

Cluster Rotamerism of a 25-Metal-atom Cluster $[(\text{Ph}_3\text{P})_{10}\text{Au}_{13}\text{Ag}_{12}\text{Br}_8]^+$ Monocation: A Molecular Rotary Unit

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Crystallographic studies of the title cluster in two crystal forms containing different anions $[\text{SbF}_6^-$ and Br^- (this work)] revealed two distinct rotamers with different metal configurations — *ses* and *sss*.

Recently, we reported the synthesis and structure of a 25-metal-atom cluster $[(\text{Ph}_3\text{P})_{10}\text{Au}_{13}\text{Ag}_{12}\text{Br}_8]^+$ as the SbF_6^- salt **1a**.¹ The metal core can be described as two icosahedra sharing a common vertex. The four metal pentagons are arranged in a staggered–eclipsed–staggered (*ses*) configuration [Fig. 1(a)]. We now report a staggered–staggered–staggered (*sss*) conformer [Fig. 1(b)] of the same cluster as the Br^- salt **1b**. The observation of both conformers (*ses* and *sss*) for the same (title) cluster **1** establishes a new type of rotamerism[†] in clusters. It occurs to us that the metal core of this class of clusters may conceptually be described as a biicosahedral rotor.² In this regard, cluster **1** may also serve as a prototype for a molecular rotary unit.^{2–4}

The title compound, as the Br^- salt **1b**, was prepared by reducing a mixture of $(\text{Ph}_3\text{P})\text{AuBr}$ and $[(\text{Ph}_3\text{P})\text{AgBr}]_4$ ⁵ ($\text{Au} : \text{Ag} = 1 : 1$) with NaBH_4 in absolute ethanol; the product was purified by recrystallization from ethanol/hexane. Fig. 2(a) and (b) depict the $\text{Au}_{13}\text{Ag}_{12}$ metal core and the $[\text{P}_{10}\text{Au}_{13}\text{Ag}_{12}\text{Br}_8]$ framework of **1b**, respectively.[‡] There are

ten triphenylphosphine and eight bromide ligands. The ten phosphine ligands coordinate to ten peripheral (surface) Au atoms in a radial fashion. As for the eight bromide ligands, two are terminal, while the remaining six are bridging, as shown in Fig. 2(b). The six bridging bromide ligands are arranged in an unprecedented fashion (two triply bridging and four doubly bridging) as depicted in Fig. 2(c).

It is interesting to compare the bridging ligand arrangements in **1a**, **1b** and $[(p\text{-tol}_3\text{P})_{10}\text{Au}_{13}\text{Ag}_{12}\text{Br}_8]^+$, as the PF_6^- salt **2**,⁶ which also has an *sss* metal configuration, as depicted in Fig. 3 (a), (b) and (c), respectively. Here we show the projection of the two silver pentagons onto the plane of the six bridging Br ligands. We note that the six Br ligands in **1a** [Fig. 3(a)] form a highly distorted hexagon connecting the two Ag pentagons. As a result, one quadruply(q) and five doubly(d) bridging bromides (qd_5) are observed. (This bridging arrangement can also be described as *ortho*- q_2d_4 if we consider one of the doubly bridging bromide ligands as semiquadruply bridging.) As shown in Fig. 3(b), a relative rotation of 36° of the two Ag pentagons (about the idealized fivefold axis) of the *ses* metal configuration (as in **1a**) gives rise to the *sss* metal

[†] In organic chemistry, *conformers* (conformational isomers) are defined as different structures of the same molecule which are interconvertible by free rotation about a bond whereas *stereoisomers* (configurational isomers) are different structures which are not interconvertible. Draft IUPAC nomenclature defines *rotamer* as one of a set of *conformers* arising from restricted rotation about one single bond. In this paper, we have extended this to encompass a new type of rotamerism with restricted rotation about a common vertex.

[‡] *Crystal data*: data were collected using an Enraf-Nonius diffractometer (Mo-K α radiation). $[(\text{Ph}_3\text{P})_{10}\text{Au}_{13}\text{Ag}_{12}\text{Br}_8]\text{Br} \cdot 3\text{EtOH}$: monoclinic $C2/c$, $a = 33.919(4)$, $b = 26.773(3)$, $c = 21.067(2)$ Å, $\beta = 93.14(3)^\circ$; $V = 19097.6$ Å³, and $Z = 4$. Anisotropic (heavy atoms)-isotropic (carbon atoms) refinement gave $R_1 = 7.6\%$ for 4423 independent reflections ($2\theta \leq 46^\circ$) with $I > 3\sigma$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

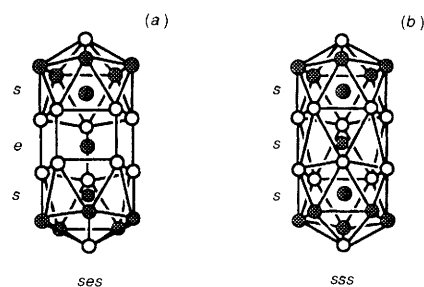


Fig. 1 The two distinct metal cores of the title cluster **1**, depicting different arrangements of the four metal pentagons in (a) the staggered–eclipsed–staggered (*ses*) rotamer **1a** and (b) the staggered–staggered–staggered (*sss*) rotamer **1b**

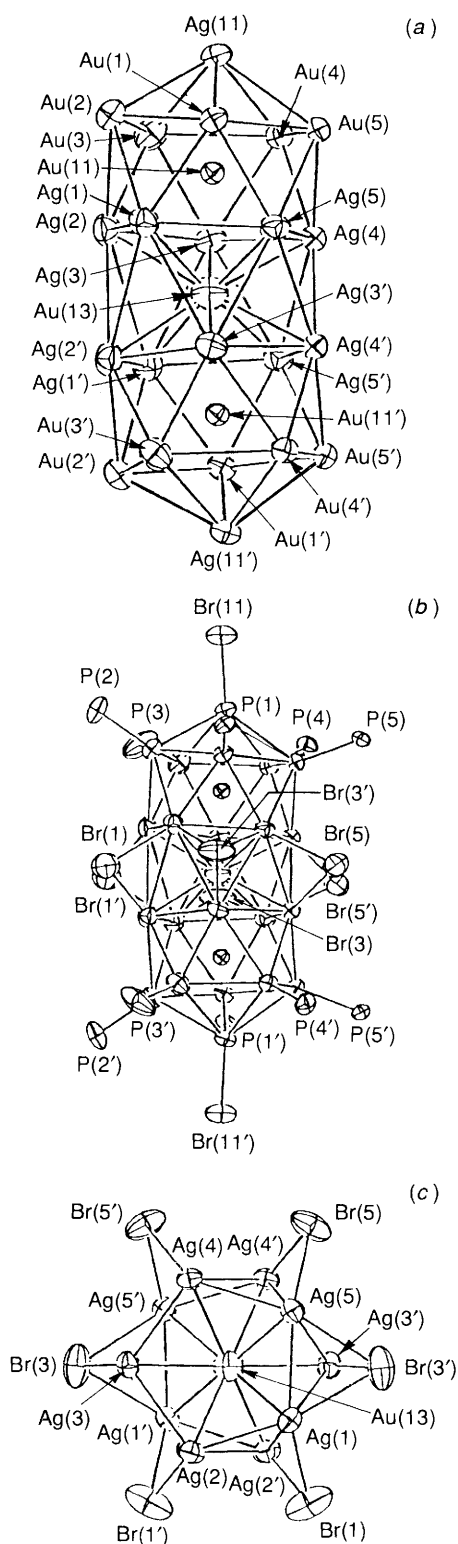


Fig. 2 Molecular architecture of the 25-metal-atom cluster $[(\text{Ph}_3\text{P})_{10}\text{Au}_{13}\text{Ag}_{12}\text{Br}_8]^+$ as the Br^- salt **1b**: (a) the metal core, $\text{Au}_{13}\text{Ag}_{12}$; (b) the metal-ligand framework, $\text{P}_{10}\text{Au}_{13}\text{Ag}_{12}\text{Br}_8$; (c) the projection of the two silver pentagons onto the plane of the six bridging Br ligands. The symmetry-related atoms are designated as primes. The metal core has an idealized fivefold rotation symmetry [passing through Ag(11), Au(11), Au(13), Au(11') and Ag(11')]. All radial bonds (12 each) from Au(11) and Au(11') (centres of icosahedra) have been omitted for clarity. All molecular parameters are normal. The important distances are: Au(11)–Au(n), 2.714(av); Au(11)–Ag(n), 2.849(av); Au(11)–Ag(11), 2.745(5); Au(11)–Au(13), 2.811(2); Au(13)–Ag(n) 2.869(av) where $n = 1-5$; Au–P, 2.30(av); Ag(11)–Br(11), 2.488(8); Ag(1)–Br(1), 2.70(1); Ag(2')–

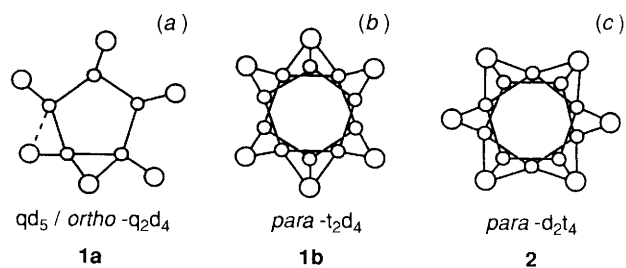


Fig. 3 The projection of the two silver (small circles) pentagons onto the plane of the six bridging halide (large circles) ligands of **1a**, **1b** and **2** (see text). The symbols d, t and q denote doubly, triply and quadruply bridging halide ligands, respectively

configuration (as in **1b**). In this process, the quadruply bridging ligand and one of the doubly bridging ligands in **1a** are transformed into two triply(t) bridging ligands, resulting in the observed *para-t*₂*d*₄ bridging environment in **1b**. Finally, a formal rotation of the nonbonding hexagon formed by the bridging ligands in **1b** by approximately 30° (with respect to the metal core) leads to the *para-d*₂*t*₄ ligand arrangement in **2** [Fig. 3(c)].

The observation of both rotamers (*ses* and *sss*) for the same cluster **1** is a strong indication that the basic building block is indeed the 13-metal-atom centred icosahedral unit, thereby lending further credence to the 'cluster of clusters' concept.^{7,8} More important, however, is the recognition that this cluster series may serve as a prototype for the construction of molecular mechanical rotary devices, with possible utility in nanotechnology.^{3,4,9,10}

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Br(1), 2.54(1); Ag(3)–Br(3), 2.532(8); Ag(1')–Br(3), 2.89(1); Ag(5')–Br(3), 2.86(1); Ag(5)–Br(5), 2.64(1); Ag(4')–Br(5), 2.554(9) Å. The six bridging bromide ligands form a slightly distorted hexagon with nonbonding distances: Br(1)⋯Br(3'), 4.211, Br(3')⋯Br(5), 4.351, Br(1)⋯Br(1'), 4.416, Br(5)⋯Br(5'), 4.621 Å.