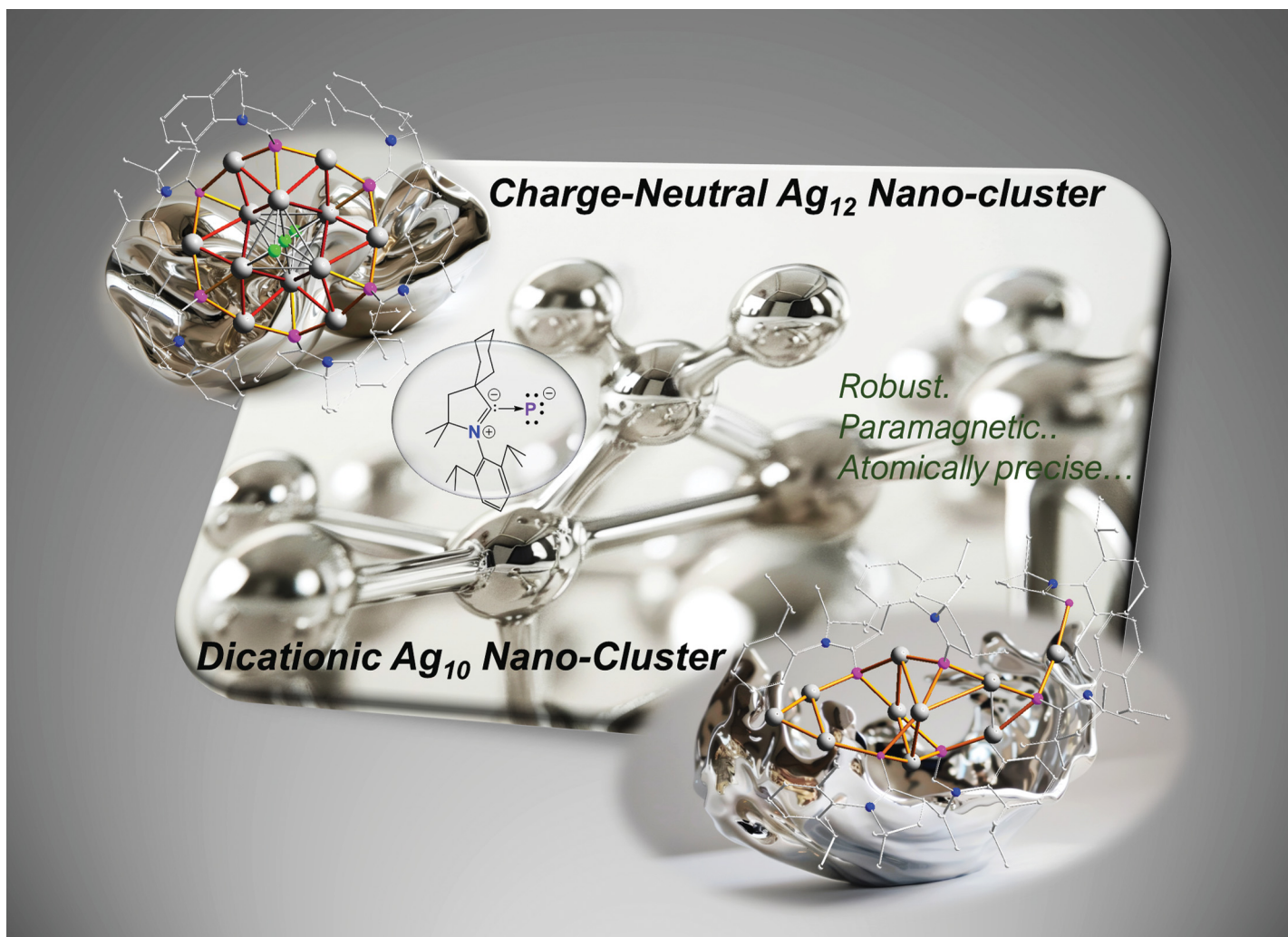




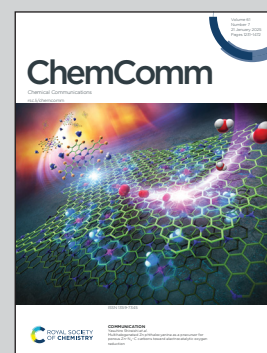
Showcasing research from Professor Sudipta Roy's laboratory, Department of Chemistry, Indian Institute of Science Education and Research (IISER) Tirupati, Andhra Pradesh, India.

Isolation of mixed valence charge-neutral Ag₁₂, and dicationic Ag₁₀ nano-clusters stabilized by carbene-phosphaalkenides

Cyclic alkyl(amino) carbene-supported phosphaalkenides were employed as ligands for isolation of two atomically precise mixed-valence nanoclusters (NCs) with Ag₁₂⁰Cl₃, and Ag₁₀²⁺ cores. The characteristic EPR signals exhibited by the NCs suggested coupling of unpaired electrons with ^{35,37}Cl, ³¹P and ^{107,109}Ag nuclei.

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Isolation of mixed valence charge-neutral Ag₁₂, and dicationic Ag₁₀ nano-clusters stabilized by carbene-phosphaalkenides†

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Siriya Jagannatha Prathapa^b and Sudipta Roy  ^a*

Cyclic alkyl(amino) carbene (cAAC)-supported phosphaalkenides (cAAC=P)[−] have been employed as ligands for the isolation of two atomically precise mixed valence paramagnetic Ag₁₂^{I/0}Cl₃, and Ag₁₀^{I/0}, nano-clusters [(Me₂-cAAC=P)₆Ag₁₂Cl₃] (2), and [(Me₂-cAAC=P)₆Ag₁₀](NTf₂)₂ (4). 2 and 4 have been structurally characterized by single-crystal X-ray diffraction revealing the presence of three Ag⁰ atoms, nine Ag^I ions (2); and two Ag⁰ atoms, eight Ag^I ions (4), respectively. The clustering inorganic unit Ag₁₂Cl₃ in 2 has been found to be surrounded by six mono-anionic μ₃-cAAC=P moieties having 3-bar symmetry. 2 and 4 have been studied by cyclic voltammetry, UV-vis, ESI-MS, XPS, EPR spectroscopy, and DFT calculations.

Silver nanoclusters (NCs) are known to exhibit unique electronic, and optical properties, such as strong photoluminescence, and various catalytic activities.¹ They are utilised as attractive luminescent probes for sensing and bioimaging.² Structurally well-defined NCs possessing Ag⁰ atoms are highly reactive, and easier to oxidize compared to their heavier Au analogues, which makes their synthesis challenging. Metallic silver is non-magnetic in its bulk form. However, Pereiro *et al.* theoretically predicted that the small nuclearity silver NCs, Ag_n, could be magnetic with variation of the magnetic moment depending on the value of *n* [*n* = 2–22].³ Liu *et al.* reported the isolation of the chiral open-shell Ag₂₃ NC with five Ag⁰ atoms, which was structurally characterized by single-crystal X-ray diffraction.⁴ The open-shell behaviour of this Ag₂₃ NC was confirmed by a weak electron paramagnetic resonance (EPR) signal, characteristic of *s* = 1/2, with *g* = 1.959 and 1.955.⁴ The first atomically precise mixed valence Ag₂₂^{0/I} NC displaying thermally activated delayed fluorescence (TADF) was reported in 2022 by Sun and

co-workers.⁵ In the same year, two other mixed valence NCs Ag₈^{0/I} and Ag₂₉^{0/I} exhibiting strong EPR signals were reported.⁶ The heavily Ag⁰-doped KCl:AgCl crystals in different chemical defect positions [cationic and anionic holes] were studied by EPR spectroscopy.^{7a} The generation of Ag₄³⁺, and Ag₆⁺ clusters was also reported under different chemical conditions.^{7b,c} However, the mixed valence silver NCs are rarely reported.⁸ The first closed-shell mixed valence Ag₂^{I/III} [Ag⋯Ag 7.4 Å] containing N₈-donor macrocyclic ligand was isolated by Qin-Hui *et al.* in 1994.^{9a} The 1D zig-zag chain of Ag₂^{I/II} (ref. 9b) stabilized by the cyclic alkyl(amino) carbene (cAAC)-supported mono-anion of the inversely polarized phosphaalkene, *viz.*, the phosphaalkenide¹⁰ was reported by Roy and co-workers. N-heterocyclic carbene (NHC), and P-SiMe₃ ligated diamagnetic Ag₁₂^I, and Ag₂₆^I clusters were reported by Corrigan *et al.*¹¹ A plethora of other Ag^I clusters have been synthesized, and characterized employing alkyne, thiolate, sulfide, selenide, phosphine, perchlorate, *etc.* as ligands.¹² Moreover, clusters with Ag–H moieties have also been isolated, and further studied by mass spectrometry.¹³ However, isolation of stable silver NCs introducing carbene-phosphaalkenides as ligands is still scarce. Herein, we report on the solid-state isolation, and structural characterization of two novel structurally well-defined mixed valence paramagnetic silver NCs with Ag₁₂^{I/0}Cl₃, and Ag₁₀^{I/0} metallic cores.

The dark red crystals of Me₂-cAAC=P–K (1)¹⁴ (Me₂-cAAC = C(N-2,6-ⁱPr₂C₆H₃)(CMe₂)₂(CH₂)) were reacted with AgNTf₂ in a 3 : 2 molar ratio in toluene at 0 °C to room temperature (rt) for 12 h to obtain a dark brown-red reaction mixture. Upon drying, the resultant crystalline solid obtained was dissolved in freshly distilled DCM, and stored for crystallization upon concentration to ~1 mL in a freezer at −40 °C. After one-week, dark red blocks of [(Me₂-cAAC=P)₆(Ag)₁₂(Cl)₃] (2) were isolated in 40% yield (Scheme 1). The presence of the three chloride ions in 2 can be attributed to the decomposition of DCM, the usage of which is found to be crucial for the isolation of 2. A different mixed valence dicationic cluster [(Me₂-cAAC=P)₆(Ag)₁₀](NTf₂)₂ (4) was isolated in 60% yield as yellow blocks when [Me₂-cAAC=P–B(N(ⁱPr)₂)₂] (3)^{9b} was reacted with AgNTf₂ in 2 : 1

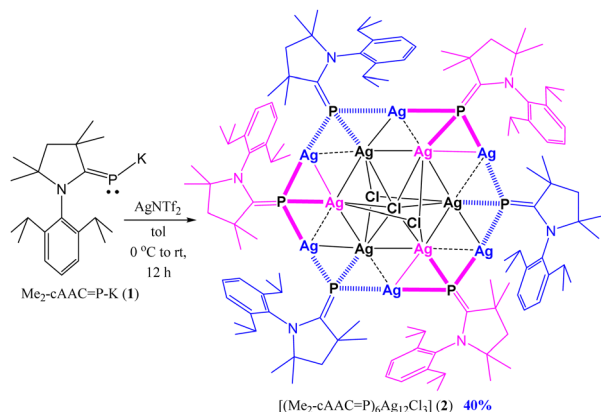
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† Electronic supplementary information (ESI) available. CCDC 2242239 (2), 2194453 (4). For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4cc05628k>

* Both authors contributed equally.



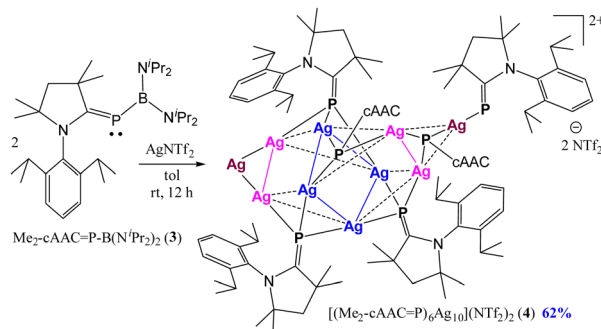


Scheme 1 Synthesis of mixed-valence neutral NC $[(\text{Me}_2\text{-cAAC}=\text{P})_6\text{Ag}_{12}(\text{Cl})_3] \text{ (2)}$.

molar ratio in toluene at rt for 12 h, followed by crystallization of the resultant precipitate from concentrated DCM solution, stored at 0 °C in a refrigerator (Scheme 2). The $(\text{cAAC}=\text{P})^-$ ligands are found to be redox non-innocent, and undergo oxidation to produce the corresponding radical followed by dimerization, resulting in the formation of $(\text{Me}_2\text{-cAAC})_2\text{P}_2$ with a subsequent reduction of Ag^{I} to Ag^0 in solution affording the mixed valence Ag-NCs **2** and **4**.⁶ The presence of Ag^0 and Ag^{I} centres in **2** and **4** is supported by XPS spectroscopy (see ESI†). The formation of $(\text{Me}_2\text{-cAAC})_2\text{P}_2$ in the reaction mixture is confirmed by ^{31}P NMR spectroscopy ($\delta = 55.1$ ppm).

The red/yellow blocks of **2/4** are found to be stable under an argon atmosphere for six months inside a glove box at rt. The powders of **2** and **4** decompose above 205 and 165 °C, respectively. **2** and **4** are found to be NMR silent, and EPR active.

2 and **4** have been structurally characterized by single-crystal X-ray diffraction. The dodeca-nuclear Ag-NC $[(\text{Me}_2\text{-cAAC}=\text{P})_6(\text{Ag})_{12}(\text{Cl})_3] \text{ (2)}$ crystallizes in the trigonal $R\bar{3}$ space group (Fig. 1). **2** comprises six $(\text{Me}_2\text{-cAAC}=\text{P})^-$ ligands, three chloride ions, and twelve Ag-atoms/ions. Fig. 2 shows that the asymmetric unit of **2** starting at position-1, generates six different symmetry equiv. points (1–6). Positions 1, 3 and 5 are non-inverted, while positions 2, 4 and 6 are three inverted-symmetry equiv. positions. There are three Ag^0 atoms in **2**, which is



Scheme 2 Synthesis of mixed-valence dicationic NC $[(\text{Me}_2\text{-cAAC}=\text{P})_6\text{Ag}_{10}(\text{NTf}_2)_2] \text{ (4)}$.

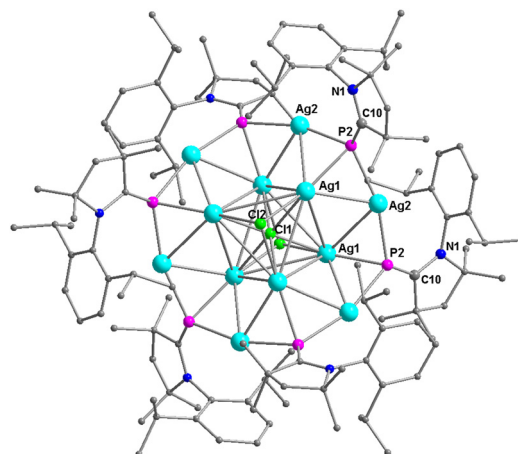


Fig. 1 Molecular structure of NC $[(\text{Me}_2\text{-cAAC}=\text{P})_6(\text{Ag})_{12}(\text{Cl})_3] \text{ (2)}$. Hydrogen atoms are omitted for clarity.

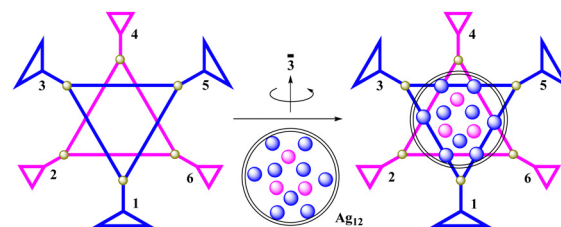


Fig. 2 Structural topology and symmetry $[3\text{-bar}]$ in NC **2**.

suggested from charge balance consideration, since there are a total of nine mono-anionic ligands present.

The space filling model of **2** has been shown in Fig. 3 (left), which represents how the central Ag_{12} metallic core is well protected by the surrounding cAAC-supported phosphaaikenide ligands. The natural bond orbital (NBO) analyses of NCs **2** and **4** at neutral doublet, and dicationic triplet states, respectively, were performed at the UB3P86-D3(BJ)/Def2-SVP level of theory (see ESI† for details). The NBO analysis of **2** revealed that the $\alpha\text{-LUMO}+1$, $\alpha\text{-LUMO}$, and $\alpha\text{-SOMO}$ are very close in energy ($\Delta E = 0.01\text{--}0.05$ eV) suggesting that the unpaired electron in **2** can span all these three orbitals involving the $\text{C}=\text{N}-\text{P}$ unit, Cl and Ag atoms (see ESI†). This is also reflected in the Mulliken α -spin densities of **2** showing delocalization of spin densities due to the unpaired electron (Fig. 3 (right), see ESI†).

The Ag–Ag distances of charge-neutral NC **2** are found to be 2.883(1), and 3.024(2) Å, which are significantly shorter than

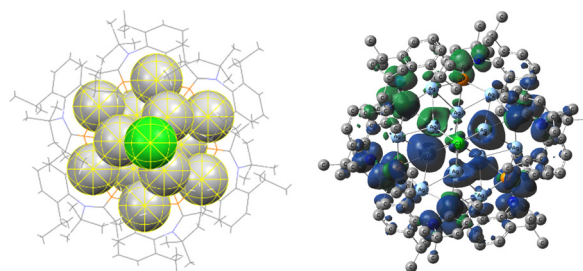


Fig. 3 Space filling model (left), and Mulliken α -spin densities (right) of $[(\text{Me}_2\text{-cAAC}=\text{P})_6\text{Ag}_{12}\text{Cl}_3] \text{ (2)}$.



those of the previously isolated tri-cationic closed-shell Ag NC $2^{3+}(\text{OTf}^-)_3$ (2.9593(14), 2.9174 (12), 3.2026(15), 3.1541(13) Å).⁶ The Ag–P distances of **2** are 2.379(4), 2.401(3), and 2.455(2) Å, which are close to those of $2^{3+}(\text{OTf}^-)_3$ (Ag–P 2.393(4)–2.431(4) Å).⁶ The C–P bond in **2** is 1.75(1) Å, which is slightly shorter than those of $2^{3+}(\text{OTf}^-)_3$ (1.780(11)–1.801(11) Å).⁶ The Ag–Cl distances in **2** are found to be 2.4530(14), and 2.572(7) Å, which are either very similar in value or significantly smaller than those of 2^{3+} (2.475(9), 2.705(5), 2.638 (4), 2.7143(11), 2.732(4), 2.8254(10) Å).⁶ The diameter of the outer/peripheral Ag₆ ring of **2** having a three-fold symmetry is 8.37 Å, which is very close to those of 2^{3+} with two-fold symmetry (8.26, 8.36, 8.48 Å).⁶ The Cl–Cl distance between the two extreme Cl-ions in **2** is 5.8 Å, which is shorter than that of 2^{3+} (6.5 Å).⁶ The P–P distance in **2** is 9.02 Å, which is slightly greater than the average value of 2^{3+} (8.46 Å; 8.26, 8.36, 4.48, 8.88, 9.22 Å).⁶ **2** represents the first example of an Ag^{I/0} based mixed valence NC, which has been structurally characterized in two different charged (0 (**2**) vs. +3 (2^{3+})), and spin states [doublet (**2**) vs. singlet (2^{3+})].⁶

The dicationic deca-nuclear Ag NC [(Me₂-cAAC=P)₆Ag₁₀](NTf₂)₂ (**4**) crystallizes in triclinic space group *P* $\bar{1}$ (Fig. 4). The entire molecule of **4** appears in the crystallographic asymmetric unit, which possesses six mono-anionic ligands (Me₂-cAAC=P)[−], and ten Ag-atoms/ions. There are two non-coordinating/free mono-anionic NTf₂[−] anions present for the electrical charge balance. The charge balance consideration suggests that there are two Ag⁰ atoms in **4**. The four arms of the central Ag₄ unit of **4** have been bridged by four P-atoms of mono-anionic Me₂-cAAC=P[−] ligands producing a (Me₂-cAAC=P)₄Ag₄ unit. Two Ag₂ units have been placed in anti-fashion above and below the irregular square-like Ag₄ unit (Fig. 4 and 5).

An additional Ag-atom is present above the Ag₂ unit (Fig. 4 and 5), while another Ag atom is bridged by a μ₃-P atom (right, Fig. 5). The Ag–Ag distances of the central four-membered Ag₄ ring in **4** are 2.90, 3.0, and 3.20 Å, which are longer than those (~2.96 Å) of the Ag₈^{0/I} complex.⁶

The Ag₂ unit, which is situated on the top of the central Ag₄ unit, possesses the Ag–Ag distance of 2.91 Å, which is

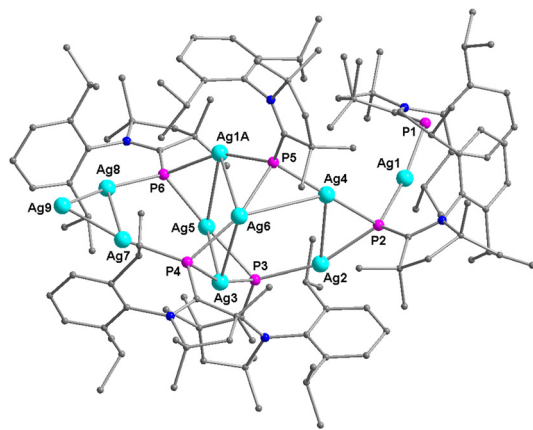


Fig. 4 Molecular structure of NC [(Me₂-cAAC=P)₆Ag₁₀](NTf₂)₂ (**4**). Hydrogen atoms are omitted for clarity. Two triflimide anions [N(SO₂CF₃)₂][−] are omitted for clarity.

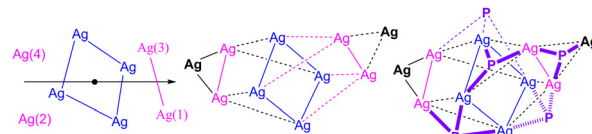


Fig. 5 Core topology of [(Me₂-cAAC=P)₆Ag₁₀](NTf₂)₂ (**4**). Two Ag₆ square prisms sharing the blue colored pseudo-Ag₄-square with a 4-bar symmetry operation.

significantly shorter than that of the Ag₃ triangle of **4** (3.04 Å). The corresponding Ag–Ag distance in previously reported Ag₈^{0/I} complexes is 3.07 Å.⁶ Notably, the distal Ag atom (Ag9) (Ag7–Ag9, Ag8–Ag9; 2.472(3), 2.458(3) Å) is significantly closer to the Ag₂ arm (Ag8–Ag9), which is situated above the central Ag₄ unit of **4**. The Ag–P bond lengths of NC Ag₁₀^{0/I} (**4**) range from 2.23 Å to 2.48 Å, and are significantly different than those of the neutral Ag₈ cluster (2.404(5)–2.417(4) Å).⁶ The space filling diagram of a ten Ag atoms/ions unit of **4** has been shown in Fig. 6 (left). The Ag atom placed above the Ag₂ unit is situated in between the two aromatic rings of the Dipp ligands. The NBO, and Mulliken spin density analyses of **4** (Fig. 6 (right)) showed the major spin densities on the C=N–P unit with very small values on the Ag-atoms except for one Ag-atom (5.6%) and thus typical EPR features of Ag–P systems were not observed⁶ in the experimental EPR spectrum of **4**.

The EPR spectra of **2** and **4** (in DCM) are shown in Fig. 7 and 8. The EPR simulation/fitting of **2** considering coupling of the unpaired electron with the nuclei of ^{107,109}Ag, ³¹P and ^{35,37}Cl atoms is quite satisfactory (Fig. 7). Three board lines near *g* = 2.0033 were observed for the previously reported Ag₈^{0/I} cluster containing four Ag⁰ atoms.^{6,9b} However, the EPR spectrum of **2** shows three sets of multiple hyperfine lines, which have been simulated with EasySpin.

The coupling constants of one ^{107,109}Ag⁰, two ³¹P and one ^{35,37}Cl nuclei are 9.43, 111.79/111.75, and 9.81 MHz, respectively, with a slight rhombic nature of *g* [*g*_x = 2.00766, *g*_y = 2.00885, *g*_z = 1.99959]. The EPR spectrum of **4** appears as unsymmetrical showing two resonances around *g* ≈ 2 [*g*_x = 2.00165, *g*_y = 2.00006, *g*_z = 1.99703] (Fig. 8). The coupling constant of Ag⁰ is 2.51 MHz, which is significantly smaller than that of **2** (9.43 MHz). The ESI-MS studies show that **2** (see ESI[†]) and **4** can fly as dications. The ESI-MS spectrum of **4**²⁺ corroborates the loss of two isopropyl groups with the intake of a sodium ion as [(Me₂cAACP)₆Ag₁₀ + Na–2C₃H₇–H]²⁺. The cyclic

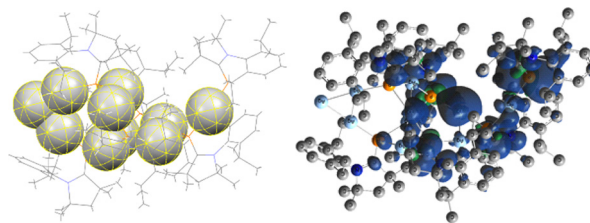


Fig. 6 Space filling model of total molecule (left), and Mulliken α -spin densities (right) of [(Me₂-cAAC=P)₆Ag₁₀](NTf₂)₂ (**4**).



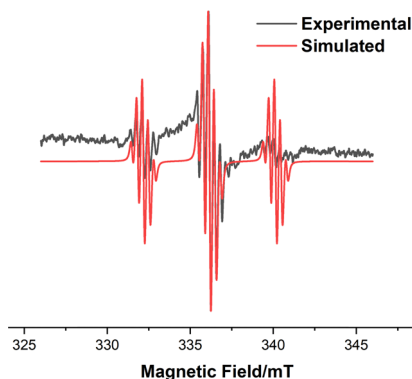


Fig. 7 Experimental (black), and simulated (red) X-band EPR spectra of $[(\text{Me}_2\text{-cAAC}=\text{P})_6(\text{Ag})_{12}(\text{Cl}_3)]$ (**2**) in DCM at 293 K. EasySpin, simulated parameters: one $^{107,109}\text{Ag}$ ($A = 9.43$ MHz), two ^{31}P ($A = 111.79$, 111.75 MHz), one $^{35,37}\text{Cl}$ ($A = 9.81$ MHz), $g_x = 2.00766$, $g_y = 2.00885$, $g_z = 1.99959$, $\text{LW1} = 0.016$ mT, $\text{LW2} = 0.166$ mT. Experimental frequency = 9.436369 GHz.

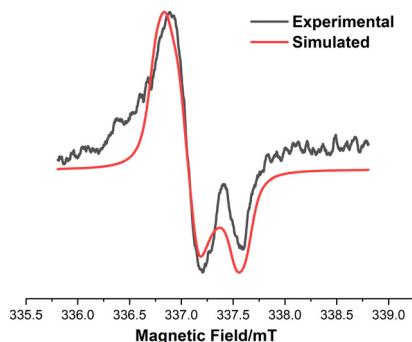


Fig. 8 X-band EPR spectrum of the NC $[(\text{Me}_2\text{-cAAC}=\text{P})_6(\text{Ag})_{10}](\text{NTf}_2)$ (**4**) in DCM at 293 K. Black line represents the experimental spectrum, and the red line represents the simulated spectrum using the EasySpin program [$g_x = 2.00165$, $g_y = 2.00006$, $g_z = 1.99703$, $\text{LWPP}_1 = 0.0678384$ mT, $\text{LWPP}_2 = 0.0817786$ mT, $A_{\text{Ag}} = 2.51891$ MHz].

voltammetry studies of **2** and **4** suggest the possible oxidation (see ESI†). The UV-vis spectra (in THF at 298 K) of **2** and **4** exhibited the absorption maxima (λ_{max}) at 365 and 367 nm, respectively (see ESI†). **2** and **4** were observed to be non-emissive.

In conclusion, two novel mixed valence Ag-NCs (Ag_{10} , **2**; Ag_{12} , **4**) were isolated as red/yellow blocks. **2** and **4** have been structurally characterized by X-ray single-crystal diffraction. The Ag_{10} , and Ag_{12} NCs possess three and two Ag^0 atoms, respectively. The NMR silent NCs **2** and **4** were found to be EPR active. The unpaired electrons couple with the $^{35,37}\text{Cl}$, ^{31}P and $^{107,109}\text{Ag}$ nuclei. The strongest coupling constant was obtained for ^{31}P -nuclei (111.75 MHz) in **2**. The coupling constant of $^{107,109}\text{Ag}$ of **2** (9.43 MHz) is four times stronger than that of **4** (2.51 MHz). The distributions of electron densities in **2** and **4** were estimated by computation of the Mulliken spin densities, and further correlated with ERP simulation.

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support. We thank Dr S. S. Sen (NCL-Pune), and KB for the XPS measurements.

Data availability

The data supporting this article (experimental details, UV-vis, HRMS, EPR, XPS, single-crystal X-ray data, and computational details) have been included as part of the ESI†. Crystallographic data for **2** and **4** have been deposited at the CCDC (2242239, 2194453†), and can be obtained from <https://www.ccdc.cam.ac.uk/>.

Conflicts of interest

There are no conflicts to declare.

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