

## X-RAY CRYSTAL STRUCTURE OF A DISTORTED TETRAHEDRAL CLUSTER IN THE SALT $[(\text{Ph}_3\text{P})_4\text{Au}_4\text{N}]^+ \text{BF}_4^-$ . GEOMETRICAL INDICATION OF STABLE ELECTRONIC CONFIGURATIONS IN POST-TRANSITION METAL COMPLEXES AND THE MAGIC NUMBER $18\bar{e}$ IN CENTRED GOLD CLUSTERS

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### Summary

According to an X-ray investigation ( $-120^\circ\text{C}$ ,  $\lambda(\text{Mo-K}_\alpha)$ , 6815 reflections, space group  $P2_1/c$ ,  $Z = 4$ ,  $R = 0.068$ ), the cation of the tetraaurated ammonium salt  $[(\text{Ph}_3\text{PAu})_4\text{N}]^+ \text{BF}_4^-$  can be considered as a distorted tetrahedral  $\text{Au}_4(\text{N})$  cluster built up of four linearly coordinated Au atoms with an interstitial N atom (Au–Au 3.012–3.504 Å, Au–N 1.93–2.10 Å). On the basis of the structural data on 14-, 16- and 18-electron mononuclear post-transition metal complexes, the magic number of 18 skeletal electrons can be suggested for  $[\text{Au}_n\text{L}_{n-1}]^{m+}$  clusters with an interstitial Au atom and a quasi-spherical peripheral  $\text{Au}_{n-1}$  polyhedron.

The organometallic and coordination chemistry of post-transition metals is particularly characterized by the frequent violation of the EAN ( $18\bar{e}$ ) rule and the increased stability of underfilled 14- and 16-electron valence shells. Being a typical post-transition metal, gold forms all the types of mononuclear complexes known in coordination chemistry, viz. complexes with 14, 16 and  $18\bar{e}$  in the valence shell of the Au atoms [1,2]. The peculiar stereochemical feature of 14-electron  $\text{Au}^{1+}$  derivatives is the capability of linearly coordinated gold atoms to an additional  $\text{Au} \cdots \text{Au}$  bonding interaction at interatomic distances of 2.8–3.5 Å [2]. In order to find out the influence of such an interaction on the structure of the earlier prepared tetraaurated ammonium cation [3], we have carried out an X-ray study of its tetrafluoroborate salt,  $[(\text{Ph}_3\text{PAu})_4\text{N}]^+ \text{BF}_4^-$  (I).

Crystals of I are monoclinic,  $a$  17.672(10),  $b$  19.166(9),  $c$  18.985(10) Å,  $\beta$   $96.03(4)^\circ$ ,  $Z = 4$ , space group  $P2_1/c$ . The cell dimensions and intensities of 8562 independent reflections were measured at  $-120^\circ\text{C}$  with a Syntex  $P2_1$  diffractometer ( $\lambda(\text{Mo-K}_\alpha)$ , graphite monochromator,  $\theta/2\theta$  scan,  $2\theta_{\text{max}}$   $46^\circ$ ), absorption-corrected according to [4]. The structure was solved by the direct method using the MULTAN

program and refined by block-diagonal least-squares in anisotropic approximation to  $R = 0.068$ .

The cation I with the preliminary geometrical parameters is shown in Fig. 1. All four Au atoms are linearly coordinated by the  $\text{PPh}_3$  ligands and the interstitial N atom. Three of the gold atoms, Au(1), Au(2) and Au(3), are drawn together to interatomic distances of 3.012–3.160 Å, which are close to those found in the aurated oxonium dimer  $[(\text{Ph}_3\text{PAu})_3\text{O}]_2^{2+}$  (3.032–3.215 Å [5]), but the Au(4) atom is distinctly further away from the three others (3.321–3.504 Å). Therefore the tetrahedral ( $sp^3$ ) environment of the interstitial N atom is strongly distorted (bond angles Au–N–Au 94.3–120.7°). A wide range of metal–metal distances has been observed in the majority of gold clusters [2]. However, the analogous tetramercury derivatives  $(\text{RHg})_4\text{C}$  are characterized by a much narrower range of Hg...Hg distances, probably due to the absence of a metal–metal bonding interaction [6,7].

On the basis of available structural data, three types of ligand coordination in mononuclear post-transition metal complexes can be distinguished, each type characterized by its own valence electron configuration (Fig. 2). They are one-dimensional or linear coordination with 14 valence electrons, two-dimensional (planar trigonal or square planar) with  $16\bar{e}$  and three-dimensional or quasi-spherical coordination with  $18\bar{e}$ . In the latter case, corresponding to the EAN rule, the coordination

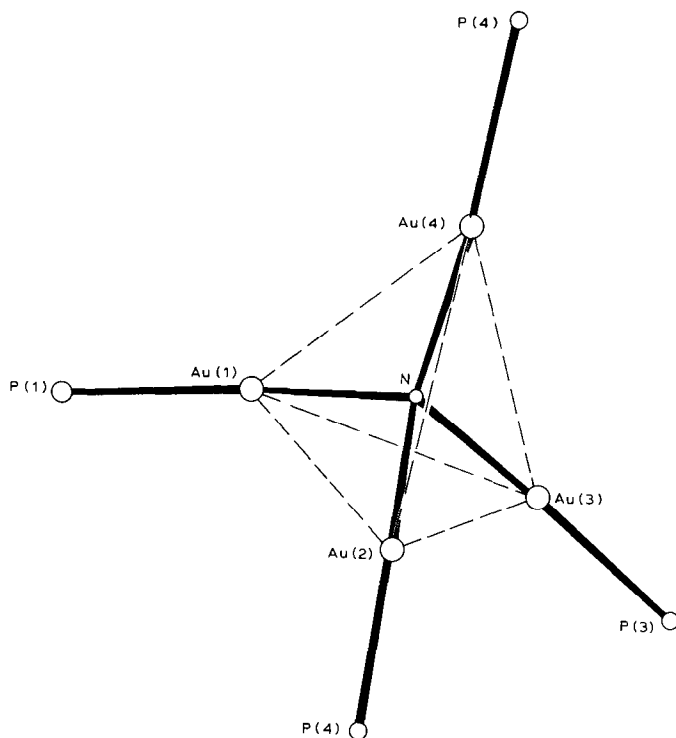


Fig. 1. Cation I (phenyl substituents omitted). Interatomic distances: Au(1)–Au(2) 3.138, Au(1)–Au(3) 3.012, Au(2)–Au(3) 3.160, Au(1)–Au(4) 3.504, Au(2)–Au(4) 3.321, Au(3)–Au(4) 3.489, Au(1)–N 2.01, Au(2)–N 1.93, Au(3)–N 2.10, Au(4)–N 2.03, Au–P 2.230–2.244 Å; e.s.d.'s Au–Au 0.002, Au–P 0.007, Au–N 0.02 Å. Bond angles: Au–N–Au 94.3–120.7, P–Au–N 171.5–177.0°; e.s.d.'s 0.8 and 0.6°, respectively.

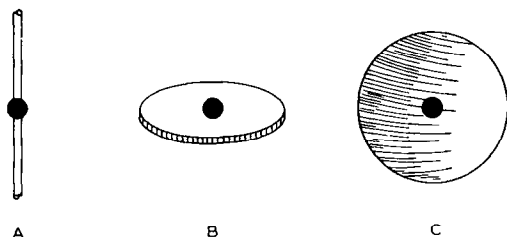


Fig. 2. Types of coordination in post-transition metal complexes and their numbers of valence electrons. (A) One-dimensional,  $14\bar{e}$  ( $\text{LAuX}$ ,  $\text{RHgX}$ ); (B) two-dimensional,  $16\bar{e}$  ( $\text{L}_3\text{Au}^+$ ,  $\text{L}_2\text{AuX}_2$ ,  $\text{L}_3\text{Pd}$ , etc.); (C) three-dimensional,  $18\bar{e}$  ( $\text{L}_4\text{Au}^+$ ,  $\text{L}_4\text{Pd}$ , etc., EAN rule).

sphere of the metal atom is uniformly filled by ligands. The cation I represents the simplest case of a centred polyhedron built up of the linearly coordinated 14-electron  $\text{Au}^{1+}$  atoms. Notwithstanding distortions in the coordination environment of the central N atom, it has an octet of valence electrons (according to Wade [8], each  $\text{Ph}_3\text{PAu}$  unit supplies one skeletal electron, in this case to the valence shell of the interstitial atom).

The structure and stoichiometry of gold clusters of higher nuclearity with an Au atom inside the polyhedron of peripheral Au atoms should evidently be determined, as well as in the case of I, by the electronic requirements of the central gold atom [2,9–11]. For clusters with the uniform (“quasi-spherical”) environment of this central atom by the peripheral ones, instead of Wade’s magic numbers of skeletal electrons, only one magic number of  $18\bar{e}$  must occur, which is not very typical for mononuclear gold complexes (see also [12], where the same magic number of  $12n + 18$  valence electrons was obtained from MO calculations, in contrast to the “toroidal” clusters with a roughly planar environment of the central atom, where calculations predict the magic number  $12n + 16$ ). Actually, all such centred clusters, for example  $[\text{Au}_8\text{L}_8]^{2+}$  [9],  $[\text{Au}_9\text{L}_8]^+$  [2],  $[\text{Au}_{11}\text{L}_{10}]^{3+}$  [10],  $[\text{Au}_{11}\text{L}_7\text{X}_3]$  [2] and  $[\text{Au}_{13}\text{L}_{10}\text{X}_2]^{3+}$  [11] (where L is a phosphine ligand and X is a halogen or pseudohalogen), do have 18 skeletal electrons. This magic number also allows the existence of as yet not obtained clusters such as  $[\text{Au}_{10}\text{L}_9]^{2+}$ ,  $[\text{Au}_{12}\text{L}_{11}]^{4+}$  and/or their isoelectronic halogen-substituted derivatives and probably the larger  $[\text{Au}_{14}\text{L}_{13-n}\text{X}_n]^{(6-n)+}$  or  $[\text{Au}_{15}\text{L}_{14-n}\text{X}_n]^{(7-n)+}$  clusters to be predicted. It is noteworthy that the EAN magic number does not determine the detailed geometrical characteristics of the peripheral polyhedron, where the  $\text{Au} \cdots \text{Au}$  edges may vary in length in a wide range, as can be seen even in cation I.

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