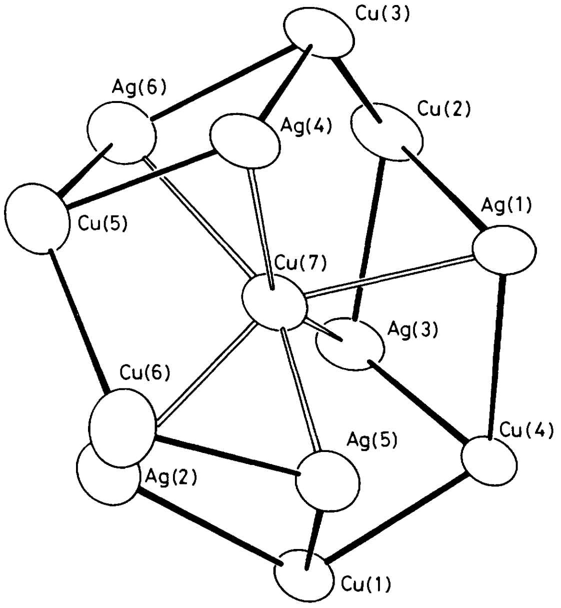

Figure 2. The central heterometallic core of the cluster.

geometry, forming three tetranuclear Ag_2Cu_2 sub-clusters interlinked through copper–copper bonds enclosing the seventh copper atom which itself is engaged in Cu–Ag interactions with all six silver atoms in the sub-clusters. The overall structure can be viewed as an 'open basket' type arrangement resulting from wrapping of three interlinked Ag_2Cu_2 sub-clusters around a copper atom. The average silver–copper distance in the three sub-clusters is 2.786 Å. The average length of the Cu–Cu bonds linking the sub-clusters is 2.826 Å, which is intermediate in the ranges of Cu–Cu separation observed[4] in copper clusters and about 0.27 Å longer than the length in copper metal (2.556 Å). There are no bonding interactions between the central copper atom Cu(7) and other copper atoms. All Cu(7) - - - Cu distances are more than 3.50 Å, whereas the Cu(7)–Ag distances lie in the range 2.915—3.070 Å with a mean value of 2.972 Å. The Ag–Cu interactions are significant for the formation and wrapping of the sub-clusters around the central copper atom, whereas the Cu–Cu interactions are important for interlinking the three sub-cluster units. The overall effect of these interactions should play a dominant role both in the formation and ultimate stability of the metallic core (Figure 2) of the anionic cluster.

Each copper atom is end-on σ-bonded to two ethynyl carbons from two acetylide groups in almost linear co-ordination. The average Cu–C distance is 1.861 Å which is significantly shorter than the Ag–C distances ranging from 2.168 to 2.289 Å. Each silver atom is side-on π-bonded to two alkyne groups, attached to the adjacent copper atoms with Ag–C distance ranging from 2.182 to 2.289 Å for the carbon atoms at β-position and above 2.650 Å for the carbons at α-position to the phenyl ring. Twelve of the fourteen acetylide groups are α-bonded to six copper atoms and act as bridging groups between copper and silver atoms in the three Ag_2Cu_2 sub-cluster units. The remaining two are non-bridging and are σ-bonded to the central 8-co-ordinated copper atom. As usually observed in these clusters, the phenyl rings surround the metallic core of the Ag_6Cu_7 cluster almost entirely covering the inner core with an extensive carbon backbone.

The structure of this cluster is novel because: (a) of its unique bonding pattern; (b) bonding similar to that of the central copper atom is not commonly observed; (c) it is the first high nuclearity heterometallic Ag–Cu cluster reported structurally; and (d) the average Cu–C bond distances are significantly shorter than usually observed.

One of the authors (O. M. A. S.) is grateful to Prof. M. F. Hawthorne, Department of Chemistry, UCLA for providing research facilities and to King Saud University for sabbatical leave. M. S. H. thanks the KFUPM Research Committee for its support of this work.

Received, 17th December 1986;‡ Com. 1790

References

1 O. M. Abu-Salah, A. R. Al-Ohaly, and C. Knobler, *J. Chem. Soc., Chem. Commun.*, 1985, 1502.
2 O. M. Abu-Salah and C. Knobler, *J. Organomet. Chem.*, 1986, **302**, C10—C12.
3 O. M. Abu-Salah, A. R., Al-Ohaly, and H. A. Al-Qahtani, *Inorg. Chim. Acta*, 1986, **117**, L29—L30.
4 P. K. Mehrotra and R. Hoffmann, *Inorg. Chem.*, 1978, **17**, 2187.

---

‡ Received in revised form, 16th September 1987.