

A series of bimetallic chain coordination polymers bearing $[\text{Ag}(\text{PPh}_3)_2]$ chromophores: Synthesis, structure and luminescence

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ABSTRACT

A series of three cyanide-bridged chain coordination compounds with the formulae $[\text{M}(\text{CN})_2(\text{PPh}_3)_2\text{Ag}]_n$ (M is Ag, Cu or Au) is presented. The compounds have been prepared by room temperature reactions of triphenylphosphane with the cyanide salts of silver(I), copper(I) and gold(I). The compounds are characterised with IR, elemental analyses, SEM-EDX and X-ray powder diffraction, and the molecular structures were elucidated by single crystal X-ray diffraction. The three compounds are best described as one-dimensional cyanide-bridged chain coordination polymers, where the tetrahedral Ag^+ ions are coordinated by 2 triphenylphosphane ligands and 2 cyanides, forming a AgN_2P_2 chromophore. The linear $\text{Ag}(\text{I})$, $\text{Cu}(\text{I})$ and $\text{Au}(\text{I})$ centers are in two-coordinate geometry with C-bound cyanides. No aurophilic or argentophilic interactions are observed, but in the lattice only C–H... π and C–H...M hydrogen bonds are present. The solid-state luminescence properties of the three compounds are discussed and assigned, in agreement with DFT calculations, to MMLCT.

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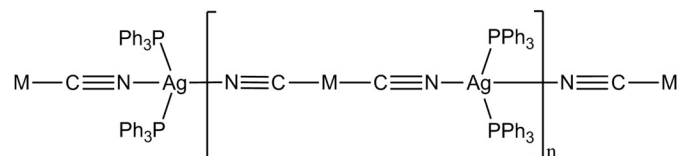
The poly- and hetero-nuclear metal complexes are known to exhibit promising performance in catalysis, magnetism and as sensors [1]. In particular, hetero-nuclear univalent coinage metal (Cu, Ag and Au) complexes are attracting great attention as therapeutics [2,3] and as photoactive agents [4]. The luminescent d^{10} closed shell $\text{Ag}(\text{I})$ or $\text{Au}(\text{I})$ compounds have been investigated over the last decades, where most studies correlated the emission properties or the electronic structure vs. the extent of argentophilic or aurophilic interactions [5,6]. These atom–atom interactions, coined by Pyykko as ‘relativistic effects’ [7,8], are known to be larger at $\text{Au}(\text{I})$ than $\text{Ag}(\text{I})$ [9], thus promoting a strong spin-orbital coupling leading to more intense emission. Such enhancement is unavailable with the analogous $\text{Cu}(\text{I})$ compounds, due to lack of the inter-chain relativistic effect stabilization, and this is also noticed at their cyanide salts. Both silver and gold cyanide crystallize as one-dimensional parallel chains, while its analogous copper crystallizes either as one-dimensional parallel chains, or two-dimensional intercalated grids [10–12].

Due to their strong σ -bonding, the linear dicyanometallates, by its bridging bidentate binding mode, is a classical ever-green building block for the construction of d^{10} – d^{10} Cu^+ , Ag^+ and Au^+ homo- and hetero-metallic coordination polymers showing interesting magnetic, vapochromic or luminescent properties [13,14]. We recently reported on a new one-dimensional coordination polymer, i.e., $[\text{Au}(\text{CN})_2\text{Ag}(\text{PPh}_3)_2]_n$ showing intense blue photoluminescence in the solid phase [15], and in this

study we extend the series $[\text{M}(\text{CN})_2\text{Ag}(\text{PPh}_3)_2]_n$, i.e., M is Ag, Cu or Au, now numbered as **1**, **2** and **3**, see Scheme 1. We are presenting here the synthesis, characterization, and molecular structures of **1** and **2**, as derived from X-ray single crystal diffraction along with their photoluminescence and DFT theoretical study, compared to those of **3**.

Details of the characterization techniques and syntheses of compounds **1** with **2** are summarized in [16]. Compound **3** was prepared as described by us before [15]. The X-ray single crystal diffraction data were collected using the CrystalClear Package [17], solved with SIR92 program [18], refined using the SHELX package [19] and graphically presented using the DIAMOND package [20]. Details are given in [21]. Photoluminescence experimental details are described in [22]. Method used for theoretical calculations is portrayed in [23,24].

A doublet at ca. 2150 and 2160 cm^{-1} is assigned to $\nu_{\text{C}\equiv\text{N}}$ stretching bands in all three compounds. Also similar $\nu_{\text{Ag-P}}$ vibrational frequencies are observed in **1**, **2** and **3** (see Fig. S1 in Supplementary data). The three compounds were prepared in excellent yields by room temperature reactions of triphenylphosphane with cyanide salts. The phase purity of the compounds **1** and **2** compared to **3** have been examined by SEM



Scheme 1. Representation of the studied polymeric compounds. M; Ag, Cu or Au.

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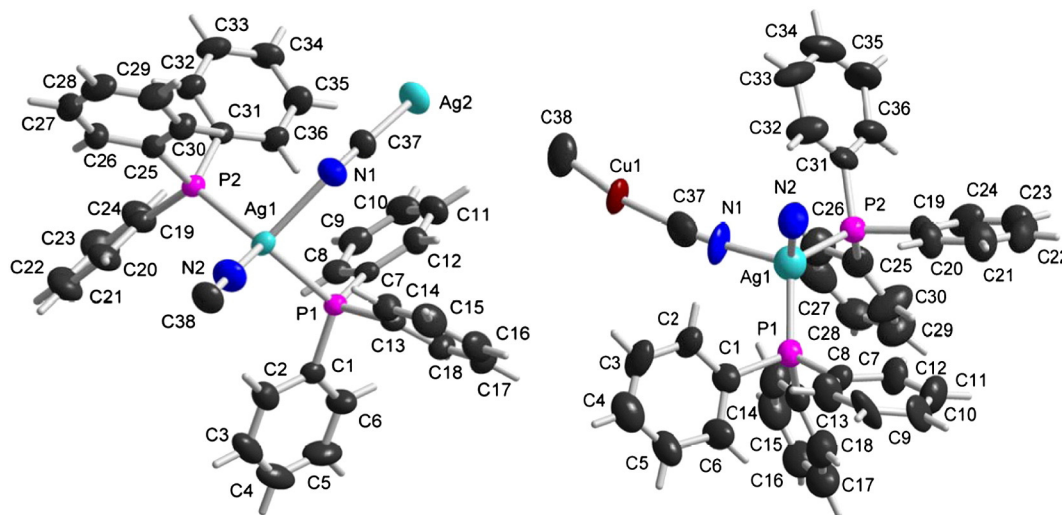


Fig. 1. Atomic displacement parameters and the used atomic numbering scheme for the asymmetric unit in the polymeric compound of **1** (left) and **2** (right). Selected bond distances (Å) and angles (°) in **1** and **2**: Ag1–P1: 2.4585, 2.2751; Ag1–P2: 2.4604, 2.2984; Ag1–N1: 2.4666, 2.0412; Ag1–N2: 2.2681, 1.9967; P1–C1: 1.8334, 1.8588; P1–C7: 1.8156, 1.7911; P1–C13: 1.8329, 1.8211; P2–C19: 1.8301, 1.8293; P2–C25: 1.8328, 1.8499; P2–C31: 1.8195, 1.8243; N1–C37: 1.1349, 1.0958; N2–C38ⁱ (**1**): 1.1409; N2–C38ⁱ (**2**): 1.1341; Ag2–C37(**1**): 2.0600; Cu1–C37(**2**): 2.0504; Ag2–C38ⁱ(**1**): 2.0586; Cu1–C38(**2**): 2.0506; P1–Ag1–P2: 129.80, 118.96; P1–Ag1–N1: 92.57, 108.19; P1–Ag1–N2: 111.93, 109.38; P2–Ag1–N: 100.40, 108.66; P2–Ag1–N2: 110.95, 105.65; N1–Ag1–N2: 105.05, 105.11; Ag1–P1–C1: 117.34, 114.04; Ag1–P1–C7: 109.56, 118.36; Ag1–P1–C13: 115.21, 114.63; C1–P1–C7: 104.09, 118.36; C1–P1–C13: 103.87, 101.35; C7–P1–C13: 105.60, 103.42; Ag1–P2–C19: 117.64, 116.01; Ag1–P2–C25: 109.71, 117.11; Ag1–P2–C31: 115.75, 113.79; C37–Ag2–C38ⁱ (**1**): 172.29; C37–Cu1–C38ⁱ (**2**): 169.44. Symmetry code(**1**): (i) $-1/2 + x, 1/2 - y, 1/2 + z$; (**2**): (i) $-x + 1, -y + 1, z + 1/2$.

and XRPD (see Figs. S2 and S3), and its analyses by EDX confirm the oxidation state of the metal ions. The molecular structures with thermal ellipsoidal numbering schemes for **1** and **2** are shown in Fig. 1. Crystallographic data are summarized in Table 1 and selected bond distances with angles are given in the caption of Fig. 1. Structure and geometrical parameters for compound **3** have been detailed elsewhere [15].

An earlier molecular elucidation of the $C_{38}H_{30}Ag_2N_2P_2$ one-dimensional polymer was earlier reported [25] in the $P2_1/c$ space group, while the present unit cell of **1**, with the glide plane along the diagonal (see Fig. 1 for symmetry codes), is exhibiting a smaller β -angle with shorter a - and c -crystallographic axes, and is also isostructural to **3**. On the other hand, compound **2** crystallizes in an inversion-twinned crystal with twinning ratio being 0.41:0.59 and is presented here for the first time. For compound **2**, the scatter plot of Bijvoet differences, prepared by using the Byvoetpair sub-routine in the PLATON [26] program, is shown in Fig. S4 (Supplementary data). As many as 4293 pairs with $\Delta_{obs} > 0.25\sigma(\Delta_{obs})$ were analyzed and 1340 reflections

confirmed the absolute structure, of which 687 and 653 reflections were of correct and wrong signs, respectively (black and red colors in the electronic version of the paper). The Hooft (y) parameter [27] of 0.500(1) and the $p3$ (racemic twinning probability) value of 1.00 confirmed the inversion-twining in compound **2** crystals.

In **1–3**, the tetrahedral Ag^I ions adopt a distorted tetrahedral geometry, while the other Ag^I, Cu^I and Au^I ions are two-coordinated in an almost linear geometry (angle C–M–C): 172.29(2)° in **1**, 169.44(8)° in **2** and 175.00(4)° in **3**, see Fig. 1. The hetero-intermetallic separation distances are 5.17(7) and 5.41(6) Å in **1**, 5.14(3) and 5.16(3) Å in **2** compared to 4.94(7) and 5.366(6) Å in **3**. In **1**, the chain propagation

Table 1
Crystallographic and refinement details for **1** and **2**.

Crystallographic parameters	1	2
Formula	$C_{38}H_{30}Ag_2N_2P_2$	$C_{38}H_{30}AgCuN_2P_2$
Formula weight	792.32	747.99
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (No. 14)	$Pna2_1$ (No. 33)
a, b, c [Å]	9.3275(5) 22.9484(13) 16.1416(11)	25.7722(10) 9.9450(3) 14.9732(6)
α, β, γ [°]	90 99.724(2) 90	90 90 90
V [Å ³]	3405.5(4)	3837.7(2)
Z	4	4
$D(\text{calc})$ [g/cm ³]	1.545	1.295
Theta min: max [°]	3.1: 27.5	3.1: 27.5
Data set (h; k; l)	–12: 10; –29: 29; –20: 20	–33: 0; –12: 0; 0: 19
Total, unique data	39538, 7757	4560, 3767
Observed data [$I > 2.0\sigma(I)$]	5818	3767
$N_{\text{ref}}, N_{\text{par}}, \text{restraints}$	7757, 398, 0	4560, 399, 1
R, wR_2, S	0.0423, 0.1245, 1.00	0.082, 0.194, 1.11
Minimum and maximum Residual Density [e/Å ³]	–0.77, 0.52	–1.7, 1.72
Flack parameter	–	0.41 (13)

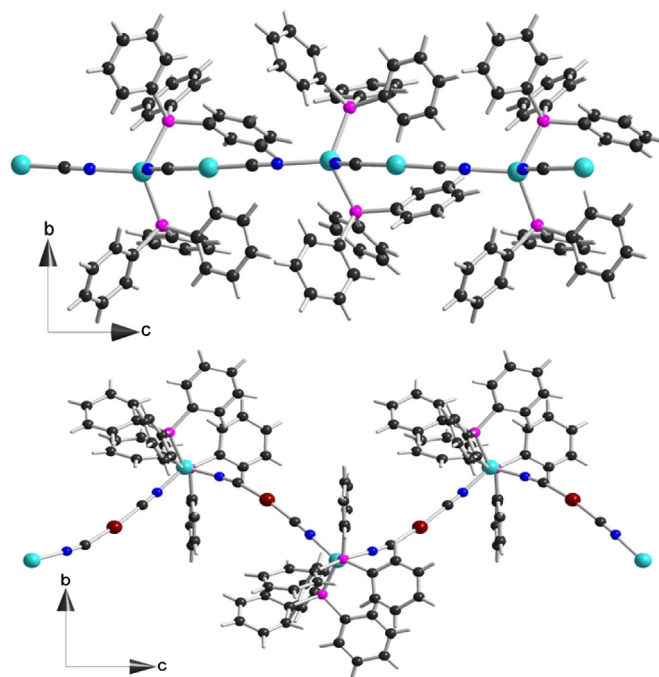


Fig. 2. Crystallographic a -axis projection, showing part of the polymeric one-dimensional chain compound in **1** (above) and **2** (below). Color codes: Ag, pale green; Cu, brown; P, purple; N, blue; C, black.

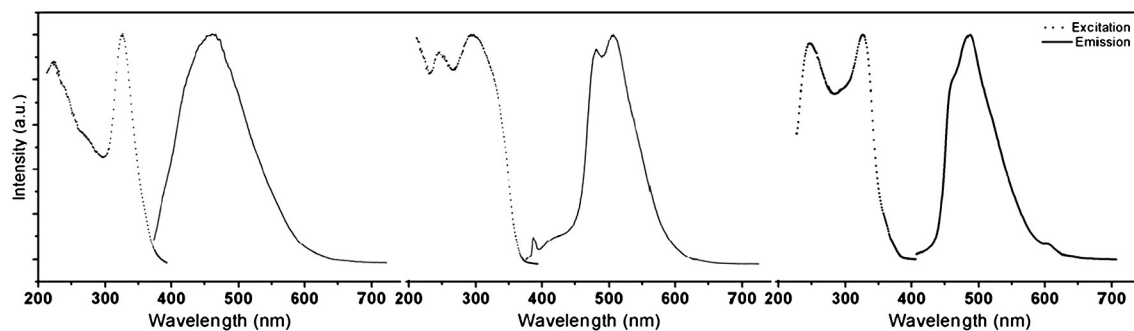


Fig. 3. Solid-state photoluminescence of the $[M(CN)_2Ag(PPh_3)_2]_n$ compounds. Left: **1**; middle: **2**; right: **3**. Intensity scales are in arbitrary units.

topology as defined by the phosphane-coordinated Ag–Ag–Ag angle is $174.55(4)^\circ$, compared to the zig-zag like one-dimensional polymer angle of $96.16(2)^\circ$ in **2** and $146.93(7)^\circ$ in **3**. The projections of the chain compounds in **1** and **2** are depicted in Fig. 2.

Both compounds are one-dimensional chain coordination polymers, i.e., in **1** along the $[10\text{--}1]$, and in **2** along the $[001]$ crystallographic vectors. In **1** and **2**, also similar to **3** [15], the chains are supported with a multitude of C–H... π and C–H...M (M in **1** is Ag, in **2** is Cu and in **3** is Au) interactions that arise from the phenyl ring hydrogen atoms. Apparently, no aurophilic or argentophilic interactions are visible, which can be attributed to the ligand bulkiness on Ag^I chromophores. In **2**, ca. 5% of unit cell volume is solvent accessible voids.

The room temperature excitation and emission spectra for **1**, **2** and **3** are given in Fig. 3. The order of emission intensity for the three compounds were as $3 > 2 > 1$. The excitation spectrum of **1** exhibits a broad band in the region from 220 to 370 nm with a distinctively sharp peak centered at 338 nm and a broader peak with its maximum <220 nm. The emission spectrum comprises a single broad band centered at 458 nm. Compared to the spectra reported earlier [15] for **3**, the maximum of the excitation peak recorded for **1** has shifted to a slightly longer wavelength (338 vs. 320 nm). The emission spectrum of **1** contains only one peak, instead of a single main peak with two shoulders. The value of the emission maximum for **1** roughly matches that of the left shoulder seen in the emission spectrum of **3**. In **2**, emission by the compound is efficiently excited in the range from 220 to 350 nm and the excitation spectrum features three discrete bands centered around <200, 253 and 300 nm. The emission spectrum shows two strong bands centered at 482 and 506 nm as well as a third weak line at 391 nm. Superficially, the emission spectrum resembles that of **3**, red-shifted by approximately 25 nm. The sample had turned yellow after the luminescence measurements, by being exposed to the excitation beam for approximately 10 minutes.

Compared to **3**, the luminescence intensity of compound **2** appears to be significantly weaker, but it is stronger than **1**.

Since compounds **1** and **3** were found as isostructural, while the structure of compound **2** differs, as it was derived from a racemic twinned monoclinic crystal simulating orthorhombic symmetry, we have calculated the frontier molecular orbitals for compound **2** and for the sake of comparison; we performed the calculation for compound **2**, adopting the same z-matrix of **1** by replacing the silver with copper. As expected, the HOMO characters of **1–3** are containing the d_{xy}^2 orbital of the AgN_2P_2 chromophore with $\sigma(Ag\text{--}P)$ bonding, π -orbital contribution from phenyl rings as well as $\pi(C \equiv N)$ -bonding. The cyanide π^* -orbital mixes with the $M^{+1} p^*$ -orbital in bonding style to form the LUMO's, see Fig. S5. The HOMO/LUMO gap of ca. 0.09 in **1** and 0.06 in **2** compared to ca. 0.03 a.u. in **3** was found in accordance with the relative emission intensities observed in photoluminescence measurements, which can be attributed, similar with other results [15,28,29], to MMLCT ($d\text{--}p^*$) transition, eventually can induce structural variations along chain polymer.

In conclusion, Three new bimetallic one-dimensional cyanide-bridged coordination polymeric compounds are presented; i.e., $Cu^I\text{--}Ag^I$, $Ag^I\text{--}Ag^I$ and the analogue $Au^I\text{--}Ag^I$. The $Ag^I\text{--}Ag^I$ compound was found to be isostructural to the $Au^I\text{--}Ag^I$ compound, whereas the $Cu^I\text{--}Ag^I$ compound was crystallized in racemic twinned crystals. The emission intensity was found in the order $Au^I\text{--}Ag^I > Cu^I\text{--}Ag^I > Ag^I\text{--}Ag^I$, also in agreement with the HOMO/LUMO energy gap, as mostly originated from MMLCT.

Acknowledgments

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Appendix A. Supplementary material

CCDC's 933281–933282 contain the supplementary crystallographic data for compounds **1–2**. These data can be obtained free of charge by <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

The supplementary data contain IR spectra of **1–3** (Fig. S1), SEM with EDX of **1–3** (Fig. S2), XRPD of **1** (Fig. S3), Bijvoet pairs scatter plot of **2** (Fig. S4) and HOMO/LUMO isosurfaces of **1–3** (Fig. S5). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2013.07.020](https://doi.org/10.1016/j.inoche.2013.07.020).

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- [16] The starting chemicals silver(I) cyanide, copper(I) cyanide, gold(I) cyanide and triphenylphosphane were used as commercially supplied (Analar grade). Hexane and dichloromethane were kept over molecular sieves and used without distillation. Elemental analyses were measured by Perkin Elmer Series II-2400 analyzer. The IR spectra were recorded in the region 4000–400 cm^{-1} using spectroscopic grade KBr-pellet on Shimadzu IRAffinity-1 with a resolution of 4 cm^{-1} . Energy Dispersive

- X-ray (EDX) spectra were collected by JEOL JSM-6380 LA Scanning Electron Microscope (SEM) and X-ray Powder Diffraction (XRPD) was measured using Cu-radiation by Bragg-Brentano focusing geometry on Rigaku Ultima-IV diffractometer. Compound 1: Silver cyanide (0.134 g, 1 mmol) was added to a clear solution of triphenylphosphane (0.786 g, 3 mmol) in dichloromethane (30 ml). Stirring continued for 10 minutes till a clear solution was obtained. 1 mmol of AgCN was added and stirring was continued for one day to give a clear solution. Filtration of non-dissolved materials and addition of hexane to the filtrate after 3 days yielded white crystals suitable for X-ray single crystal diffraction. White crystals of $C_{38}H_{30}Ag_2N_2P_2$ (0.737 g, ca. 93%), m.p. 231 °C, Elem. Anal. for $C_{38}H_{30}Ag_2N_2P_2$: Found (calc.): 57.85 (57.6) %C, 3.54 (3.8) %H, 3.64 (3.5) %N. IR (KBr) ν_{max} cm^{-1} : 501 (s) (M-N), 690 (s), 735 (s), 950 (m), 1080 (s), 1420 (s), 1470 (s), 2100 (m) (C \equiv N), 3033 (m). Compound 2: Silver cyanide (0.134 g, 1 mmol) was added to clear solution of triphenylphosphane (0.786 g, 3 mmol) in dichloromethane (30 ml). Stirring continued for 10 minutes till a clear solution was obtained. Cuprous cyanide $CuCN \cdot H_2O$ (0.108 g, 1 mmol) was added and stirring was continued for one day to yield a clear solution. Filtration and addition of hexane to the filtrate after 2 days resulted in white crystals suitable for X-ray single crystal diffraction. White crystals of $C_{38}H_{30}AgCuN_2P_2$ (0.726 g, ca. 97.1%), m.p. 197 °C, Elem. Anal. for $C_{38}H_{30}AgCuN_2P_2$: Found (calc.): 61.41 (61.0) %C, 3.73 (4.0) %H, 3.75 (3.7) %N. IR (KBr) ν_{max} cm^{-1} : 503 (s) (M-N), 691 (s) (C-H), 733 (s), 953 (m), 1079 (s), 1418 (s), 1468 (s), 2096 (m) (C \equiv N), 3032 (m).
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- [21] Suitable crystals were selected under optical microscope, glued and mounted on thin glass capillaries. Diffraction data were collected using a Rigaku R-axis RAPID diffractometer equipped with imaging plate area detector utilizing Mo-K α radiation ($\lambda = 0.71075$ Å) with a graphite monochromator. The data were collected in ω -scans at a temperature of 294 ± 2 K to a maximum 2θ of 55.0° . The intensity data were corrected for Lorentz and polarization effects, also for absorption and extinction. Structures were refined by full-matrix least squares on all $|F^2|$ data. All non-hydrogen atoms were refined anisotropically. All aromatic H-atoms were geometrically fixed using appropriate riding approximations.
- [22] The excitation and emission spectra were recorded at room temperature using a Shimadzu RF-5301PC spectrofluorophotometer equipped with a solid state sample holder. The excitation spectra were recorded by constantly monitoring the emission spectra at the wavelength of most intense luminescence while scanning the excitation wavelength from 220 to 400 nm. The excitation spectra were corrected for the response of the detector using an 8 mg/ml solution of rhodamine-B in ethylene glycol as a standard.
- [23] Single point *ab-initio* molecular electronic calculations were performed on ground state geometry truncated from X-ray structure z-matrix of $d^{10} [Ag(PPh_3)_2 M(CN)]$ cationic fragment (M is Ag, Cu or Au) with tetrahedral Ag^I and linear M^I coordination environments are sustained by two HCN, while the two hydrogen atoms geometrical positions were optimized. The exchange correlation energy was calculated without geometrical constraints, employing the hybrid exchange functional B3LYP, augmented with the scalar zeroth-order regular approximation (ZORA) triple- ζ -plus two polarization function (TZ2P) basis set, as implemented. The A-DIIS restricted SCF relativistic calculations were performed, employing a Slater Type Orbital (STO) double- ζ -plus one polarization function (DZP) for metal ions.
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