Linear One-Dimensional Coordination Polymers Constructed by Dirhodium Paddlewheel and Tetracyanido-Metallate Building Blocks

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Abstract: In this article, we describe the preparation of anionic heteronuclear one-dimensional coordination polymers made by dirhodium paddlewheels and tetracyanido-metallate building blocks. A series of complexes of $[\text{PPh}_4]^2n[\text{Rh}_2(\mu-O_2CCH_3)_4][\text{M(CN)}_4]_n$ ($\text{M} = \text{Ni}$ (1), Pd (2), Pt (3)) formulae were obtained by reaction of $[\text{Rh}_2(\mu-O_2CCH_3)_4]$ with $[\text{PPh}_4]^2[\text{M(CN)}_4]$ in a 1:1 or 2:1 ratio. Crystals of 1–3 suitable for single crystal X-ray diffraction were grown by slow diffusion of a dichloromethane solution of the dirhodium complex into a chloroform solution of the corresponding tetracyanido–metallate salt. Compounds 1 and 2 are isostructural and crystallize in the triclinic $P1$ space group, while compound 3 crystallizes in the monoclinic $P2_1/n$ space group. A detailed description of the structures is presented, including the analysis of the packing of anionic chains and $\text{PPh}_4^+$ cations.

Keywords: dirhodium compounds; tetracyanido-metallate complexes; one-dimensional coordination polymers

1. Introduction

Dinuclear complexes with a paddlewheel structure show a rich chemistry and different electronic configurations as a consequence of the distribution of the energy levels and the number of electrons in the dimetallic unit [1,2]. Dirhodium complexes and, in particular, the tetracarboxylato derivatives, are among the most important and versatile paddlewheel compounds [1,2], and their reactivity has been explored in several fields such as catalysis [3–9] or bioinorganic chemistry [10–13]. The ground state electron configuration for most of these complexes is $\sigma^2\pi^4\delta^2\delta^*\pi^4$ for a diamagnetic $\text{Rh}_2^{4+}$ unit, which, therefore, displays a single metal-metal bond order [1,2].

Many dirhodium molecular complexes have been reported owing to the facility of the rhodium ions to coordinate monodentate donor ligands at the axial positions of the paddlewheel structure [1,2,14–17]. Moreover, dirhodium units have been used to form one-dimensional coordination compounds using bridging ligands between the dimetallic cores [18–21]. The use of other metal complexes as connectors between the paddlewheel units can lead to the formation of heterometallic one-dimensional coordination polymers, whose versatile chemical and physical properties, such as temperature dependent luminescence or modulation of their electronic structures, make those polymers promising materials [22–25]. An interesting approach to obtain this kind of
heterometallic one-dimensional polymers is the use of platinum complexes to form \([\text{Rh}_2]\cdot[\text{Pt}_2]\cdot[\text{Pt}_2]\) chains, in which the different dimetallic units show direct Rh-Pt metal-metal bonds \([26–29]\). Paramagnetic \([\text{Rh}_2]\cdot[\text{Pt-Cu-Pt}]\) chains can be synthesized, also inserting a copper complex \([30,31]\). In addition, several heterometallic one-dimensional polymers using dicyanidoaurate, \([\text{Au(CN)}_2]^-\) \([32]\), or dicyanidoargentate, \([\text{Ag(CN)}_2]^-\) \([33]\), as bridging axial ligands have been reported by our research group. The use of cyanide-bridged cyanidometallates to form heterometallic complexes has been widely reported in the literature, owing to the diversity in the topologies and dimensionalities found in those complexes and to the interesting magnetic or optical properties showed by some of them \([34–40]\).

The use of charged cyanidometallates to bridge the neutral Rh(II)-Rh(II) units requires the presence of counter-cations to compensate the negative charge, which can simply be alkali cations \([32]\) or bulkier groups like tetraphenylphosphonium \([33]\). The interest of the latter lays in its higher arrangement diversity owing to the supramolecular structures that can be formed by phenyl–phenyl interactions through double, quadruple, or sextuple phenyl embraces \([33,41–44]\).

In this work, we examine the reaction of \([\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)_4]\) with \((\text{PPh}_4)_2[\text{M(CN)}_4]\) \((\text{M} = \text{Ni, Pd, Pt})\). The presence of four \(\text{CN}^-\) groups in the \([\text{M(CN)}_4]^-\) ion gives a great coordination versatility that could lead to discrete molecular compounds, one-dimensional structures, or bi-dimensional structures. Thus, in this paper, we describe the synthesis, characterization, and structural description of the heterometallic one-dimensional complexes
\[(\text{PPh}_4)_2[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)_4][\text{M(CN)}_4]_n\] \((\text{M} = \text{Ni (1), Pd(2), Pt(3)})\), using \([\text{M(CN)}_4]^-\) groups as bridging ligands.

2. Materials and Methods

2.1. Materials and Physical Measurements

\((\text{PPh}_4)_2[\text{M(CN)}_4]\) \((\text{M} = \text{Ni, Pd})\) salts were prepared by reaction of a 15 mL water solution of 0.100 g of the corresponding \(\text{K}_2[\text{M(CN)}_4]\) \((\text{M} = \text{Ni, Pd})\) compound with a 15 mL water solution of two equivalents of \(\text{PPh}_4\text{Br}\). The mixture was stirred for 30 min and the white solid obtained was filtered and washed with water and diethyl ether. Yield: \((\text{PPh}_4)_2[\text{Ni(CN)}_4], 0.200 \text{ g (57%)}. (\text{PPh}_4)_2[\text{Pd(CN)}_4], 0.230 \text{ g (75%)}. (\text{PPh}_4)_2[\text{Pt(CN)}_4]\) was prepared by the following procedure: a solution of 0.100 g of \(\text{K}_2[\text{PtCl}_4]\) \((0.24 \text{ mmol})\) in 10 mL of water was mixed with a solution of 0.120 g of \(\text{NaCN}\) \((2.45 \text{ mmol})\) in 10 mL of water. The mixture was stirred for 24 h and a solution of 0.200 g of \(\text{PPh}_4\text{Br}\) \((0.48 \text{ mmol})\) in 15 mL of water was added, immediately obtaining a white precipitate. The stirring was kept for 30 min and the solid was filtered and washed with water and diethyl ether. Yield: 0.170 g (72%). The rest of the reactants and solvents were obtained from commercial sources and used as received.

The elemental analysis measurements were carried out by the Elemental Analysis Service of the Universidad Complutense of Madrid. The FTIR spectra were collected with a Perkin-Elmer Spectrum 100 Spectrometer equipped with a universal ATR accessory in the 4000–650 cm\(^{-1}\) range. The mass spectra were collected by the Mass Spectrometry Service of the Universidad Complutense of Madrid using the electrospray ionization (ESI) technique and an ion trap-Bruker Esquire-LC spectrometer. Single crystal X-ray diffraction data were collected using an Oxford Diffraction Atlas diffractometer with Mo K\(_\alpha\) \((\lambda = 0.71073)\) Å radiation at room temperature. CCDC 1954793–1954795 contain the crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. A summary of some crystal and refinement data can be found in Table 1, and more information is collected in the Supplementary Material in Tables S1–S6.
Table 1. Crystal and refinement data for 1–3.

| Formula                  | 1 (M = Ni) | 2 (M = Pd) | 3 (M = Pt) |
|--------------------------|------------|------------|------------|
| fw                      | 1283.51    | 1331.21    | 1419.90    |
| Space group              | P-1        | P-1        | P2_1/n     |
| a/Å                      | 12.669(1)  | 12.636(1)  | 13.0959(4) |
| b/Å                      | 12.840(8)  | 13.095(2)  | 11.7615(4) |
| c/Å                      | 14.640(1)  | 14.524(2)  | 25.132(1)  |
| α°                      | 84.405(5)  | 85.137(9)  | 90         |
| β°                      | 67.765(7)  | 68.479(9)  | 101.613(4) |
| γ°                      | 70.795(7)  | 70.436(9)  | 90         |
| V/Å³                    | 2080.7(3)  | 2104.7(4)  | 3791.8(2)  |
| Z                       | 1          | 1          | 2          |
| d calc/g·cm⁻³            | 1.024      | 1.052      | 1.244      |
| µ/mm⁻¹                  | 0.694      | 0.676      | 2.356      |
| R indices (I > 2σ(I))    | R1 = 0.0740 | R1 = 0.0662 | R1 = 0.0395 |
| wR2 = 0.2276            | wR2 = 0.1699 | wR2 = 0.1046 |
| GooF on F²               | 1.017      | 1.005      | 1.008      |

2.2. Synthesis

Synthesis of (PPh₄)₂[Ni(μ-O₂CCH₃)₄][M(CN)₄]₄ (M = Ni (1), Pd(2), Pt(3))

A solution of 0.11 mmol (PPh₄)₂[MCN]₄ (M = Ni, Pd, Pt) in 15 mL of CH₂Cl₂ was added to a solution of 0.050 g of [Rh₂(μ-O₂CCH₃)₄] (0.11 mmol) in 15 mL of CH₂Cl₂, immediately obtaining a pink precipitate. The mixture was stirred for 24 h and the solid was filtered and washed with CH₂Cl₂.

(1) Yield. 0.068 g (48%). Anal.Calcd. (%) for 1-CH₂Cl₂: C, 53.54; H, 3.98; N, 4.09. Found (%): C, 53.26; H, 4.05; N, 4.20. FT-IR (cm⁻¹): 3061 w, 2992 w, 2137 w, 2120 w, 1597 s, 1484 w, 1436 s, 1408 s, 1342 w, 1315 w, 1108 s, 997 m, 760 m, 721 vs, 690 vs. ESI⁻, m/z = 501 [(PPh₄)Ni(CN)₄]⁻; 943 [M-(PPh₄)]⁻; 1385 [M+Rh₂(O₂CCH₃)₄](PPh₄)]⁻.

(2) Yield. 0.082 g (56%). Anal.Calcd. (%) for 2-CH₂Cl₂: C, 49.61; H, 3.76; N, 3.73. Found (%): C, 49.82; H, 3.82; N, 3.92. FT-IR (cm⁻¹): 3065 w, 2992 w, 2150 w, 2130 w, 1595 s, 1484 w, 1436 s, 1408 s, 1345 w, 1316 w, 1108 s, 995 m, 757 m, 730 w, 687 vs. ESI⁻, m/z = 549 [(PPh₄)Pd(CN)₄]⁻; 991 [M-(PPh₄)]⁻; 1433 [M+Rh₂(O₂CCH₃)₄](PPh₄)]⁻.

(3) Yield. 0.060 g (38%). Anal.Calcd. (%) for 3-CH₂Cl₂: C, 48.69; H, 3.62; N, 3.72. Found (%): C, 49.06; H, 3.74; N, 3.87. FTIR (cm⁻¹): 3063 w, 2927 w, 2167 w, 2146 w, 1584 vs, 1484 w, 1434 s, 1407 vs, 1344 m, 1108 s, 997 m, 756 m, 722 vs, 690 vs. ESI⁻, m/z = 638 [(PPh₄)Pt(CN)₄]⁻; 1080 [M-(PPh₄)]⁻; 1522 [M+Rh₂(O₂CCH₃)₄](PPh₄)]⁻.

Purple crystals of 1–3 suitable for single crystal X-ray diffraction were obtained after one week by slow diffusion of a solution of 0.050 g of [Rh₂(μ-O₂CCH₃)₄] (0.11 mmol) in 25 mL of CH₂Cl₂ into a solution of 0.06 mmol of the corresponding (PPh₄)₂[M(CN)₄] compound in 20 mL of CHCl₃.

3. Results and Discussion

3.1. Synthesis, Spectroscopic Characterization, and Spectrometric Characterization

The synthesis of compounds 1–3 was initially attempted using a 2:1 ratio of [Rh₂(μ-O₂CCH₃)₄] and the corresponding (PPh₄)₂[M(CN)₄] compound in order to prepare 2D coordination polymers. However, these reactions led to 1D coordination polymers in all cases, as shown by the crystal structures obtained. The presence of bulky PPh₄⁺ cations in the structure probably hinders the coordination of [M(CN)₄]²⁻ to four [Rh₂(O₂CCH₃)₄] units, leading to 1D arrangements instead. The reactions were repeated using a 1:1 ratio, obtaining products whose elemental analyses and IR spectra indicate both similar composition and coordination modes to those found in the crystal structures. Unfortunately,
the lack of crystallinity in the obtained products from the 1:1 reactions does not allow the structural comparison of the solid state arrangement with the crystals from the 2:1 reactions.

Compounds 1–3 can be obtained by stirring a mixture of the reactants at room temperature. However, following this procedure, the products are obtained as solids that cannot be recrystallized because of the low solubility of the polymeric species in common solvents. In order to obtain single crystals of the products that allowed the structural determination of the compounds, slow diffusion of a solution of \( \text{[Rh}_2(\mu-O_2\text{CCH}_3)_4]\) in \( \text{CH}_2\text{Cl}_2 \) into a solution of the corresponding \( \text{(PPh}_4)_2\text{[M(CN)]}_4 \) salts was employed. \( \text{(PPh}_4)_2\text{[M(CN)]}_4 \) salts were used instead of the commercially available \( \text{K}_2\text{[M(CN)]}_4 \) salts in order to use organic solvents in the reactions.

The IR spectra of all the compounds display bands corresponding to the symmetric and asymmetric stretching modes of the carboxylate groups: \( \text{COO}^\text{as} (1597–1584 \text{ cm}^{-1}) \); \( \text{COO}^\text{sym} (1450–1400 \text{ cm}^{-1}) \). The C-H stretching bands of the aliphatic and aromatic groups appear below and above 3000 cm\(^{-1}\), respectively. Moreover, two bands are observed between 2167 and 2120 cm\(^{-1}\) in all cases corresponding to the CN\(^-\) groups. The lower energy band corresponds to terminal CN\(^-\) ligands (not coordinated to Rh\(_2\) units), while the higher energy band corresponds to bridging CN\(^-\) ligands, coordinated to Rh\(_2\) units.

The base peak of the ESI\(^-\) mass spectra of 1–3 corresponds to \( \text{[(PPh}_4)\text{M(CN)]}_4^- \). A peak close to the base peak that corresponds to \( \text{[M-(PPh}_4)]^- \) is also present in all the spectra, as well as a peak assigned to \( \text{[M+Rh}_2(\text{O}_2\text{CCH}_3)_4-(\text{PPh}_4)]^- \). This last peak indicates polymerization of the complexes, although it could also be caused by an association process during the measurements.

3.2. Structural Description

The crystal structures of 1–3 were determined by single crystal X-ray diffraction. Complexes 1 and 2 are isostructural and crystallize in the \( \text{P}-1 \) space group, while compound 3 crystallizes in the \( \text{P}_2_1/\text{n} \) space group (Table 1). The three compounds comprise anionic 1D chains with the formula \( \text{[Rh}_2(\mu-O_2\text{CCH}_3)_4][\text{M(CN)]}_4 \text{n}^{2n^-} \) and interstitial PPh\(_4^+\) cations to balance the negative charges.

The structure of the 1D anionic polymer is remarkably similar in the two structural types and consists of dirhodium paddlewheel units joined by \( \text{[M(CN)]}_4 \) moieties. Figures S1–S3 show the asymmetric units of 1, 2, and 3, Figures S4 and S5 show their coordination environments, and Table 2 shows a selection of bond lengths and angles in 1–3; collected in more detail in Sections S4 and S5, Tables S7–S10. There are highly disordered solvent molecules in the crystals, which could not be satisfactorily modelled, and were removed with SQUEEZE software [45].

|                | 1 (M = Ni) | 2 (M = Pd) | 3 (M = Pt) |
|----------------|------------|------------|------------|
| Rh-Rh          | 2.394(1)   | 2.3968(9)  | 2.4007(8)  |
| Rh-N           | 2.275(6)   | 2.246(5)   | 2.209(5)   |
| Rh-O           | 2.019(5)   | 2.020(4)   | 2.026(4)   |
| Rh-O           | 2.024(5)   | 2.031(4)   | 2.029(4)   |
| M-C5 (bridge CN)| 2.035(5) | 2.040(4)   | 2.035(4)   |
| M-C6 (bridge CN)| 2.041(5) | 2.052(4)   | 2.042(4)   |
| M-C5 (bridge CN)| 1.888(8)  | 2.080(6)   | 1.998(6)   |
| M-C6 (terminal CN)| 1.850(8) | 1.960(8)   | 1.979(8)   |
| C5-N1 (bridge CN)| 1.062(9) | 1.031(7)   | 1.144(8)   |
| C6-N2 (terminal CN)| 1.14(1)  | 1.151(9)   | 1.127(9)   |
| Rh-Rh-N        | 178.4(2)   | 179.1(1)   | 178.2(1)   |
| Rh-N-C         | 178.0(8)   | 172.5(5)   | 175.8(5)   |
| C5-M-C6        | 88.8(3)    | 88.9(2)    | 89.9(3)    |

Concerning the \( \text{[Rh}_2(\mu-O_2\text{CCH}_3)_4] \) paddlewheel dimers, the rhodium atoms are joined by a single metal-metal bond and bridged by four acetate ligands, with an inversion center.
located in the middle of the Rh–Rh bond. Regarding the Rh coordination environment geometry, Rh-Rh bond (2.394(1)–2.4007(8) Å) values are very similar in the three cases to those found in the literature for similar compounds: $K_n\{[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)_4]\{\text{Au(CN)}_2\}_2\}_{n}^{2-}$ [32], $[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)_4]\{\text{PtCl}_4\}_n$ [46], (PPh$_4$)$_n\{[\text{Rh}_2(\mu-\text{O}_2\text{CR})_4]\{\text{Ag(CN)}_2\}_2\}_n$ (R = Me, Ph, CH$_2$OEt) [33], [K(18-crown-6)(H$_2$O)$_2$]$\text{K}(\text{18-crown-6})(\text{H}_2\text{O})_2\text{[Rh}_2(\mu-\text{O}_2\text{CPh})_4\text{]}\{\text{Fe(CN)}_6\}_2\text{]}\_8\text{nH}_2\text{O}$ [47], and $K_n\{[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)_4]\{\text{Co(CN)}_6\}_2\}_n$ [48]. The Rh-O distances in 1–3 (2.019(5)–2.052(4) Å) are also very similar to the values found in these analogous compounds.

In the tetracyano-metallate units, the metal atom is located at an inversion center, and these fragments bridge two dimetallic units by two CN$^-$ groups in trans disposition coordinated to the axial positions of the rhodium atoms. The Rh-N distances range from 2.209(5) to 2.275(6) Å, close to those of $K_n\{[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)_4]\{\text{Au(CN)}_2\}_2\}_n$ [32], (PPh$_4$)$_n\{[\text{Rh}_2(\mu-\text{O}_2\text{CR})_4]\{\text{Ag(CN)}_2\}_2\}_n$ [33], [K(18-crown-6)(H$_2$O)$_2$]$\text{K}(\text{18-crown-6})(\text{H}_2\text{O})_2\text{[Rh}_2(\mu-\text{O}_2\text{CPh})_4\text{]}\{\text{Fe(CN)}_6\}_2\text{]}\_8\text{nH}_2\text{O}$ [47], and $K_n\{[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)_4]\{\text{Co(CN)}_6\}_2\}_n$ [48].

The smaller size of Ni compared with Pd logically affects the M-C distance in the structures of 1 and 2. However, this effect is not observed when the structures of 2 (M = Pd) and 3 (M = Pt) are compared. The C5-N1 distance in the bridge CN$^-$ is slightly different depending on the M atom (1.062(9) Å for 1, 1.031(7) Å for 2, and 1.144(8) Å for 3). However, the C6–N2 distance in the terminal CN$^-$ ligands is very similar in the three compounds (1.14(1) Å for 1, 1.151(9) Å for 2, and 1.127(9) Å for 3). These C6-N2 distances are very similar to the values found in other complexes with terminal CN$^-$ ligands, such as $[\text{Ni(PhCN)}_2]\text{n}[\text{Ni(CN)}_4\text{n}](1.14–1.15 \text{ Å})$ [49] and $[\text{Hg(CN)}_2\{\text{NO}_3\}_2\text{n}(1.12 \text{ Å and 1.11 Å})$ [50].

The structure of the chains of 1–3 is almost linear (Figure 1), in contrast to the structure of $K_n\{[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)_4]\{\text{Au(CN)}_2\}_2\}_n$ [32], $[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)_4]\{\text{PtCl}_4\}_n$ [46], and (PPh$_4$)$_n\{[\text{Rh}_2(\mu-\text{O}_2\text{CR})_4]\{\text{Ag(CN)}_2\}_2\}_n$ (R = Me, Ph, CH$_2$OEt) [33], which are formed by zigzag chains. The Rh–Rh–N angles in 1–3 (M = Ni, 1; Pd, 2; Pt, 3) are 178.4(2)$^\circ$, 179.2(2)$^\circ$, and 178.2(1)$^\circ$, respectively, while Rh–N–C angles are 178.0(8)$^\circ$ for 1, 172.5(5)$^\circ$ for 2, and 175.8(5)$^\circ$ for 3. The M–M distance of the metals in $[\text{M(CN)}_4]^{-2}n$ groups is 12.840 Å for 1, 13.095 Å for 2, and 13.096 Å for 3. This distance is logically much longer than that found for similar chains with a zigzag disposition, for example, $K_n\{[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)_4]\{\text{Au(CN)}_2\}_2\}_n$ (Au-Au distance = 8.365 Å) [32].

Figure 1. View of the $[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)_4]\{\text{M(CN)}_4\}_2^n$ chains: left, chain in 1 (up) and 3 (down); right, view along the chain axis, b in 1 (up) and a in 3 (down).

An important structural difference is observed in the angle between the $[\text{M(CN)}_4]$ plane and one of the planes in the paddlewheel molecule: in compounds 1 and 2, the two are almost parallel (10.30$^\circ$
in 1 and 6.23° in 2), while in compound 3, the value is considerably higher (22.64°), as can be seen in Figure 1 (right).

However, the main difference between the two structural types lies in the arrangement of the anionic chains and the molecular cations in the crystal (see Figure 2). The packing is achieved in the three compounds by C–H···π interactions between hydrogen atoms from the acetate ligands and some of the rings in the PPh₄⁺ cations (Figures S6 and S7, and Tables S11 and S12). In the structure of compounds 1 and 2, only four hydrogen atoms in each paddlewheel unit participate in these interactions, while in compound 3, six C–H···π interactions are established, resulting in a denser packing.

![Figure 2. View along the chain axis of the packing of the anionic 1D polymers and the PPh₄⁺ counterions in the structures of 1 and 2 (left) and 3 (right).](image)

4. Conclusions

The room temperature reaction of [Rh₂(μ-O₂CCH₃)₄] with (PPh₄)₂[M(CN)₄] (M = Ni, Pd, Pt) leads to the formation of the one-dimensional complexes (PPh₄)₂[(Rh₂(μ-O₂CCH₃)₄)(CN)₄]ₙ. The formation of 2D coordination polymers was not observed, regardless of the reagent ratio used. Probably, the presence of bulky PPh₄⁺ groups hinders the formation of two-dimensional networks. The crystal structure of these polymers consists of almost linear chains formed by [Rh₂(μ-O₂CCH₃)₄] paddlewheel units axially bridged by two trans cyanide groups of the tetracyano-metallate moieties. The phenyl rings of the PPh₄⁺ cations are involved in C–H···π interactions with the hydrogen atoms from the acetate ligands, so the higher the number of involved hydrogen atoms, the denser the resulting packing.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/9/12/614/s1, Figure S1: Asymmetric unit of compound 1. Table S1: Sample and crystal data for 1. Table S2: Data collection and structure refinement for 1. Figure S2: Asymmetric unit of compound 2. Table S3: Sample and crystal data for 2. Table S4: Data collection and structure refinement for 2. Figure S3: Asymmetric unit of compound 3. Table S5: Sample and crystal data for 3. Table S6: Data collection and structure refinement for 3. Figure S4: Coordination environments of metal atoms in 1 and 2. Table S7. Coordination environment distances (Å) in 1 and 2. Figure S5. Coordination environments of metal atoms in 3. Table S8. Coordination environment distances (Å) in 3. Table S9. Coordination environment angles (°) in 1 and 2. Table S10. Coordination environment angles (°) in 3. Figure S6. C–H···π interactions in 1 and 2. Table S11. Supramolecular interactions in 1 and 2. Figure S7. C–H···π interactions in 3. Table S12. Supramolecular interactions in 3.

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