The Mackay-type cluster \([\text{Cu}_{43}\text{Al}_{12}](\text{Cp}^*)_{12}\): Open-shell 67 electron superatom with emerging metal-like electronic structure.

Jana Weßing, Chelladurai Ganesamoorthy, Samia Kahlal, Rémi Marchal, Christian Gemel, Olivier Cador, Augusto C. H. Da Silva, Juarez L. F. Da Silva, Jean-Yves Saillard* and Roland A. Fischer*

Abstract: The paramagnetic cluster \([\text{Cu}_{43}\text{Al}_{12}](\text{Cp}^*)_{12}\) was obtained from the reaction of \([\text{CuMes}]_{5}\) and \([\text{AlCp}^*]_{12}\) \( (\text{Cp}^* = \tfrac{3}{2}\text{C}_5\text{Me}_3; \text{Mes} = \text{mesityl}) \). This all-hydrocarbon ligand-stabilized \(M_{68}\) magic atom-number cluster features a Mackay-type nested icosahedral structure. Its open-shell 67 electron superatom configuration is unique. Three unpaired electrons occupy weakly antibonding jellium states. The situation prefigures the formation of a conduction band, which is in line with the measured temperature independent magnetism. Steric protection by twelve \text{Cp}^* ligands annihilates the intrinsic polyradical reactivity of the \text{Cu}_{43}\text{Al}_{12}\) core.

The superatom theory, based on the spherical jellium model, has evolved to a concept of choice for understanding stability and chemistry of a wide range of naked and also ligated metal clusters. Superatoms feature atom-like cluster orbital shells following the energy order 1S<1P<1D<2S<1F<2P<1G<... for which particular stability is related to electronic shell closing at transition metal centers (TM), and, over time, this particular stability is related to electronic shell closing at transition metal centers (TM), and, over time, it cannot be re-dissolved in any solvent without decomposition, a property which prohibited its extensive characterization with high-resolution mass spectrometry or solution NMR spectroscopy. Single-crystals suitable for X-ray diffraction structural analysis were obtained by carefully tuning the reaction conditions in order to allow for a slow crystallization of pure one directly from the reaction mixture. However, the compound notoriously forms relatively small, weakly diffracting cubes. Supporting information (SI) for this article is given via a link at the end of the document (analytical and crystallographic data and computational details).

[a] Dr. J. Weßing, Dr. C. Gemel, Prof. Dr. R. A. Fischer, Chair in Inorganic and Metal-Organic Chemistry Technical University of Munich, Lichtenbergstr. 4, D-85748 Garching, Germany. E-mail: roland.fischer@tum.de
[b] Dr. C. Ganesamoorthy, University of Duisburg-Essen Faculty of Chemistry, Universitätsstr. 5-7, D-45141 Essen, Germany.
[c] Dr. R. Marchal, Dr. S. Kahlal, Prof. Dr. O. Cador, Prof. Dr. J.-Y. Saillard, Univ Rennes, CNRS, IScR-UMR 6226, F-35000 Rennes, France. E-mail: jean-yves.saillard@univ-rennes1.fr
[d] Dr. A. C. H Da Silva, Prof. Dr. J. L. F. Da Silva São Carlos Institute of Chemistry, University of São Paulo PO Box 780, 13560-970, São Carlos, São Paulo, Brazil.

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The non-stoichiometric reaction of \([\text{AlCp}^*]_{12}\) with \([\text{CuMes}]_{5}\) in benzene at 78°C reproducibly yields analytically pure one as a black crystalline solid, albeit in low yields of 10–17 % (scheme 1). The compound is highly air and moisture sensitive, whereat the isolated crystals are pyrophoric upon exposure to air. Isolated \(1\) cannot be re-dissolved in any solvent without decomposition, a property which prohibited its extensive characterization with high-resolution mass spectrometry or solution NMR spectroscopy. Single-crystals suitable for X-ray diffraction structural analysis were obtained by carefully tuning the reaction conditions in order to allow for a slow crystallization of pure one directly from the reaction mixture. However, the compound notoriously forms relatively small, weakly diffracting cubes. Despite all efforts, thus obtained crystallographic data falls short of routinely accepted, high quality requirements. Accordingly, the following, quantitative discussions provide an approximation, obtained by careful tuning the reaction conditions in order to allow for a slow crystallization of pure \(1\) directly from the reaction mixture. However, the compound notoriously forms relatively small, weakly diffracting cubes. Despite all efforts, thus obtained crystallographic data falls short of routinely accepted, high quality requirements. Accordingly, the following, quantitative discussions provide an approximation, only, and given bond lengths and angles are to be considered carefully, whereas the proposed core composition of \text{Cu}_{43}\text{Al}_{12}\) as well as the overall molecular structure of \(1\) are unambiguously supported by the compiled experimental data, as well as structure optimizations on the DFT level of theory.

Scheme 1. Synthesis of \([\text{Cu}_{43}\text{Al}_{12}](\text{Cp}^*)_{12}\) (1).

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Figure 1. Molecular structure of \(1\) in the solid state, viewed along the five-fold rotational axis. H atoms and co-crystallized benzene molecules have been omitted for clarity, ellipsoids are drawn at the 30 % probability level. Al, Cu, C are depicted in blue, orange and grey, respectively.
Figure 2. Naked metal cores and underlying tetrahedral M₁₂ subunits of [Cu₄Al₁₂(Cp*)₄]- (1, left) and [Pd₄(μ²-P₃H₃)₄(μ²-CO)₈] (right) with highlighted M₄12M₄42M polyhedral shell geometries. The Mackay-type two-shell icosahedra are essentially isosctructural. For [Cu₄Al₃(Cp*)₄], the outer shell is constructed from a Cu₄12icosidodecahedron embedded inside an Al₃12icosahedron.

Cluster 1 crystallizes in the cubic space group Im-3 with two molecules per unit cell along with twelve solvate molecules of benzene. Its molecular structure features a unique highly symmetric, discrete heterometallic M₈S unit which is embedded into the all-enclosing hydrocarbon shell of twelve Cp* ligands. To date, the only other example of a crystallographically characterized, icosahedral M₈S magic atom-number ligated metal cluster is the recently reported homometalic [Pd₄S(μ²-P₃H₃)₄(μ²-CO)₈]. Similar to this Pd₄S core, the Cu₄Al₁₂ core adopts a Mackay-type two-shell icosahedron (figure 2), an arrangement which is considered to be particularly stable owing to its high sphericity and the accompanying minimization of surface energies according to classical Wulff construction principles. It has been predicted the preferred structure for M₈S clusters of a variety of metals by quantum chemical calculations. And was also experimentally observed in the interior shells of the rare examples of structurally elucidated multi-shell TM₄ clusters, like [Pd₄S(μ²-P₃H₃)₄(μ²-CO)₈] or [Cu₄Al₁₂(S₂C=H-H=Si)]₄. Accordingly, the Cu₄Al₁₂ core of 1 is composed of a body-centered Cu₁₃icosahedron (Cu₄@12Cu₈) that is encapsulated by a second, heterometallic (Cu₂Al)₁₂ shell. Herein, the Al-atoms are symmetrically distributed on the outer sphere of the Cu core to occupy the icosahedral shell of benzene, a geometrical preference which has also been reported for ligand-free 55 and 561 atom Cu/Al clusters based on quantum chemical calculations. While the lower surface energy of Al with regard to Cu was held responsible for the latter, in the case of 1, the symmetric arrangement of the aluminum atoms is certainly strongly influenced by the steric demand of the Al-bound Cp* ligand. The Al-atoms are thus embedded into an almost ideal pentagonal bipyramidal environment between the η⁵-Cp* and the η⁵-Cu₅ face with dCu₁Al of 2.622(3) to 2.655(4) Å. These values are similar to the typical dCu₁Al of the intermetallic solid state reference compounds Cu₄Al₂ (2.587(4) Å) and Cu₃Al₄ (2.486(2)-2.737(3)). The Al-Cp* centre distance of 1.923 Å is within the expected range, and only slightly elongated with regards to the smaller cluster [Cu₄(AlCp*)₄(N=CHPh)₄]₂, probably due to the higher steric crowding in case of 1. The Cu₄Al-Cp* centre angle of 179.4° is almost linear.

Following the formal description of a two-shell Mackay cluster in terms of face-sharing distorted tetrahedra, twenty tetrahedral 10-atom units can be defined, which are constructed from the innermost central Cu₄Al atom and three neighboring Al vertices of the outer shell (figure 2, middle). The radial Cu₄Al-Al edges are 5.006 Å in length and slightly shorter than the tangential Al-Al distances of av. 5.270 Å. This distortion of 5.3 % is in good agreement with the 5 % deviation predicted by Mackay based on angular strain considerations, and was also found for the cluster [Pd₄S(μ²-P₃H₃)₄(μ²-CO)₈]. Deviations from the distorted tetrahedron predicted by Mackay in terms of angles and edge ratios are small, and assumed to result from the packing of distinguishable spheres with different atomic radii (Cu 140 ppm, Al 184 ppm). The interatomic Cu-Cu distances range from 2.430(2) to 2.569(5) Å, which values are considerably shorter than the sum of the van der Waals radii for Cu atoms (2.80 Å) and match well with the Cu contacts of the ccp structure of elemental copper (2.55 Å). These contacts are also similar to those of ligated homometallic Cu (nano)clusters, like [Cu₄Al₁₂(PPh₃)₂H₂]Cl (av. 2.635 Å) or [Cu₂₄Al₆H₂(Ph,phen)₃]Cl (av. 2.65 Å). The shortest dCu-Cu found for 1 are the radial spacings between the central Cu atom and the inner Cu₁₂ shell (dCu₁₂Cu₁₂ 2.434(2) Å), along with those of the inner Cu₁₈ atoms and the outer Cu₄Al₁₂ shell (dCu₄Al₁₂ 2.430(2)-2.436(3) Å), a situation which is in full agreement with the strain-induced compression discussed above. In contrast, the tangential dCu-Cu within the icosahedral shells are slightly elongated (dCu₄Al₁₂/Cu₄Al₁₂ 2.555(2)-2.569(5) Å).

Elemental analysis and X-ray powder diffraction studies (SI), along with solid-state MAS NMR and IR spectroscopic confirm the composition of the bulk sample as deduced from single crystal X-ray diffraction. The ¹H MAS NMR spectrum shows one broad singlet at 1.72 ppm, assigned to the methyl groups of the 12 Cp* ligands, in accordance with the icosahedral symmetry. The additional signal at 6.95 ppm arises from co-crystallization of benzene (see SI for matching ¹⁳C MAS NMR data). As we were unable to reproducibly detect a broad feature around -97 ppm in the ²⁷Al MAS NMR experiment, we hesitate to unambiguously assign this signal to the AlCp* ligands. Note that the ²⁷Al chemical shifts of the pertinent reference compounds [AlCp*]₄ and [Al₂(AlCp*)₂] are -990 ppm and 200 ppm, respectively. IR spectroscopic analysis reveals the characteristic set of bands for Cp* ligands, being the νC-H and νC-C vibrational modes at 2872 and 2818 cm⁻¹ and 1412 and 1358 cm⁻¹. An additional very strong absorption is observed at 391 cm⁻¹ which is assigned to the Al-Cp* vibration. Note, neither NMR nor IR data gave us hints for the presence of hydride ligands. The total elemental analysis (determined values for Al, Cu, C, H; Σ = 99.64%) supports the composition of the compound as a benzene solvate of cluster 1 with the empirical formula of [Cu₄Al₁₂(AlCp*)₁₂] 3C₆H₆ (4885.30 g mol⁻¹) (Table S4).

The electron-count of 1 is somehow disconcerting. Looking at the [Cu@Cu₁₂@Cu₄Al₄@AlCp*]₁₂ concentrated shell description, one is tempted to consider the peripheral AlCp* units as neutral 2-electron ligands, leaving the [Cu₄Al] superatomic core with the “non-magic” 43-electron count. Including the Al atoms as part of the metal core, the resulting [Cu₄Al₁₂]₁₂ electron count reaches...
67, a value close to the “magic” number 68. However, this cluster electron count appears rather unlikely at first sight, owing to the fact that in a first approximation only one orbital per atom, i.e., one 4s(Cu) and one sp(Al) hybrid AO, is expected to contribute significantly to the building up of the jellium-type orbitals. Indeed, with only 55 combinations, occupation of antibonding jellium-type orbitals is expected for this electron count. In order to shed some light on the electronic structure of \([\text{Cu}_3\text{AlCp}_2]\), we have performed spin-polarized density functional theory (DFT) calculations on the simplified model \([\text{Cu}_3\text{AlCp}_2]\) (1*) by replacing \(\text{Cp}^*\) with \(\text{Cp} = \text{C}_5\) and \(\text{AlCp}\) with \(\text{Al}^3\) functionals, respectively (see SI for computational details).

The ground state was found to be a quadruplet with 3 unpaired electrons of \([\text{Cu}_3\text{AlCp}_2]\) (58 electrons, “magic” number). The possibility for \([\text{Cu}_3\text{AlCp}_2]\) (58 electrons, “magic” number) to reach such closed-shell configurations has been tested by DFT priori expected antibonding nature (see above) is tempered by the stabilizing participation of 4p(Cu) orbitals. Thus, \(1^*\) (or 1) can be considered as an open-shell 67 electron superatom complex, made of a \([\text{Cu}_3\text{AlCp}_2]\) jellium-type core and “passivated” by 12 \(\text{Cp}^*\) (or \(\text{Cp}^+\)) ligands.

It is important to note that the nearest favorable closed-shell situations would be \([1^*]^+\) (64 electrons, “non-magic” number) or \([1^*]^9^-\) (58 electrons, “magic” number). The possibility for 1 bearing 3 or even 9 additional hydride ligands, thus allowing it to reach such closed-shell configurations has been tested by DFT and it was not possible to find any closed-shell situation for any of the tested models. This result is consistent with the MAS NMR and IR data, which gave no indications for hydrides.

The thermal variation of the magnetization, \(M\), of 1 has been investigated between 2 and 300 K at variable magnetic field, \(H\). The product of molar magnetic susceptibility, \(\chi_M = MH\), by the temperature, \(T\), is plotted in Figure 3. In the low temperature regime, \(\chi_M T \approx 1.5 \text{ cm}^3 \text{K mol}^{-1}\) approaches the expected value for an isolated spin 3/2 with a Zeeman factor \(g = 2\) (1.875 cm \(T^{-1}\)). This observation corroborates the existence of three unpaired electrons. \(\chi_M T\) increases almost linearly on warming which might be the signature of low lying energy levels coupled with the ground state through Zeeman perturbation, known as the Temperature Independent Paramagnetism (TIP).

To summarize, cluster 1 is the largest Cu superatom reported to date and it is completely new from the point of view of two features. Firstly, it has a very large electron count of 67, as compared to 22 in case of \((\text{Au}_{10}\text{Cu}_{30})(\text{CCl})_{32} (\text{PPH}_3)_2\text{Cl}_2\)\(^{33}\), as the only other heterometallic example,\(^{46}\) or only 2 for the known homonuclear copper superatoms.\(^{31, 32, 47-49}\) Secondly, this non-magnetic number is associated with an open-shell configuration (S = 3/2) with an unprecedented electronic structure in which 9 electrons occupy discrete levels preferrig the bottom of a metallic-like conduction band. Such a situation is largely favored by the presence of a densely packed protecting shell of \(\text{Cp}^*\) ligands which provide the cluster core with sufficient kinetic stability and annihilates the intrinsic polyradicalar reactivity of the superatom core.\(^{50}\) Together with the emblematic \(\text{Au}_{20}\)\(^{44}\) and \([\text{Cu}_2\text{Zn}_3]\)(\text{C}^+\text{H})(\text{CNR})_{12}\)\(^{53}\) cluster 1* is a rare example of a group 11-containing superatom in which the group-11 metal oxidation state is equal to zero. Indeed, such superatom cluster complexes are usually bearing formally anionic ligands (e.g.
thiolates) directly bonded to the metal core, giving rise to metal average oxidation states comprised between +I and 0.47, 53, 54
Our synthetic approach, which consists in using sources of
neutral (r.t.) 2936 (w), 2872 (w), 2818 (w), 1463 (w), 1412 (m), 1358 (m), 18. E. G. Mednikov, M. C. Jewell, L. F. Dahl, 20.
The reaction of [AlCp*]_4 and [CuMes]_5 yields the Mackay 55-metal atom two-shell icosahedral [Cu_{43}Al_{12}](Cp*)_{12}. The intermetalloid cluster possesses a unique 67 electron open shell superatomic [Cu_{43}Al_{12}]^{12+} core, embedded inside an all-hydrocarbon shell of twelve Cp* ligands. Its electronic structure comprises a set of entangled HOMO und low-lying LUMOs, prefiguring the formation of a conduction band.


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