

Coordination Chemistry

Linking of Cu^I Units by Tetrahedral Mo₂E₂ Complexes (E = P, As)

Jana Schiller⁺, Andrea Schreiner⁺, Michael Seidl, Gábor Balázs, and Manfred Scheer^{*[a]}

Dedicated to Professor F. Ekkehardt Hahn on the occasion of his 65th birthday

Abstract: The reaction of [Cp₂Mo₂(CO)₄(μ,η^{2,2}-E₂)] (**A**: E = P, **B**: E = As, Cp = C₅H₅) with the WCA-containing Cu^I salts ([Cu(CH₃CN)₄][Al{OC(CF₃)₃}]₄ (CuTEF, **C**), [Cu(CH₃CN)₄][BF₄] (**D**) and [Cu(CH₃CN)_{3.5}][FAI{OC₆F₁₀(C₆F₅)₃}]₃ (CuFAI, **E**) affords seven unprecedented coordination compounds. Depending on the E₂ ligand complex, the counter anion of the copper salt and the stoichiometry, four dinuclear copper dimers and three trinuclear copper compounds are accessible. The latter complexes reveal first linear Cu₃ arrays linked by E₂ units (E = P, As) coordinated in an η^{2:1:1} coordination mode. All compounds were characterized by X-ray crystallography, NMR and IR spectroscopy, mass spectrometry and elemental analysis. To define the nature of the Cu...Cu...Cu interactions, DFT calculations were performed.

During the last two decades, the number of organometallic aggregates bearing Cu^I units has rapidly increased, owing to their wide range of applications and their versatile coordination chemistry.^[1] Cu^I compounds have proven to be useful in mimicking enzyme interactions,^[1a] as anticancer drugs,^[1b] and in other materials.^[1c] Furthermore, Cu^I derivatives turned out to be smart and novel solid-state emitters because of their accessibility and low costs.^[2] Therefore, the development of inter alia extended linear Cu^I arrays for potential applications in molecular electronics and luminescent materials has become more and more important. Some linear trinuclear cationic Cu^I complexes bridged by P/N hybrid ligands, such as 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine,^[3] N,N,N',N'',N''-pentamethyl-diethylentriamine,^[4] diphosphine/N-heterocyclic-carbene hybrid ligands^[5] or the synthesis of halide-bridged trinu-

clear Cu^I complexes connected by (diphenylphosphinomethyl)-phenyl-phosphine^[6] with Cu...Cu distances below the sum of the van der Waals radii were reported. However, Cu...Cu interactions were not confirmed by calculations. A variety of compounds containing different Cu^I and organometallic polyphosphorus ligand complexes were previously reported by our group.^[7] We were able to show the formation of 1D, 2D and even 3D coordination polymers,^[8] organometallic-based nano-sized capsules^[9] and inorganic spherical supramolecules.^[10] In addition to polyphosphorus complexes, organometallic polyarsenic ligand complexes have been known for many years.^[11] However, their coordination chemistry has been a rather unexplored area so far.^[12] To bring metals in close proximity to allow for metallophilic interactions, special building blocks are needed. One of such potential materials is the tetrahedral Mo₂E₂ moiety in the compounds [Cp₂Mo₂(CO)₄(μ,η^{2,2}-E₂)] (E = P (**A**), As (**B**)).^[13] Until now, basically three coordination modes have been observed for these E₂ ligand complexes (Figure 1).^[7c,e]

The lone pairs of one or two E atoms can either coordinate towards one or two metal centers via σ-coordination of the lone pairs (type I and II), or the E-E σ-orbital binds in a π-coordination to the metal center (type III).^[7c,e] However, to bring metal cations in close proximity, the coordination modes IV and V are needed, which are unknown for homoelement Mo₂E₂ compounds. Note that the coordination mode IV has so far only been observed for mixed EE' derivatives (E = P, E' = As, Sb).^[7b]

Herein, we report the reactions of the polypnictogen ligand complexes [Cp₂Mo₂(CO)₄(μ,η^{2,2}-E₂)] (**A**: E = P, **B**: E = As, Cp = C₅H₅) with the Cu^I salts [Cu(CH₃CN)₄][BF₄], [Cu(CH₃CN)_{3.5}][FAI{OC₆F₁₀(C₆F₅)₃}]₃ (CuFAI) and ([Cu(CH₃CN)₄][Al{OC(CF₃)₃}]₄ (CuTEF) which lead, by variation of the stoichiometry of the used reactants, to seven unprecedented coordination compounds (1–7, Scheme 1), showing a novel η^{2:1:1}-(V) and η^{2:1}-(IV) coordination

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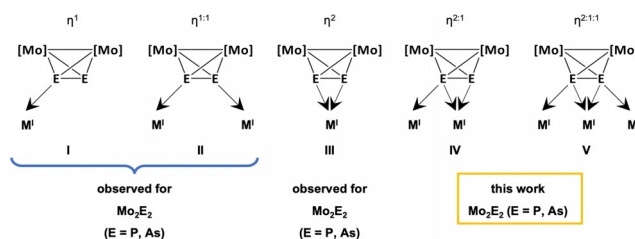
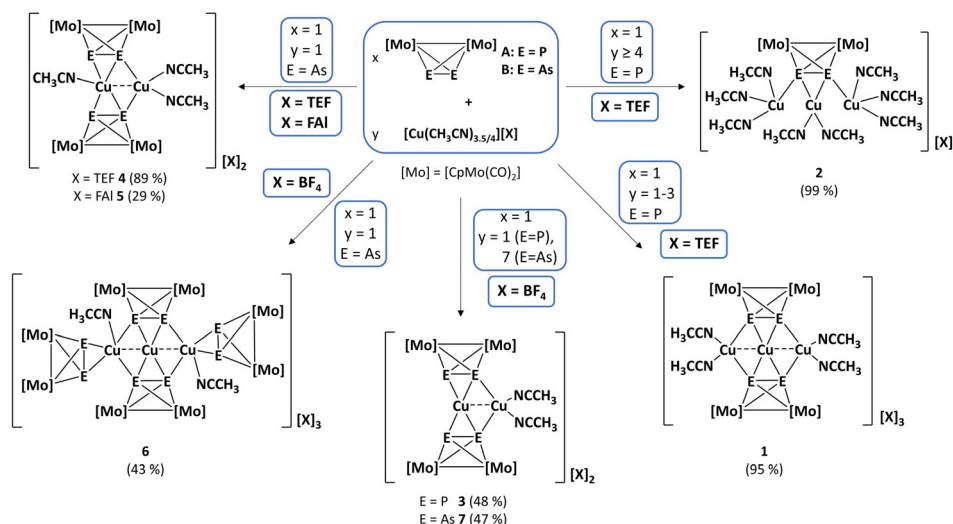


Figure 1. Reported and new coordination modes of Mo₂E₂ complexes. M^I = Ag^I, Cu^I, Au^I. [Mo] = [CpMo(CO)₂].^[7c,e]



Scheme 1. Products of the reaction of **A** with $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (depending on the stoichiometry) and with $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$, and of the reaction of **B** with the Cu^I salts $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$, $[\text{Cu}(\text{CH}_3\text{CN})_3][\text{FAI}\{\text{OC}_6\text{F}_5\}_3]$ (**5**) and $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ (depending on the stoichiometry). Yields are given in parentheses.

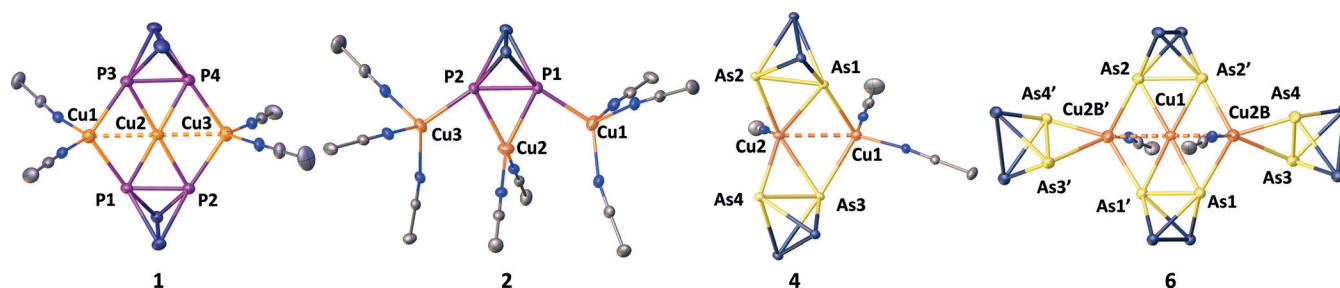


Figure 2. Molecular structures of the cationic parts of compounds **1**, **2**, **4** and **6** in the solid state. Cp- and CO-ligands and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability level. Only the major part of compound **6** is depicted (for further information see Supporting Information).

behavior, respectively, of the E_2 ligand complexes ($\text{E} = \text{P}$). Moreover, compounds **1** and **6** reveal $\text{Cu}\cdots\text{Cu}\cdots\text{Cu}$ interactions which were analyzed by DFT calculations. For the first time, an $\eta^{2:1:1}$ -coordination mode **V** was detected for the two complexes **A** and **B** to which both P/As atoms contribute via σ -bonding and π -coordination. That way, linear Cu_3 chains stabilized only by polynictogen ligand complexes are accessible.

The reaction of $[\text{Cu}(\text{o-DFB})][\text{TEF}]$ with **A** to give the dimeric compound $[\text{Cu}_2(\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_4, \eta^{2:2:1:1}\text{-P}_2)_2(\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_3, \eta^{2:2:1:1}\text{-P}_2)_2)][\text{TEF}]$ (**F**), containing a P_4Cu_2 6-membered ring, was reported some time ago (Figure 3).^[8c]

When using the different Cu^I source $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{TEF}]$ (**C**)^[7a] in the reaction with **A**, we were surprised at receiving the new coordination compound $[\text{Cu}\{\text{Cu}(\text{CH}_3\text{CN})_2\}_2\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_5, \eta^{2:2:2:1:1}\text{-P}_2)\}_2][\text{TEF}]_3$ (**1**, Figure 2). Crystals of **1** as orange blocks (**1a**) in the trigonal space group $P3_2$ were obtained by diffusion of *n*-pentane or toluene into the crude reaction mixture. When using *n*-pentane, **1** crystallizes as red plates (**1b**) in the monoclinic space group $P2_1/c$. In compound **1**, two P_2 ligand complexes **A** are coordinated to a molecular chain of three copper atoms ($\text{Cu}\cdots\text{Cu}$ 2.4344(10)–2.4537(19) Å). The peripheral copper atoms

Cu_{per} are coordinated by two acetonitrile ligands each. Unlike other known structures, which feature a characteristic six-membered Cu_2P_4 ring with **A** being coordinated in a type I–III coordination mode,^[8c,7c] in **1**, a third additional copper atom is located in the center of this six-membered ring with an unprecedented type **V**-coordination (Figure 1). Therefore, the P–P bonds in **1** (2.4344(10)–2.4537(19) Å) are elongated compared to the free **A** (2.0798(3) Å).^[13a] The bonds between the peripheral copper atoms and the respective phosphorus atoms are between 2.3830(19) and 2.460(3) Å, and are thus significantly longer than those in the dimer **F** (2.240(3)–2.277(2) Å). The Cu–Cu–Cu angles in **1** are between 177.95(9)° and 180°, depending on the crystallographic space group of the product, and the angles around the central copper atom are between 57.70(6) and 62.39(9)°. Compound **1** presents the first trinuclear Cu^I complex with such short $\text{Cu}\cdots\text{Cu}$ distances, stabilized by an unprecedented $\eta^{2:1:1}$ coordination of a polynictogen unit.

By using an excess of the Cu^I salt **C** in the reaction with **A** (CH_2Cl_2 , room temperature), the compound $[\{\text{Cu}(\text{CH}_3\text{CN})_2\}_2\{\text{Cu}(\text{CH}_3\text{CN})_3\}_2\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_5, \eta^{2:2:2:1:1}\text{-P}_2)\}][\text{TEF}]_3$ (**2**, Figure 2) was obtained. Compound **2** crystallizes as yellow blocks and consists of only one complex **A** coordinated to

three copper atoms in the coordination mode type **V**. The peripheral copper atoms are further saturated with three acetonitrile ligands each; the central copper atom has two acetonitrile ligands attached. The Cu...Cu distances in **2** (3.0013(6) Å and 3.0593(6) Å) are significantly elongated compared to **1**. The distance between the two peripheral copper atoms is also significantly larger in **2** (5.8238(8) Å; **1**: 4.869(2)–4.904(2) Å). The Cu–P bonds are slightly longer for Cu_{cen}–P (2.3706(8) and 2.3909(8) Å), but shorter for Cu_{per}–P (2.2446(8) and 2.2520(8) Å) as compared to **1**. Also, the Cu–Cu–Cu angle is with 147.861(19)° significantly more bent. The angles around the central copper atom possess values between 47.55(2) and 53.56(3)°.

Furthermore, we were interested in the reactivity of the As₂ ligand complex [Cp₂Mo₂(CO)₄(μ₄η^{2,2}-As₂)] (**B**) towards [Cu(CH₃CN)₄][TEF] (**C**). In a straightforward synthetic approach, mixing **B** with an equimolar amount of **C** in CH₂Cl₂ at room temperature, the new compound [{{CpMo(CO)₂}}₂(μ₅η^{2,2:2:1}-As₂)]₂[Cu(CH₃CN)₂ Cu(CH₃CN)][TEF]₂ (**4**) was obtained. Layering with *n*-pentane afforded **4** in a moderate yield as red needles suitable for X-ray structure analysis (Figure 2).^[14] The solid state structure of **4** reveals a Cu dimer stabilized by two As₂ ligands **B**. Additionally, the copper atom Cu1 is coordinated by two acetonitrile ligands and the copper atom Cu2 by one such ligand. Cu1 is η¹-coordinated by one As atom from both As₂ ligand complexes **B**, Cu2 is η²-coordinated by two complexes **B** in a novel η^{2:1} coordination mode **IV**. The Cu...Cu distance (2.6925(7) Å) is elongated compared to **1**. The As–As bonds (2.3905(5)–2.3901(5) Å) are slightly elongated compared to the uncoordinated complex **B** (2.311(3) Å).^[15] Additionally, the distances of the coordinating As atoms to Cu2 (η²-coordination) are slightly longer (2.4849(6)–2.5312(6) Å) than the As–Cu1 distances (η¹-coordination, 2.4582(6)–2.4850(6) Å). A compound **5**, isostructural to **4**, containing a different counterion, was formed by the reaction of **B** with the Cu^I salt [Cu(CH₃CN)₃][FAI] (**E**) (cf. Supporting Information).

Moreover, the trinuclear complex **6** was obtained by reacting **B** with [Cu(CH₃CN)₄][BF₄] in CH₂Cl₂ at room temperature using equimolar amounts. By diffusion of *n*-pentane into the crude reaction mixture, **6** crystallizes as dark red blocks. X-ray crystallography of **6** revealed that the central Cu atom has an occupancy of 0.8. Therefore, a complex with only the peripheral copper atoms is present with an occupancy of only 0.2 (**F**-like). Furthermore, the acetonitrile molecules coordinated to the outer Cu atoms have an occupancy of 0.59 (for further details see Supporting Information). The major part (Figure 2) consists of a Cu₃ (d(Cu–Cu) = 2.587(4) Å) chain coordinated by four As₂ ligand complexes **B**, with the peripheral copper atoms (Cu2B and Cu2B') additionally coordinated by one acetonitrile ligand each. While Cu2B and Cu2B' are η²-*side-on*-coordinated by one molecule of **B** and η¹-*end-on*-coordinated by two other [Cp₂Mo₂(CO)₄(μ₄η^{2,2}-As₂)] moieties, Cu1 shows only η²-*side-on*-coordination by two molecules of **B**. The As–As bonds of the *side-on*-coordinated molecules **B** are tilted by an angle of 133° in relation to the plane As1–Cu1–As2'–Cu2B and accordingly tilted to an angle of 47° to the symmetry-generated plane.

By using a 1:1 stoichiometry of **B** and **D**, product **6** was obtained containing a 4:3 composition of **B** and **D**. It was expected that a higher ratio of **D** would lead to a product that is similar to complex **1**. Quite contrary to expectations, when using an excess of **D**, compound **7** was formed. The structure of **7** is comparable to the structures of compounds **4** and **5**, respectively, with the difference that the Cu₂ atom is not coordinated by a CH₃CN molecule. However, the synthesis of the Mo₂P₂-containing compound [Cu(CH₃CN)₂{Cu{Cp₂Mo₂(CO)₄(μ₄η^{2,2:2:1}-P₂)}₂][BF₄]₂ (**3**) (Figure 2), which is isostructural with **7**, was achieved by reacting equimolar amounts of **A** with **D**. The use of two equivalents of **A** leads to a compound containing a P₄Cu₂ 6-membered ring similar to compound **F** (Figure 3).^[8c] Compounds **3** (orange plates) and **7** (red plates) crystallize both in the monoclinic space group *I2/m*. For detailed information on their structures, see the Supporting Information.

The products **1**–**7** are well soluble in donor solvents such as CH₃CN and slightly soluble in CH₂Cl₂, but insoluble in other common organic solvents such as THF, toluene and *n*-pentane. The NMR spectra of all compounds were recorded in [D₃]acetonitrile at room temperature. The ¹H and ¹³C{¹H} NMR spectra of compounds **1**–**7** indicate decomplexation by showing signals corresponding to the proton and carbon nuclei of the Cp and CO ligands of **A** or **B**, respectively. The ³¹P NMR spectra of the compounds **1**–**3** show broad signals that are up-field shifted compared to the free P₂ ligand complex **A** (δ = –43.2 ppm).^[13a] The broad signals in combination with former *variable-temperature* NMR studies on the Ag-dimer [Ag₂{Cp₂Mo₂(CO)₄(μ₄η^{2,2:1:1}-P₂)}₂{Cp₂Mo₂(CO)₄(μ₄η^{2,2:1}-P₂)}₂][TEF]₂^[7c] indicate a dynamic behavior in solution between **1**–**3** and monomeric fragments of them. Therefore, with acetonitrile being a coordinating solvent, it is most likely decomplexation that is observed in solution. In the ESI mass spectra of **1**–**3**, peaks for the cationic fragments ([Cu{Cp₂Mo₂(CO)₄P₂}]⁺, [Cu(CH₃CN){Cp₂Mo₂(CO)₄P₂}]⁺ and [Cu(CH₃CN)₂]⁺) were detected. While the ESI mass spectra of **4**–**5** show peaks for the cationic fragments [{Cp₂(CO)₄Mo₂As₂}₂Cu]⁺ and [{Cp₂(CO)₄Mo₂As₂}Cu(CH₃CN)]⁺, compounds **6**–**7** reveal an additional peak for [Cp₂(CO)₄Mo₂As₂]⁺. All compounds are air- and light-stable in the solid state for several days, but decompose within hours in solution when exposed to air.

The Cu...Cu distances in **1** and **6** are below the sum of the van der Waals radii^[16] suggesting intramolecular metallophilic interactions. In order to elucidate the bonding situation in [{{CpMo(CO)₂}}₂(μ₅η^{2,2:2:1}-P₂)]₂[Cu(CH₃CN)₂]₂Cu³⁺ (**1**) and

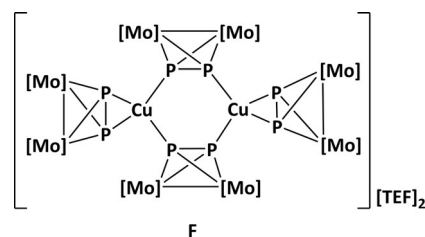


Figure 3. Structure of the dimeric compound **F**.^[8c]

$[\{\{\text{CpMo}(\text{CO})_2\}_2(\mu_5, \eta^{2:2:2:1:1}\text{-P}_2)\}\{\text{Cu}(\text{CH}_3\text{CN})_3\}_2\text{Cu}(\text{CH}_3\text{CN})_2]^{3+}$ (2), DFT calculations at the B3LYP/def2-TZVP level of theory were performed. The Cu...Cu distances in the gas phase optimized geometry in **1** (2.559 Å) are similar to the experimentally determined distances in the solid state (2.4344(10)–2.4537(19) Å). For **2**, the Cu...Cu distances are even longer in the gas phase optimized geometry (3.380 and 3.384 Å) compared to the solid state (3.0013(6) and 3.0593(6) Å). When dispersion effects are included in the calculations, the Cu...Cu distance in **1** decreases to 2.483 Å, indicating that dispersion plays an important role in the geometry of **1**. A similar effect, although less accentuated has also been observed for **2**. The calculations also show that the bonding of the peripheral Cu ions to the P₂ ligands in **1** takes place via the coordination of the phosphorus lone pairs, while the central Cu ion binds to the P–P σ-orbital of the P₂ unit. This is clearly revealed by the localized molecular orbitals (LMOs) (Figure 4).

A small orbital contribution of the central Cu ion to the LMOs of the P–Cu_{per} bond of roughly 7% was detected for **1**. A comparison of the LMOs of **1** with that of $[\{\{\text{CpMo}(\text{CO})_2\}_2(\mu_4, \eta^{2:2:1:1}\text{-P}_2)\}_2\{\text{Cu}(\text{CH}_3\text{CN})_2\}_2]^{2+}$ (**G**)^[7a] shows that the bonding of the P₂ ligand **A** to the peripheral Cu ions is very similar (Figure S3). The Wiberg bond indexes (WBIs) of the P–P bond in **G** are close to unity (1.06), while in **1** and **2** the WBIs of the P–P bonds are lower (0.78 in **1**; 0.72 in **2**), indicating a weaker P–P bond. This is not unexpected if considering the coordination of the P–P σ-bond additionally to the central Cu ion, which leads to the depletion of the electron density in this bonding orbital. The WBIs of the peripheral Cu–P bonds in **1**, that is, 0.40–0.44, are slightly lower than in **G** (0.53–0.55) and **2** (0.55), respectively. The WBIs of the Cu_{cen}–P bonds in **1** are 0.29 (Cu9–P6, Cu9–P8) and 0.40 (Cu9–P5, Cu9–P7), pointing to a slightly asymmetric bonding and a preference for a linear coordination geometry of the central Cu ion. This is an explanation for the elongation of the P–P bond in **1** (WBI 0.78) compared to **G** (1.06). The calculations indicate that between the three Cu ions in **1** an interaction is present since a WBI of 0.11 was found. In order to obtain deeper insight into the nature of

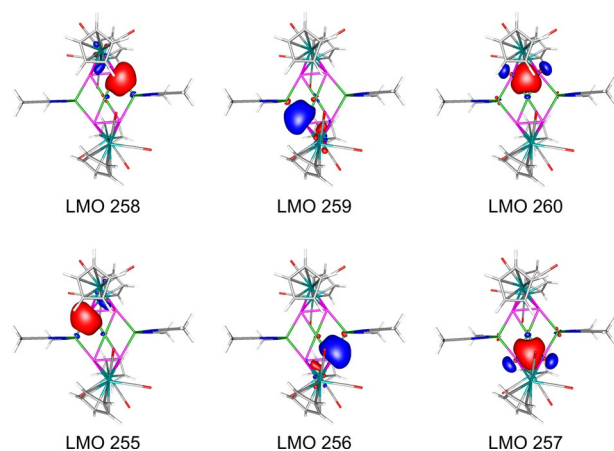


Figure 4. Selected Localized Molecular Orbitals (LMOs) representing the Cu–P bonding in $[\{\{\text{CpMo}(\text{CO})_2\}_2(\mu_5, \eta^{2:2:2:1:1}\text{-P}_2)\}\{\text{Cu}(\text{CH}_3\text{CN})_2\}_2\text{Cu}]^{3+}$, calculated at the B3LYP/def2-TZVP level of theory.

the Cu–Cu interaction, we investigated the topology of the electron density of **1** by means of the atoms in molecules (AIM) method and were able to locate bond critical points (BCPs) between the Cu atoms. The electron density at these BCPs is rather low and the Laplacian of the electron density is positive, which nevertheless indicates that interaction is present (for details see SI). The ratio of the potential energy density ($|V|$) and the kinetic energy density (G) at the bond critical point of 1.20 is characteristic of intermediate interactions between typical covalent and closed shells, for which the $|V|/G$ ratio lies between 1 and 2. Interestingly, the ellipticity at the BCP is rather high ($\epsilon = 2.13$) pointing to a kind of π -type interaction. The interaction between the Cu atoms is also supported by the density overlap regions indicator (DORI) analysis which clearly identifies regions of overlapping electron density (see Supporting Information).

In conclusion, we synthesized seven unprecedented coordination compounds (**1**–**7**), obtained by reacting the P₂ (**A**) and As₂ (**B**) ligand complexes with three different Cu^I salts (**C**, **D** and **E**) containing a WCA as counterion. Thus, four dinuclear copper dimers (**3**, **4**, **5** and **7**) and three trinuclear copper complexes (**1**, **2** and **6**) were obtained. For the first time, tetrahedral Mo₂E₂ ligand complexes are able to connect different metal atoms forming a chain of three Cu atoms. The formation of these complexes reveal the decisive influence of WCAs as counterion in the used Cu^I salts with different coordinating solvents, as $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{TEF}]$ forms a trinuclear Cu^I chain coordinated by two **A** units and $[\text{Cu}(\text{o-DFB})][\text{TEF}]$ forms a Cu₂P₄ ring.^[8c] The Cu...Cu distances in the trinuclear copper complexes **1** and **6** (2.4344(10)–2.4537(19) Å; 2.587(4) Å) are below the sum of the van der Waals radii, suggesting intramolecular metallophilic interactions. DFT calculations for **1** at the B3LYP/def2-TZVP level of theory reveal that the bonding of the peripheral Cu ions to the Mo₂P₂ ligands in **1** takes place via the coordination of the phosphorus lone pairs, while the central Cu ion binds to the P–P σ-orbital of the Mo₂P₂ unit in an unprecedented coordination mode. As WBIs of 0.11 were found between the central and peripheral Cu ions, an interaction can be concluded, which are supported by AIM analysis bond critical points between the Cu atoms could be located. Moreover, under the same reaction conditions, the As₂ ligand complex **B** reveals a higher tendency to coordinate in an η^2 -fashion and additionally in an $\eta^1:\eta^1$ -mode in comparison to the P₂ complex **A**.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: coordination chemistry · copper · heterometallic complexes · polyniactogen complexes · WCA

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