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A novel high nuclearity bimetallic cluster: the crystal structure of $[N(PPh_3)_2][Ag_6Cu_7(C_2Ph)_{14}]$

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Abstract

An X-ray diffraction study of the high nuclearity complex $[N(PPh_3)_2][Ag_6Cu_7(C_2Ph)_{14}]$ has shown it to be a novel 13-atom bimetallic anionic cluster $[Ag_6Cu_7(C_2Ph)_{14}]^-$ with two types of copper atoms, one inside the body of the cluster and six on its surface. The surface atoms have a distorted trigonal bipyramidal geometry whereas the internal copper atom is linearly coordinated by two C_2Ph groups in addition to displaying six Cu–Ag bonding interactions with three tetranuclear $[Ag_2Cu_2(C_2Ph)_4]$ subclusters. Thus the internal copper atom essentially exhibits eight-coordination. All the silver atoms have a bent two-coordinate geometry as far as Cu–Ag–Cu metal bonding is concerned. These atoms are also asymmetrically π bonded to alkyne groups on the phenyl moieties attached to the adjacent copper atoms. This complex represents a new class of Group 1B metal clusters with a bonding pattern not observed previously.

1. Introduction

High nuclearity, close-packed, heterometallic cluster compounds have recently attracted considerable attention, particularly in relation to catalysis and surface science [1,2]. The synthesis, characterization and structures of the pentanuclear anionic cluster $[Au_3Cu_2(C_2Ph)_6]^-$, the tetranuclear cluster $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$, the novel high nuclearity bimetallic cluster $[Ag_6Cu_7(C_2Ph)_{14}]^-$ and the analogous trimetallic cluster $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ have recently been reported [3–5]. We have also published a preliminary communication [6] on the structure of the 13-atom anionic cluster $[Ag_6Cu_7(C_2Ph)_{14}]^-$, which was prepared by the reaction of the linear complex $[Ag(C_2Ph)_2]^-$ and a mixture of $[\{Cu(C_2Ph)_n\}_n]$ and $[\{Ag(C_2Ph)_n\}_n]$. This cluster represents a new type of species formed from Group 1B metal arylacetylides and so knowledge of its molecular structure would seem desirable. We report below the results of a single-crystal X-ray diffraction study of $[N(PPh_3)_2][Ag_6Cu_7(C_2Ph)_{14}]$ which contains the 13-atom anionic cluster $[Ag_6Cu_7(C_2Ph)_{14}]^-$.

2. Experimental details

The compound was prepared by the procedure reported recently in ref. 6. The crystal structure determination was carried out with a spherical crystal of about 1.87 mm^3 volume mounted on a glass fibre in an arbitrary orientation. The same crystal was used for lattice and intensity data measurements. The lattice parameters were obtained from a least-squares (LS) refinement of the setting angles of 25 reflections with $2\theta > 25°$ and located by the programme SEARCH in a CAD4-SDP diffractometer system. The crystal density was measured by the flotation method. Intensity data were collected with an Enraf–Nonius CAD4-SDP diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) and the zigzag method in the ω–2θ scan mode. Background counts were measured for half the total scan time by extending the scan range by 25% on either side of the scan limits. Three standard reflections were monitored every 6000s of X-ray

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TABLE 1. Crystal data and details of data collection and structure solution and refinement for $[N(PPh_3)_2][Ag_6Cu_7(C_2Ph)_{14}]$

Formula	$Ag_6Cu_7P_2NC_{148}H_{100}$
F.W.	3047
Space group	$P2_1/n$
a	13.950(3) Å
b	34.787(8) Å
c	25.681(4) Å
β	90.03°
U	12308(8) Å^3
Z	4
D_{obs}	1.69 g cm^{-3}
D_{calc}	1.668 g cm^{-3}
$F(000)$	6040
Crystal shape	Spherical
Crystal size	1.2 mm × 1.2 mm × 1.3 mm
Wavelength MoKα	0.71073 Å
Max. 2θ limit	36.6°
Min. *hkl* values	$h = 0, k = 0, l = -22$
Max. *hkl* values	$h = 12, k = 30, l = 22$
Interval for measuring standard reflection	75
Absorption coefficient μ	22 cm^{-1}
Min. and max. decay corrections	0.8274, 0.9995
Min. and max. transmission factors	89.25, 99.98
Total no. of reflections measured, including standards	9667
No. of unique reflections	9143
No. of observed reflections	4607
Criterion for observed reflections	$I > 2\sigma(I)$
Method for structure solution	MULTAN 82
Use of F or F^2 in LS refinement	F^2
Method of hydrogen positions	Calculated and ΔF map positions
No. of variables refined	732
Value of R	0.058
Value of $R(w)$	0.062
Ratio of max. shift to error	1.58
Error in observation of unit weight	2.22
Extinction coefficient	1.0×10^{-6}
Max. height in final ΔF map	< 0.91 e Å^{-3}
Computer program used	SDP 82

exposure time. No crystal deterioration was observed over the entire period of data collection. The intensities were corrected for the background, Lorentz and polarization effects, crystal decay and absorption corrections. The absorption corrections were based on ψ scans of six reflections. The structure was solved with MULTAN and some metal atom positions were further confirmed by the heavy atom method. A difference Fourier (ΔF map) phased on the metal atoms revealed the positions of the atoms in the cation $[N(PPh_3)_2]^+$ and most of the carbon atoms of the anionic cluster. The remaining carbon atoms were obtained by successive ΔF maps. The silver, copper and phosphorus atoms were refined anisotropically and the other atoms isotropically. Several hydrogen atoms were located from the ΔF maps and the remainder were placed in calculated positions. The lattice parameters, intensity data collection parameters and details of the solution and refinement of the structure are given in Table 1. Final atomic coordinates for the metal atoms along with their B_{eq} values are listed in Table 2. The anisotropic thermal parameters; the positional and thermal coordinates for the non-metal atoms and the structure factors are available from the authors.

3. Results and discussion

Selected interatomic distances and angles for $[Ag_6Cu_7(C_2Ph)_{14}]^-$ are listed in Table 3, where similar bond lengths and angles in each subcluster are grouped together for comparison purposes. The structural analysis shows the presence in $[Ag_6Cu_7(C_2Ph)_{14}]^-$ of one internal and 12 surface metal atoms as depicted in Fig. 1, with the inner metallic core shown in Fig. 2. There are 14 C_2Ph groups attached to 13 metal atoms. Twelve of the C_2Ph groups are σ bonded to six peripheral (surface) copper atoms, Cu(1) to Cu(6), in almost linear fashion. These groups also act as bridging moieties between copper and the adjacent silver atoms in the three tetranuclear subclusters $[Ag_2Cu_2(C_2Ph)_4]$, one of which (cluster A) is shown in Fig. 3. The silver atoms are within π-bonding distance of the two C_2Ph units bonded to the adjacent copper atoms. The remaining two C_2Ph units are σ bonded to the bulk Cu(7) atom. The overall structure can be viewed in terms of three slightly skewed tetranuclear $[Ag_2Cu_2(C_2Ph)_4]$ subclusters, labelled A, B and C in Figs. 1 and 2, interlinked through copper–copper bonds entrapping the bulk

TABLE 2. Atomic coordinates for metal atoms of inner core of $[Ag_6Cu_7(C_2Ph)_{14}]^-$ anionic cluster

Atom	x	y	z	B_{eq} (Å^2)
Ag(1)	0.4250(2)	0.1811(9)	0.6650(1)	5.98(8)
Ag(2)	0.1775(2)	0.1031(8)	0.7920(1)	5.79(8)
Ag(3)	0.2926(2)	0.2117(9)	0.7420(1)	5.75(8)
Ag(4)	0.5228(2)	0.0795(9)	0.7662(1)	6.08(8)
Ag(5)	0.2212(2)	0.0871(8)	0.6739(1)	5.77(8)
Ag(6)	0.4787(2)	0.1358(9)	0.8549(1)	6.26(9)
Cu(1)	0.1033(3)	0.1459(1)	0.6981(2)	4.9(1)
Cu(2)	0.4950(3)	0.2166(1)	0.7599(2)	5.5(1)
Cu(3)	0.6016(3)	0.1531(1)	0.7805(2)	5.5(1)
Cu(4)	0.2251(3)	0.1850(1)	0.6413(2)	4.6(1)
Cu(5)	0.4170(4)	0.0606(1)	0.8480(2)	6.4(1)
Cu(6)	0.2522(3)	0.0375(1)	0.7615(2)	5.5(1)
Cu(7)	0.3538(3)	0.1315(1)	0.7501(2)	5.1(1)

TABLE 3. Some relevant bond lengths (Å) and angles (°) for the $[Ag_6Cu_7C_2Ph)_{14}]^-$ cluster. Bond lengths and angles of the same type within each sub-cluster are grouped together. Estimated standard deviations are given in parentheses

Subcluster A			
Cu(1)–Ag(2)	2.884(5)	Cu(1)–C(1)	1.757(6)
Cu(1)–Ag(5)	2.760(6)	Cu(1)–C(9)	1.866(7)
Cu(6)–Ag(2)	2.678(5)	Cu(6)–C(81)	1.960(6)
Cu(6)–Ag(5)	2.824(6)	Cu(6)–C(89)	1.892(5)
Cu(1)–Cu(4)	2.765(5)		
Cu(6)–Cu(5)	3.044(6)		
Ag(2)–C(1)	2.223(7)	Ag(2)–C(81)	2.252(6)
Ag(5)–C(89)	2.248(6)	Ag(5)–C(9)	2.353(7)
Ag(2)–Cu(1)–Ag(5)	70.2(7)	Ag(2)–Cu(6)–Ag(5)	72.2(7)
Cu(1)–Ag(2)–Cu(6)	107.5(6)	Cu(1)–Ag(5)–Cu(6)	107.0(8)
Ag(2)–Cu(1)–Cu(4)	121.7(7)	Ag(5)–Cu(6)–Cu(5)	115.2(7)
Ag(2)–Cu(6)–Cu(5)	81.1(7)	Ag(5)–Cu(1)–Cu(4)	78.8(7)
C(1)–Cu(1)–C(9)	158.0(7)	C(81–Cu(6)–C(89)	164.5(8)
Cu(1)–C(1)–Ag(2)	92.1(8)	Cu(1)–C(9)–Ag(5)	80.8(7)
Cu(6)–C(8)–Ag(2)	79.4(7)	Cu(6)–C(89)–Ag(5)	85.5(6)
Cu(1)–C(9)–C(10)	163.0(9)	Cu(1)–C(1)–C(2)	167.9(7)
Cu(6)–C(81)–C(82)	154.5(6)	Cu(6)–C(89)–C(90)	175.5(6)
Cu(1)–Ag(2)–C(81)	152.8(8)	C(9)–Ag(5)–C(89)	143.1(7)
Subcluster B			
Cu(2)–Ag(1)	2.771(6)	Cu(2)–C(17)	1.882(7)
Cu(2)–Ag(3)	2.793(5)	Cu(2)–C(25)	1.919(7)
Cu(4)–Ag(1)	2.763(7)	Cu(4)–C(57)	1.861(7)
Cu(4)–Ag(3)	2.770(6)	Cu(4)–C(49)	1.887(8)
Cu(2)–Cu(3)	2.670(6)		
Ag(1)–C(17)	2.289(7)	Ag(1)–C(57)	2.269(8)
Ag(3)–C(25)	2.249(6)	Ag(3)–C(49)	2.218(7)
Ag(1)–Cu(2)–Ag(3)	67.7(6)	Ag(1)–Cu(4)–Ag(3)	68.1(8)
Ag(1)–Cu(2)–Cu(3)	85.0(9)	Ag(3)–Cu(4)–Cu(1)	79.6(8)
Cu(4)–Ag(1)–Cu(2)	112.1(8)	Cu(4)–Ag(3)–Cu(2)	111.2(9)
Ag(3)–Cu(2)–Cu(3)	119.9(7)	Ag(1)–Cu(4)–Cu(1)	122.9(7)
C(17)–Cu(2)–C(25)	152.9(8)	C(49)–Cu(4)–C(57)	150.3(7)
Cu(2)–C(17)–Ag(1)	82.6(7)	Cu(2)–C(25)–Ag(3)	83.8(8)
Cu(4)–C(49)–Ag(3)	84.5(8)	Cu(4)–C(57)–Ag(1)	83.4(7)
Cu(2)–C(17)–C(18)	178.7(9)	Cu(2)–C(25)–C(26)	171.4(6)
Cu(4)–C(57)–C(58)	172.9(8)	Cu(4)–C(49)–C(50)	166.6(7)
C(57)–Ag(1)–C(17)	149.1(8)	C(25)–Ag(3)–C(49)	142.3(7)
Subcluster C			
Cu(3)–Ag(4)	2.790(5)	Cu(3)–C(33)	1.835(7)
Cu(3)–Ag(6)	2.826(7)	Cu(3)–C(41)	1.759(8)
Cu(5)–Ag(4)	2.828(7)	Cu(5)–C(65)	1.878(7)
Cu(5)–Ag(6)	2.748(8)	Cu(5)–C(73)	1.838(7)
Ag(4)–C(33)	2.294(6)	Ag(4)–C(73)	2.215(7)
Ag(6)–C(41)	2.182(6)	Ag(6)–C(65)	2.168(8)
Ag(4)–Cu(3)–Ag(6)	67.9(8)	Ag(4)–Cu(5)–Ag(6)	68.5(7)
Ag(6)–Cu(3)–Cu(2)	86.1(7)	Ag(6)–Cu(5)–Cu(6)	119.6(7)
Cu(3)–Ag(4)–Cu(5)	110.8(8)	Cu(3)–Ag(6)–Cu(5)	112.1(6)
Ag(4)–Cu(5)–Cu(6)	86.6(6)	Ag(4)–Cu(3)–Cu(2)	122.6(7)
C(33)–C(3)–C(41)	154.8(6)	C(65)–Cu(5)–C(73)	149.6(7)
Cu(3)–C(41)–Ag(6)	91.0(7)	Cu(5)–C(73)–Ag(4)	87.9(7)
Cu(3)–C(33)–Ag(4)	84.2(8)	Cu(5)–C(65)–Ag(6)	85.3(7)
Cu(3)–C(33)–C(34)	176.2(6)	Cu(3)–C(41)–C(42)	171.6(8)
Cu(5)–C(65)–C(66)	163.2(8)	Cu(5)–C(73)–C(74)	169.8(8)
C(73)–Ag(4)–C(33)	154.6(7)	Cu(41)–Ag(6)–C(65)	146.9(8)

TABLE 3. (continued)

Coordination around central Cu(7) atom			
Cu(7)–Ag(1)	3.070(5)	Cu(7)–Ag(2)	3.002(6)
Cu(7)–Ag(3)	2.915(5)	Cu(7)–Ag(4)	2.949(5)
Cu(7)–Ag(5)	2.923(7)	Cu(7)–Ag(6)	2.972(7)
Cu(7)–C(97)	1.945(6)	Cu(7)–C(105)	1.959(7)
Ag(1)–Cu(7)–Ag(2)	144.5(8)	Ag(2)–Cu(7)–Ag(3)	95.3(7)
Ag(3)–Cu(7)–Ag(4)	144.7(7)	Ag(4)–Cu(7)–Ag(5)	100.3(8)
Ag(5)–Cu(7)–Ag(6)	148.9(9)	Ag(6)–Cu(7)–Ag(1)	144.1(7)
C(97)–Cu(7)–C(105)	178.5(9)		

copper atom. Each subcluster has a nearly rectangular arrangement of metal atoms with copper–silver bond length ranging from 2.678 to 2.884 Å, indicating an appreciable Cu–Ag metal–metal bonding [1]. There is no bonding interaction between Cu · · · Cu and Ag · · · Ag atoms within any of the subclusters. The structure of the subcluster observed here resembles that of the gold–silver cluster $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$ described previously [4].

The internal copper atom Cu(7) encapsulated in the cage formed by the interlinking subclusters is within the bonding distance of all six silver atoms but beyond that for bonding interaction with any of the surface copper atoms. The average Cu(7)–C bond length of 1.952 Å and C(97)–Cu(7)–C(105) angle of 178.5° indicate a linear copper atom in the $[Cu(C_2Ph)_2]$ moiety which is within the metal–metal bonding distance of the six Ag atoms, thus imposing an unusual eight-coordination geometry on the internal Cu(7) atom. The six Cu(7)–Ag bond lengths range from 2.915 to 3.070 Å (mean value 2.972 Å), indicating a relatively weaker Cu(7)–Ag interaction compared with the range 2.678–2.884 Å for Cu–Ag distances in the subcluster. The two Cu(7)–C(acetylide) bond distance are 1.945 and 1.959 Å, corresponding to quite strong metal–carbon bonds. There are no surface copper atoms within the bonding distance of Cu(7); all the copper atoms lie more than 3.50 Å away from Cu(7). The Cu(7)–Ag interactions contribute towards the wrapping of $[Ag_2Cu_2(C_2Ph)_4]$ subclusters around the internal Cu(7) atom, whereas the Cu–Cu interactions hold the three subclusters in place to form an "open basket" type of arrangement. The overall effect of these interactions must be responsible for the formation and stability of the metallic core of the cluster. In terms of metal frameworks, the structure of the inner metal core can be visualized as an assembly of three square pyramids (Fig. 2) connected at a common apex situated at Cu(7), while the pyramids themselves are connected through copper–copper bonds with an average length of 2.826 Å, which is within the range of Cu–Cu distances usually observed in other copper clusters.

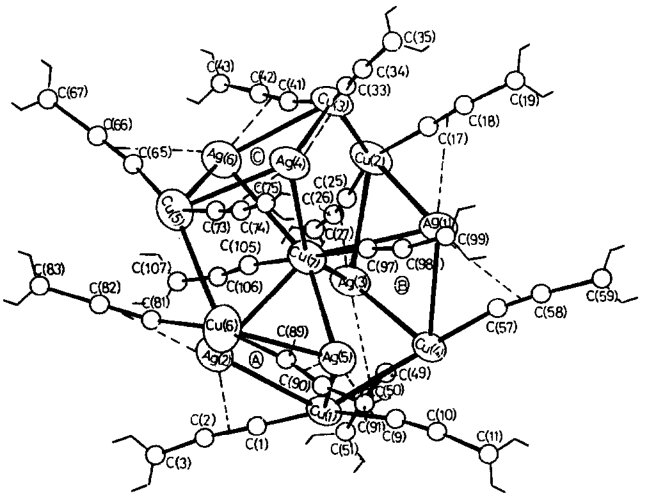

Fig. 1. Molecular structure of $[Ag_6Cu_7(C_2Ph)_{14}]^-$ anionic cluster. Only one carbon atom of the phenyl rings in the C_2Ph groups is shown, the rest of the ring being omitted for clarity. The silver–carbon π bonds are shown as broken lines and the copper–carbon σ bonds as solid lines. The subclusters are labelled A, B and C.

The formation of the 13-atom cluster can be accounted for in terms of the anionic character of the internal copper atom in the linear $[Cu(C_2Ph)_2]$ moiety. The presence of a negative charge raises the energy of the d-electrons of the Group 1B metals and so renders them suitable for further metal–metal bonding. The formation of such metal–metal bonds has been reported previously [7] in binuclear complexes obtained by depolymerization of both gold phenylacetylide and silver *p*-tolylacetylide by use of $[Au(C_2Ph)_2]^-$. Such anion cationic interaction with asymmetric π bonding is an inherent bonding feature of acetylide-containing Group 1B complexes and has been observed previously in several other cluster compounds [8–11].

The Cu–Cu–C angles for the surface copper atoms range from 149.6° to 164.5°. The average σ-bonding (structure **1**) Cu–C distance is 1.861 Å. This distance is significantly shorter than the Ag–C distances of 2.168–

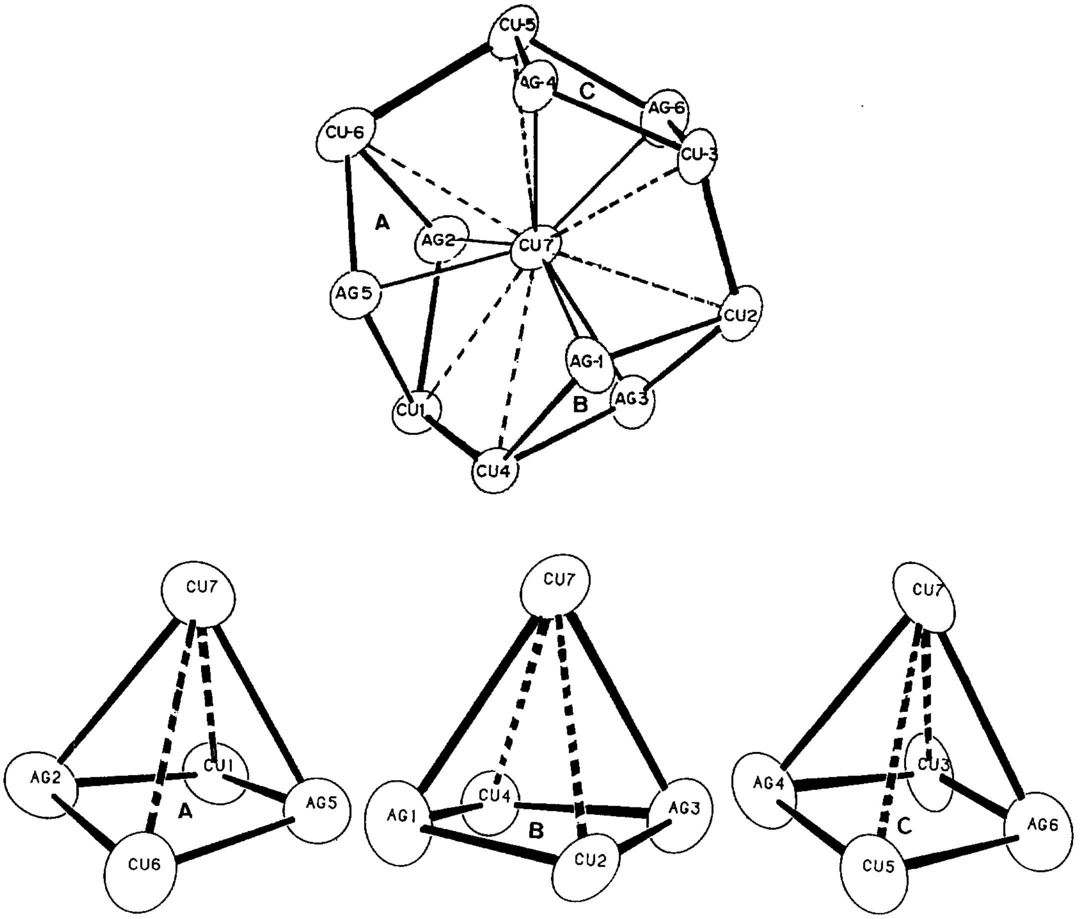

Fig. 2. The inner 13-atom bimetallic core of $[Ag_6Cu_7(C_2Ph)_{14}]^-$ showing eight-coordination around the internal copper atom in the linear $[Cu(C_2Ph)_2]$ moiety. The metal framework can be viewed as an assembly of three distorted square pyramids joined at a common apex at the central Cu(7) atom. Weak metal–metal interactions are indicated by broken lines.

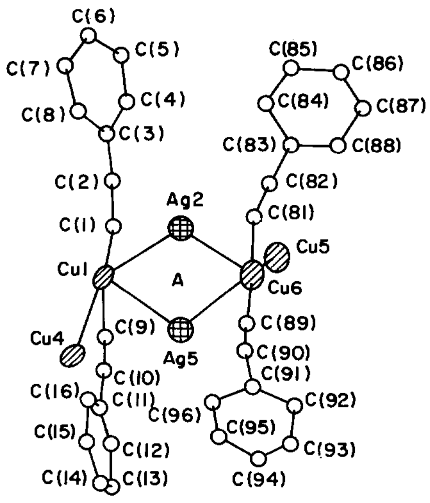

Fig. 3. One of the tetranuclear $[Ag_2Cu_2(C_2Ph)_4]$ subclusters depicting the approximately trigonal pyramidal geometry around the surface copper atoms.

2.289 Å involving the carbon atoms at β positions of C_2Ph groups and those of 2.644–2.849 Å involving the carbon atoms at α positions. In all the C_2Ph groups (except for the two attached to the internal Cu(7) atom) the C≡C moiety lies nearly perpendicular to the Ag–Cu vector, indicating asymmetric π bonding (structure 2) with Ag atoms through the acetylide group.

$$\mathrm{M} \longleftarrow \mathrm{C{\equiv}C{-}R} \qquad \mathrm{M} \longleftarrow \mathrm{C{\equiv}C{-}R}$$

σ bonding
1

M

asymmetric π bonding
2

The C≡C bond lengths, ranging from 1.112 to 1.275 Å, provide further evidence for asymmetric π bonding of the type shown in structure 2, since any contribution from the σ-bonding structure of type 1 with Ag through π-bonding, would result in lengthening of the C≡C bond. A similar bonding pattern with a C≡C bond length of 1.117 Å has also been observed in other clusters [12].

As usual for these compounds, the phenyl rings surround the inner Ag_6Cu_7 metal core, almost covering it entirely with a carbon backbone. The bond lengths and angles in the $[(Ph_3P)_2N]^+$ cation are as expected and the cation lies well outside the bonding distance from the anionic cluster. The phenyl rings are planar and all C–C and C=C bond distances and angles are as expected.

The structure of the $[N(PPh_3)_2][Ag_6Cu_7(C_2Ph)_{14}]$ complex is important because (a) it reveals a previously unknown bonding pattern (eight-coordinated bonding such as displayed by the internal copper atom is uncommon) and (b) it is the first high nuclearity bimetallic Ag–Cu cluster to be structurally characterized.

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