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Unique Copper-Organic Networks Self-Assembled from 1,3,5-Triaza-7-Phosphaadamantane and its Oxide: Synthesis, Structural Features, Magnetic and Catalytic Properties

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ABSTRACT

Three new coordination compounds, namely a 0D dicopper(II) complex $[Cu_2(\mu -$ MeCOO)₄(MeOH)₂](PTA=O)₂ (1), a 3D copper(II)-organic framework [Cu₃(µ-MeCOO)₆(µ₃-PTA=O]_n·3.5nMeCN (2), and a mixed-valence copper(I/II) 1D coordination polymer [Cu₃(μ -MeCOO)₄(MeCOO)(μ -PTA)₂(PTA)]_n (3), were self-assembled from copper(II) acetate and cage-like aminophosphine 1,3,5-triaza-7-phosphaadamantane (PTA) or its P-oxide (PTA=O). The obtained products were isolated as air-stable crystalline solids and characterized by IR and EPR spectroscopy, thermogravimetric and elemental analysis, as well as single crystal Xray diffraction. Although all compounds bear dicopper(II) paddle-wheel tetraacetate $[Cu_2(\mu -$ MeCOO)₄] blocks, they are arranged into very distinct metal-organic architectures. The structure of 2 reveals an intricate 3D metal-organic framework (MOF) driven by the μ_3 -PTA=O spacers acting in an unusual N, N, O-tridentate mode, whereas the compound **3** discloses an infinite 1D wave-like metal-organic chain with the dicopper(II) [Cu₂(u-MeCOO)₄] and monocopper(I) [Cu(PTA)(MeCOO)] blocks being interlinked by the μ -PTA linkers acting in an N,P-bidentate mode. Topological analysis of underlying nets was performed, revealing a decorated uninodal 3-connected framework with the ths topology in 2 and a uninodal 2-connected chain with the 2C1 topology in 3. Compounds 2 and 3 broaden a still very limited family of MOFs or coordination polymers assembled from PTA or its Poxide building blocks, also showing that PTA can be applied for the generation of unusual mixed-valence copper(I/II) derivatives. Besides, 2 represents the first example of a coppercontaining 3D MOF that is driven by PTA=O or any other PTA-derived block. Magnetic properties of 1-3 were investigated, modelled, and discussed in detail, resulting in the exchange coupling parameters $(J = -310, -320 \text{ cm}^{-1})$ that indicate a strong antiferromagnetic interaction within the dicopper(II) paddle-wheel blocks. Moreover, the compounds 1 and 2 show a notable catecholase activity in the aerobic oxidation of 3,5-di-tert-butyl-catechol to 3,5-di-*tert*-butyl-o-benzoquinone; turnover frequency values of up to 81 min⁻¹ were attained.

Introduction

Synthesis of novel copper-based coordination compounds using *P*,*N*- and *N*,*O*donating building blocks has become a popular research direction, especially aiming at the generation of coordination polymers (CPs) that possess a wide structural diversity and notable magnetic, catalytic, optical, host-guest, and therapeutic properties.¹⁻⁶ Many coordination polymers are often prepared by complicated and multistage synthetic procedures, or require the use of very complex building blocks. In this regard, 1,3,5-triaza-7-phosphaadamantane (PTA) and its *P*-oxide derivative (PTA=O) represent a very interesting class of cage-like *P*,*N*-

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or *N*,*O*-donor building blocks on account of their stability, aqueous solubility, and rich coordination chemistry.⁷⁻¹⁹ However, the application of such building blocks for the synthesis of functional coordination polymers is much less explored if compared with the conventional aromatic polycarboxylate or *N*-heterocyclic ligands.

On the other hand, copper is a bioessential element that is present in all organisms living in oxygen-rich environments. In particular, catechol oxidase is a type III active site metalloprotein that contains copper and shows catecholase activity.²⁰ In nature, such metalloproteins are very efficient catalysts for the oxidation of *o*-diphenols to the corresponding *o*-diquinones via the reduction of molecular oxygen to water.^{21,22} Therefore, studies on the model compounds as bioinspired catalysts with catecholase activity are promising for the evolution of new catalytic systems.^{23,24} Despite a good number of copper complexes that were tested as catalysts for the oxidation of catechols, catalytic systems based on copper coordination polymers are still scant.²⁵⁻²⁷

Following our interest in the self-assembly synthesis of copper coordination compounds driven by PTA or derived building blocks, we have reported some unique mixed-valence copper(I/II) derivatives, namely a tetranuclear complex $[Cu_4I_4(\mu-N_3)_2(N_3)_4(\mu-mPTA)_2(mPTA)_2]\cdot 2H_2O^9$ and a 1D coordination polymer $[Cu_3(\mu-HCOO)_2(HCOO)_3(\mu-PTA)_3(PTA)]_n \cdot nH_2O$,¹⁰ which are driven by *N*-methyl-1,3,5-triaza-7-phosphaadamantane(1+) (mPTA) or PTA blocks, respectively.

Inspired by these results and aiming at extending the series of such compounds to other PTA-based building blocks and to more complex structures including 3D metal-organic frameworks, we have attempted a number of self-assembly reactions using dicopper(II) paddle-wheel tetraacetate blocks and cage-like PTA=O or PTA spacers. As a result, three novel compounds were generated. Their structures range from a 0D dicopper(II) compound $[Cu_2(\mu-MeCOO)_4(MeOH)_2](PTA=O)_2$ (1) to a 3D copper(II)-organic framework $[Cu_3(\mu-MeCOO)_6(\mu_3-PTA=O)]_n \cdot 3.5nMeCN$ (2), and a mixed-valence copper(I/II) 1D coordination polymer $[Cu_3(\mu-MeCOO)_4(MeCOO)(\mu-PTA)_2(PTA)]_n$ (3). Hence, the present work describes the self-assembly synthesis, full characterization, structural and topological features, thermal and magnetic properties, as well as catecholase catalytic activity of these compounds. It should be highlighted that compound **2** represents the first 3D copper-based MOF driven by any cage-like derivative of PTA, as attested by a search of the Cambridge Structural Database.

Experimental

Materials and Methods. Syntheses of 1 and 2 were performed in air, while 3 was obtained under dry dinitrogen, using standard Schlenk techniques. All reagents and solvents were obtained from commercial sources and used as received, except from 1,3,5-triaza-7phosphaadamantane (PTA) and 1,3,5-triaza-7-phosphaadamantane-7-oxide (PTA=O) that were synthesized in accord with literature methods.^{28,29} The infrared spectra ($4000-400 \text{ cm}^{-1}$) were recorded on a Bruker Vertex 70 FTIR instrument in KBr pellets. Elemental analyses were performed on a CHNS Vario EL CUBE apparatus. Thermal analyses were run on a TG-DTA Setaram SETSYS 16/18 equipment using 10.694 (1), 11.358 (2), or 9.500 (3) mg of the compound sample (N₂ atmosphere, heating rate 10 °C/min). Powder X-ray analyses were performed with a Bruker D8 ADVANCE diffractometer using a Cu K α radiation ($\lambda = 1.5418$ Å) filtered with Ni. The diffractograms were recorded with a step size of $2\theta = 0.024^{\circ}$ to 0.048° over the range of $2\theta = 5-60^{\circ}$ and ratio 0.5. The calculated patterns were obtained from the single-crystal X-ray data using the MERCURY CSD 3.9 package. It should be noted that the compounds 1-3 are soluble in water and their single crystals are sensitive to the presence of moisture in air, can adsorb additional H₂O molecules from air, and/or can lose solvent molecules during storage. Hence, in some cases (in particular, for 2), the PXRD data of bulk samples do not exactly match the theoretical plots calculated from the single-crystal X-ray data. Catecholase activity studies were performed using an Agilent Cary 8454 UV-Visible Spectrophotometer with Agilent 89090A Peltier temperature controller with magnetic stirrer controller, and 845x UV-Vis System.

Synthesis and Analytical Data

[Cu₂(*μ*-MeCOO)₄(MeOH)₂](PTA=O)₂ (1). To a methanol solution (50.0 mL) of anhydrous [Cu(MeCOO)₂]₂ (182 mg, 0.50 mmol) was added a solution of PTA=O (179 mg, 1 mmol) in methanol (100.0 mL). The reaction mixture was stirred at room temperature (r.t., ~25 °C) for 30 min and then filtered off. The filtrate was left to evaporate in air for several days at r.t., producing blue X-ray quality single crystals. These were dried in air to furnish **1** in 55% yield, based on PTA=O. Compound **1** is soluble in H₂O, DMSO, MeOH and warm MeCN. Anal. Calcd for C₂₂H₄₄Cu₂N₆O₁₂P₂ (MW 773.5), %: C 34.16; H 5.68; N 10.85; found, %: C 34.15; H 5.73; N 10.86. IR (KBr, cm⁻¹): 3435 (s br.) and 3135 (s br.) *v*(OH), 2961 (m), 2927 (m), 2831 (m), 1610 (vs) and 1421 (vs) v_{as} (COO), 1364 (m) v_s (COO), 1297 (s), 1282 (vs), 1238 (s), 1156 (vs), 1097 (m), 1026 (s), 1007 (s), 978 (vs), 943 (w), 912 (s), 818 (m), 814 (m), 786 (w), 739 (m), 683 (s), 632 (m), 580 (s), and 453 (m). TG-DTA (N₂, 10 °C/min):110–160 °C (–2MeOH, Δm: 8.35% exptl., 8.28% calcd.), >200 °C (dec.).

[Cu₃(*μ*-MeCOO)₆(*μ*₃-PTA=O)]_n·3.5nMeCN (2). Solid PTA=O (352 mg, 2 mmol) was added to an acetonitrile solution (50.0 mL) of anhydrous [Cu(MeCOO)₂]₂ (182 mg, 0.50 mmol). The obtained mixture was refluxed for 1 h and then filtered off. The filtrate was left to slowly evaporate at ~4 °C for several days, producing green X-ray quality single crystals of **2**. If these crystals are dried and kept in air, a monohydrate derivative [Cu₃(MeCOO)₆(PTA=O)]_n·nH₂O (**2**') is produced in 46% yield, based on the copper(II) acetate. Compound **2** is soluble in H₂O, MeOH, MeCN, and DMSO. Anal. Calcd for C₁₈H₃₀Cu₃N₃O₁₃P·H₂O (MW 736.1), %: C 29.60, H 4.40, N 6.00; found, %: C 29.37, H 4.38, N 5.71. IR (KBr, cm⁻¹): 3435 (w br.) v(H₂O), 1620 (vs) and 1437 (vs) v_{as} (COO), 1299 (m), 1277 (w), 1221 (w), 1182 (m), 1085 (w), 1003 (w), 987 (w), 966 (m), 905 (vw), 795 (w), 684 (s), 627 (w), and 605 (w). TG-DTA (N₂, 10 K/min): 50–190 °C (-1.5H₂O, Δm: % 3.51 exptl., 3.63 % calcd.), >190 °C (dec.).

[Cu₃(*μ*-MeCOO)₄(MeCOO)(*μ*-PTA)₂(PTA)]_n (**3**). An excess of fine Cu powder (317 mg, 5 mmol) was added to an acetonitrile solution (50.0 mL) of anhydrous [Cu(MeCOO)₂]₂ (182 mg, 0.5 mmol). The reaction mixture was stirred at r.t. overnight, resulting in a gradual color change from green to colorless, and then was filtered off. Solid PTA (321 mg, 2 mmol) was added to the obtained filtrate. The resulting mixture was refluxed under dinitrogen for 15 min and then filtered off in air. The filtrate was left to evaporate for several days in air at r.t., resulting in green X-ray quality single crystals. These were collected and dried in air to furnish **3** in 10% yield, based on the copper(II) acetate. Compound **3** is soluble in H₂O, sparingly soluble in warm DMSO (slow decomposition occurs), and insoluble in MeOH and MeCN. Anal. Calcd for C₂₈H₅₁Cu₃N₉O₁₀P₃ (MW 957.3), %: C 35.30; H 5.28; N 13.24; found, %: C 35.13; H 5.37; N 13.17. IR (KBr, cm⁻¹): 2968 (m), 2936 (m), 1616 (vs) and 1426 (vs) ν_{as}(COO), 1372 (s) and 1349 (s) ν_s(COO), 1289 (s), 1237 (s), 1100 (m), 1050 (m), 1036 (m), 1015 (vs), 1000 (m), 992 (m), 972 (vs), 957 (s), 949 (vs), 887 (w), 810 (m), 799 (s), 763 (m), 745 (m), 681 (s), 629 (w), 608 (s), 582 (s), and 564 (m). TG-DTA (N₂, 10 °C/min): >190 °C (dec.).

Refinement Details for X-ray Analysis. The diffraction data for 1–3 were collected using an Oxford Xcalibur2 KM4 diffractometer with graphite-monochromated Mo-K α radiation. The collection and integration of crystal data were performed with the CrysAlis CCD, CrysAlis RED and CrysAlisPro systems at 100(2) K.^{30,31} The absorption correction was executed with the CrysAlis RED and CrysAlisPro software.³¹ The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 with the SHELXL-2016/6 program package.³² The non-hydrogen atoms were refined anisotropically, except of the C100, C101, C102, C103, N100 and N101 atoms of acetonitrile solvent in **2**. Three of five

acetonitrile molecules in 2 (C104, C105, N102; C106, C107, N103 and C108, C109, N104) were considered to possess 0.5 sites occupation, forming a disordered model (Figure S2). All hydrogen atoms were placed at calculated positions and refined using a riding model with $U_{iso} = nU_{eq}$ (n = 1.2 for H atoms of methylene groups and n = 1.5 for other H atoms), except of H1 atom in 1, which was located in the difference map and refined.

Crystal data for 1: $C_{22}H_{44}Cu_2N_6O_{12}P_2$, M = 773.65, a = 10.9387(4) Å, b = 9.5736(6)Å, c = 14.7979(5) Å, $a = 90^\circ$, $\beta = 90.604(4)^\circ$, $\gamma = 90^\circ$, V = 1549.59(12) Å³, T = 100(2) K, space group I2/m, Z = 2, 12949 reflections measured, 4054 independent reflections ($R_{int} = 0.0528$). The final R_I values were 0.0497 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1207 (all data). The goodness of fit on F^2 was 1.036. Crystal data for **2**: $C_{25}H_{40.5}Cu_3N_{6.50}O_{13}P$, M = 861.73, a = 15.154(3) Å, b = 25.427(3) Å, c = 19.928(3) Å, $a = 90^\circ$, $\beta = 104.366(17)^\circ$, $\gamma = 90^\circ$, V = 7438(2) Å³, T = 100(2) K, space group C2/c, Z = 8, 16682 reflections measured, 8382 independent reflections ($R_{int} = 0.0460$). The final R_I values were 0.0673 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1746 (all data). The goodness of fit on F^2 was 1.030. Crystal data for **3**: $C_{28}H_{51}Cu_3N_9O_{10}P_3$, M = 957.30, a = 8.0542(6) Å, b = 25.5933(13) Å, c = 9.6214(6) Å, $a = 90^\circ$, $\beta = 113.794(8)^\circ$, $\gamma = 90^\circ$, V = 1814.7(2) Å³, T = 100(2) K, space group P21/m, Z = 2, 16751 reflections measured, 5955 independent reflections ($R_{int} = 0.0852$). The final R_I values were 0.0521 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1746 independent reflections ($R_{int} = 0.0852$). The final R_I values were 0.0521 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1046 (all data). The goodness of fit on F^2 was 0.811.

CCDC 1541175 (1), 1541176 (2), 1541177 (3) contain the supplementary crystallographic data. Ellipsoid plots for 1–3 are given in Figures S1–S3, respectively (SI).

Magnetic and EPR Studies. The magnetization of powdered samples 1–3 was measured over the temperature range 1.8–300 K using a Quantum Design SQUID – based MPMSXL–5-type magnetometer. The superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Measurements were made at magnetic field 0.5 T. The SQUID magnetometer was calibrated with the palladium rod sample. Corrections are based on subtracting the sample – holder signal and the contribution of χ_D was estimated from the Pascal's constants.³³ EPR spectra of powdered samples 1–3 were recorded at room temperature and 77 K on a Bruker ELEXSYS E 500 CW-EPR spectrometer operating at X-band frequency and equipped with an ER 036TM NMR Teslameter and E41 FC frequency counter.

Catecholase Activity Studies. The catecholase activity of the copper(II) compounds was evaluated in the oxidation of 3,5-di-*tert*-butyl-catechol (3,5-DTBC) as a model substrate to give the corresponding quinone, 3,5-di-*tert*-butyl-o-benzoquinone (3,5-DTBQ). The experiments were performed under aerobic conditions at constant stirring and temperature 25

°C, and monitored by a contact thermometer dipped into the reaction solution. Measurements were made in a 1 cm path length quartz cuvette. In a typical test, 1.0 mL MeOH solution of catalyst $(6.53 \times 10^{-5} \text{ M} \text{ for } 1, 6.50 \times 10^{-5} \text{ M} \text{ for } 2)$ was treated with 0.01-2.00 mL MeOH solution of 3,5-DTBC $(6.77 \times 10^{-5}-1.35 \times 10^{-2} \text{ M} \text{ for } 1; 6.67 \times 10^{-5}-1.33 \times 10^{-2} \text{ M} \text{ for } 2)$ in air at 25 °C. Due to a lack of solubility of **3** in MeOH, the catalytic activity of this compound was not investigated. The absorbance was measured as a function of time, over the first 5 min, at 390 nm (ε =1734.49 M⁻¹cm⁻¹) immediately after the addition of catalyst. For comparative purposes, Cu(MeCOO)₂ (1.0 mL of MeOH solution, $6.80 \times 10^{-5} \text{ M}$) and a freshly prepared mixture of Cu(MeCOO)₂ and PTA=O (1.0 mL of MeOH solution, $6.23 \times 10^{-5} \text{ M}$) were also tested as reference catalysts in the oxidation of 3,5-DTBC (0.03–1.80 mL in MeOH, 1.99×10^{-4} – 1.19×10^{-2} M for copper(II) acetate; 0.02–2.00 mL in MeOH, 1.33×10^{-4} – 1.33×10^{-2} M for copper(II) acetate; 0.02–2.00 mL in MeOH, 1.33×10^{-4} – 1.33×10^{-2} M for copper(II) acetate; 0.02–2.00 mL in MeOH, 1.33×10^{-4} – 1.33×10^{-2} M for copper(II) acetate; 0.02–2.00 mL in MeOH, 1.33×10^{-4} – 1.33×10^{-2} M for copper(II) acetate; 0.02–2.00 mL in MeOH, 1.33×10^{-4} – 1.33×10^{-2} M for copper(II) acetate; 0.02–2.00 mL in MeOH, 1.33×10^{-4} – 1.33×10^{-2} M for copper(II) acetate; 0.02–2.00 mL in MeOH, 1.33×10^{-4} – 1.33×10^{-2} M for copper(II) acetate; 0.02–2.00 mL in MeOH, 1.33×10^{-4} – 1.33×10^{-2} M for copper(II) acetate and PTA=O in 1:1 molar ratio). Control experiments were carried out under typical reaction conditions but in the absence of copper(II) catalyst, and showed no conversion of 3,5-DTBC to 3,5-DTBQ.

Results and Discussion

Self-assembly Synthesis and Characterization. Reaction of copper(II) acetate with PTA=O in MeOH medium leads to the self-assembly of a discrete dicopper(II) complex $[Cu_2(\mu-MeCOO)_4(MeOH)_2](PTA=O)_2$ (1) (Scheme 1). A resembling reaction but using acetonitrile instead of methanol as a solvent resulted in the generation of a 3D copper(II) MOF $[Cu_3(\mu-MeCOO)_6(\mu_3-PTA=O)]_n$ ·3.5nMeCN (2). Interestingly, the μ_3 -PTA=O spacer in 2 is connected to axial positions of metal centers (Scheme 1), whereas in 1 the axial positions of copper centers are blocked by methanol molecules; as a result, PTA=O remains uncoordinated. A different self-assembly reaction in MeCN using both copper(II) acetate and metallic copper(0) powder as metal sources and PTA as a building block furnished a mixed-valence Cu(II)/Cu(I) 1D coordination polymer $[Cu_3(\mu-MeCOO)_4(MeCOO)(\mu-PTA)_2(PTA)]_n$ (3) (Scheme 1), wherein PTA moieties act as both *P*,*N*-linkers and terminal *P*-ligands. All the compounds 1–3 were isolated as air-stable crystalline solids, their molecular structures were established by single crystal X-ray diffraction and further supported by elemental analysis, TGA, IR and EPR spectroscopy.





Scheme 1. Synthesis and structural formulae of 1–3.

The IR spectra of 1-3 exhibit a set of vibrations in the 1450–550 cm⁻¹ range typical for PTA and PTA=O moieties,⁷⁻¹⁹ as well as several highly intense bands due to the $v_{as}(COO)$ (1620–1421 cm⁻¹) and v_s (COO) (1372–1337 cm⁻¹) vibrations of acetate ligands.³⁶ Other characteristic vibrations concern the weak v(CH) bands in the 2968–2831 cm⁻¹ range.³⁷ Additionally, the IR spectrum of 2 shows a characteristic band of the P=O group at 1182 cm⁻¹, which is shifted in comparison to that in an uncoordinated or N-coordinated PTA=O (1165 cm⁻¹) moiety.¹¹ The IR spectrum of **1** exhibits a P=O band at 1156 cm⁻¹ due to H-bonding interaction between the PTA=O and $[Cu_2(\mu-MeCOO)_4(MeOH)_2]$ units. The distances of P=O bonds in the crystal structures of 1 and 2 are equal to 1.4985(18) and 1.495(4) Å, respectively. These distances differ just by 0.004 Å, although from the different coordination modes of the PTA=O moieties in 1 and 2 (non-coordinated in 1 and copper-coordinated in 2) as well as from the different wavelengths of their v(P=O) IR bands (1156 and 1182 cm⁻¹, respectively), one may expect a larger difference in the P=O bond lengths. However, this observation is in accord with the statistical distribution obtained from the Cambridge Structure Database (Table S4), which reveals average P=O bonds lengths of 1.490 and 1.497 Å for PTA=O having noncoordinated oxygen and that coordinated to a transition metal, respectively. Moreover, the P=O bond distances range from ca. 1.47 to 1.51 Å in both cases (Table S4), thus not allowing to build a clear correlation between the coordination mode of PTA=O and its P=O separation.

Structural and Topological Description

Compound $[Cu_2(\mu-MeCOO)_4(MeOH)_2](PTA=O)_2$ (1). The crystal structure of 1 is composed of a discrete 0D $[Cu_2(\mu-MeCOO)_4(MeOH)_2]$ unit and two uncoordinated PTA=O

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moieties (Figure 1). The copper(II) dimer represents a neutral paddle-wheel tetraacetate block wherein each Cu1 center also has a terminal methanol ligand. The Cu1...Cu1 separation of 2.6041(5) Å lies within the typical values observed in other dicopper(II) paddle-wheel derivatives.³⁸ If the Cu1...Cu1 interaction is not taken into consideration, the geometry around the five-coordinate Cu1 centers can be described as a distorted square-pyramid with a {CuO₅} environment, which is filled by four acetate O2–O5 oxygen atoms [avg. Cu–O 1.964(7) Å] and the O6 atom from the MeOH ligand [2.1607(18) Å]. Besides, two symmetry equivalent PTA=O moieties are H-bonded to a dicopper(II) unit.



Figure 1. Structure of **1** showing a dicopper(II) paddle-wheel unit $[Cu_2(\mu-MeCOO)_4(MeOH)_2]$ and its H-bonding interaction with PTA=O moieties. Further details: H atoms (apart from those participating in H-bonds) are omitted for clarity, color codes: Cu (green), O (red), N (blue), P (orange), C (gray), H (dark gray).

Compound [*Cu*₃(μ -*MeCOO*)₆(μ ₃-*PTA*=*O*)]_n·3.5*nMeCN* (**2**). In contrast to **1**, the crystal structure of **2** is significantly more complex, given the presence of three structurally distinct copper(II) atoms (Cu1, Cu2, and Cu3) interconnected by the μ -acetate linkers and the μ ₃-PTA=O spacers (Figure 2a). The latter act as unusual tridentate *N*,*N*,*O*-ligands and sew adjacent dicopper(II) paddle-wheel blocks into an intricate 3D metal-organic framework (Figure 2b). Within the three different [Cu₂(μ -MeCOO)₄] blocks based on a pair of symmetry equivalent Cu1, Cu2, or Cu3 atoms, the Cu...Cu separations vary from 2.5732(13) to 2.5936(14) and 2.6146(14) Å, respectively. The five-coordinate copper centers show the slightly distorted {CuNO₄} (Cu1 and Cu2) or {CuO₅} (Cu3) coordination environments. The coordination sphere of the Cu1 atom is filled by four acetate O1–O4 atoms [avg. Cu1–O 1.971(4) Å] and an axial N1 atom from the μ ₃-PTA=O block [Cu1–N1 2.221(4) Å]. Similarly, the coordination environment of the Cu3 center is taken by four acetate O9–O12 atoms [avg. Cu3–O1 4.970(4) Å] and an axial O13 atom from the phosphine oxide ligand [Cu3–O13 2.171(4) Å]. Compound **2** represents the first example of a copper-containing 3D MOF that is driven by a PTA=O or any other PTA-derived block.

(a)



Figure 2. Structural fragments of **2**: (a) coordination environment around Cu1, Cu2, and Cu3 atoms, (b) 3D metal-organic framework, and (c) its topological representation showing a decorated uninodal 3-connected underlying net with the **ths** topology. Further details: (a, b) H atoms are omitted for clarity, color codes: Cu (green), O (red), N (blue), P (orange), C (gray); (b, c) views along the *a* axis; (c) Cu atoms (green), centroids of PTA=O nodes (cyan), centroids of acetate moieties (gray).

To better understand the framework structure of **2**, we have performed its topological analysis by applying the concept of the simplified underlying net.³⁹⁻⁴² Such a net has been generated by reducing the μ -MeCOO and μ_3 -PTA=O ligands to respective centroids and maintaining their connectivity. From the topological viewpoint, the resulting underlying framework (Figure 2c) can be considered as a combination of the 2-connected [Cu₂(μ -MeCOO)₄] secondary building units (SBUs) and 3-connected μ_3 -PTA=O nodes. Hence, the topological analysis reveals a decorated uninodal 3-connected net with the **ths** (ThSi₂) topology³⁹⁻⁴² and point symbol of (10³).



Figure 3. Structural fragments of **3**: (a) coordination environment around Cu1 and Cu2 atoms, (b) 1D wave-like metal-organic chain, and (c) its topological representation showing a uninodal 2-connected underlying net with the **2C1** topology. Further details: (a, b) H atoms are omitted for clarity, color codes: Cu (green), O (red), N (blue), P (orange), C (gray); (b, c) views along the *c* axis; (c) Cu atoms (green), centroids of PTA (cyan) and acetate (gray) moieties.

Compound $[Cu_3(\mu-MeCOO)_4(MeCOO)(\mu-PTA)_2(PTA)]_n$ (**3**). This structure represents a rare example of a mixed-valence Cu(II)/Cu(I) 1D coordination polymer driven by the μ -PTA linkers. It bears three Cu atoms (two divalent Cu1 and one monovalent Cu2), four μ bridging and one terminal acetate ligands, as well as two μ -bridging *N*,*P*-bound and one terminal *P*-bound PTA ligands, per formula unit (Figure 3a,b). As in the case of **1** and **2**, the copper(II) atoms in **3** are arranged into paddle-wheel dimeric units with the Cu1...Cu1 separation of 2.5951(10) Å. Each Cu1 atom can be considered as five-coordinate with a distorted square-pyramidal {CuNO₄} environment, filled by four acetate O1–O4 atoms [avg. Cu1–O 1.968(3) Å] in equatorial sites and a nitrogen atom from the μ -PTA moiety [Cu1–N4 2.225(3) Å] in the axial site. The four-coordinate Cu2 atoms reveal a distorted tetrahedral {CuP₃O} environment, which is taken by a pair of symmetry generated P2 atoms [Cu2–P2 2.2739(12) Å] from the μ -PTA spacers and the P1 and O5 atoms from the terminal PTA and acetate ligands [Cu2–P1 2.2664(17), Cu2–O5 2.024(5) Å], respectively. The monocopper(I)

[Cu(PTA)(MeCOO)] and dicopper(II) [Cu₂(μ -MeCOO)₄] blocks are interconnected by the μ -PTA spacers to generate an infinite 1D wave-like chain (Figure 3b). From the topological perspective,^{39,40} this chain can be considered as a uninodal 2-connected underlying net (Figure 3c) with a decorated **2C1** topology. An unusual feature of this structure concerns the presence of monovalent and divalent copper centers, as well as two different *N*,*P*- and *P*-bound PTA ligands.

Magnetic Studies. The magnetic properties of 1–3 were investigated over the temperature range of 1.8–300 K. Plots of magnetic susceptibility χ_m and $\chi_m T$ product vs. $T(\chi_m$ is the molar magnetic susceptibility for two Cu(II) ions) are given in Figures S4 (SI) and 4, respectively. For 1–3, the $\chi_m T$ values at 300 K are much below those expected for two magnetically isolated spin doublets [$\chi_m T = 2(N\beta^2 g^2/3k)S(S+1) = 0.749$ cm³mol⁻¹K, wherein g = 2.1 is the spectroscopic splitting factor, N – the Avogadro's number, β – the Bohr magneton, k – the Boltzmann's constant, and $S = \frac{1}{2}$],⁴³ being equal to 0.538, 0.584, and 0.621 cm³mol⁻¹K, respectively (Figure 4). The $\chi_m T$ plots continuously decrease on lowering the temperature reaching almost zero below 50 K. These features are indicative of a strong antiferromagnetic ground state is completely populated below 50 K. Additionally, the susceptibility curves for 1–3 exhibit the maximum that confirms the presence of a strong antiferromagnetic ordering with a Neel temperature (T_N) about 300 K (Figure S4).

The variation of the magnetization (*M*) with respect to the field (*H*), at 2 K, also confirms the nature of the ground state in 1–3. The results are depicted in Figure 5, where the molar magnetization *M* (per Cu₂ entities) is expressed in μ_B units. The compounds 1–3 do not attain the saturation in the applied field range and the magnetization values at 5 T are much below 1 μ_B . The magnetization curves for 1–3 are reproduced by the equation $M = g\beta SNB_s(x)$ ($S = 2S_{Cu}$), where $B_s(x)$ is the Brillouin function and $x = g\beta H/kT$.⁴³ The experimental values are much inferior than those calculated using the Brillouin function for two non-interacting copper(II) ions. This further indicates that 1–3 behave as antiferromagnets.



Figure 4. Temperature dependence of experimental $\chi_m T$ (χ_m per 2Cu^{II} atoms) for 1–3. The solid lines are the calculated curves derived from equation (1).

Although all compounds display distinct metal-organic architectures, they bear similar dicopper(II) paddle-wheel tetraacetate $[Cu_2(\mu-MeCOO)_4]$ blocks. The shortest Cu···Cu distances between the adjacent dicopper(II) units in **1–3** (8.5069(6), 5.9956(11), and 6.4411(6) Å, respectively) are large enough to consider the dinuclear core as magnetically isolated. Hence, the magnetic data of **1–3** were analysed using the isotropic spin Hamiltonian $H = -J\overline{S_1} \cdot \overline{S_2}$ that results in the Bleaney-Bowers expression for two interacting spin doublets, eq (1).^{43,44} The paramagnetic monomeric impurity ρ was introduced in eq (1) to obtain satisfactory results.⁴⁴

$$\chi_{m} = \frac{2N\beta^{2}g^{2}}{kT[3 + \exp(-J/kT)}(1-\rho) + \frac{N\beta^{2}g^{2}}{2kT}\rho$$
(1)

In equation (1), *J* is an intradimer exchange coupling constant, ρ stands for the molar fraction of the monomeric form, while the other parameters have their usual meaning. A least-squares fitting of the experimental data leads to the following values: $J = -320(1) \text{ cm}^{-1}$, g = 2.20(1), $\rho = 0.024$, and $R = 3.75 \cdot 10^{-4}$ for **1**, $J = -310(2) \text{ cm}^{-1}$, g = 2.24(1), $\rho = 0.016$, and R = $2.91 \cdot 10^{-4}$ for **2**, and $J = -320(1) \text{ cm}^{-1}$, g = 2.25(2), $\rho = 0.022$, and $R = 1.08 \cdot 10^{-4}$ for **3**. The calculated curves very well reproduce the magnetic data in the whole temperature range (Figure 4). The criterion applied to determine the best fit was based on the minimization of the sum of squares of the deviation, $R = \Sigma(\chi_{exp}T - \chi_{calc}T)^2 / \Sigma(\chi_{exp}T)^2$. Results of the magnetic data calculations for **1–3** indicate a strong antiferromagnetic coupling between the copper(II) ions transmitted through μ -acetate linkers.

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The magneto-structural relationship in the carboxylato-bridged copper(II) compounds shows that the nature and the strength of magnetic exchange coupling can depend on the type of bridging mode, the coordination geometry of copper(II) centers, the Cu···Cu distances, and mainly on the bond angles at bridging atoms and the number of bridges.⁴⁵⁻⁵⁹ Typically, an exchange coupling constant significantly declines when the number of carboxylate bridges decreases from 4 to 1.⁵⁸ Furthermore, Wieghardt⁵⁹ proposed a relationship between *J/n* and the Cu–O–C bond angle (α) in which *n* is the number of carboxylate bridges. Larger α angles thus lead to smaller coupling values. The results obtained for **1–3** are consistent with a more general observation that the tetra- μ -carboxylate-bridging species strongly mediate an exchange coupling. The mechanism of the antiferromagnetic coupling between the copper(II) ions in **1–3** is an effect of the interaction of the $d_x^2 - y^2$ orbitals positioned in the square base via the acetate oxygen atoms.



Figure 5. Field dependence of the magnetization (*M* per Cu₂ entities) for 1–3. The solid line is the Brillouin function curve for the system of two uncoupled spins with $S = \frac{1}{2}$ and g = 2.0.

EPR Spectra. The EPR spectra of solid samples **1–3** at 298 and 77 K additionally confirm the properties determined by direct magnetic measurements (Figure S5). The polycrystalline X-band EPR spectra of compounds **1–3** show no significant difference between room temperature and 77 K. Compared with the spectrum at 77 K, the signals at 298 K are much sharper and stronger. The EPR spectra of **1–3** are typical for compounds where an unpaired electron is in a $d_x^2 - y^2$ ground state.⁶⁰⁻⁶⁵ The EPR spectra are also typical for dimeric copper(II) species with an O-environment.^{60-63,66,67} The spectra exhibit transitions in low and high field regions (380 G and 4700 G). The observed hyperfine pattern in low field region proves the presence of intradimer magnetic exchange interactions as detected by the direct

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magnetic measurements. The spectra also display a line at 3200 G that can be attributed to a monomeric impurity (g = 2.08 for 1, g = 2.06 for 2, and g = 2.07 for 3).

Catecholase Activity Studies. Good solubility of 1 and 2 in non-aqueous solvents encouraged us to investigate their catalytic activity under homogeneous conditions in the aerobic oxidation of 3,5-di-tert-butyl-catechol (3,5-DTBC) to the corresponding diketone, 3,5-di-tert-butyl-o-benzoquinone (3,5-DTBQ) as a model reaction (Scheme 2).68-72 Product formation was monitored by UV-Vis spectroscopy in MeOH at 25 °C in air. Control experiments carried out under similar reaction conditions but in the absence of copper catalyst confirmed no conversion of 3,5-DTBC to 3,5-DTBQ. Upon addition of the 3,5-DTBC substrate to a MeOH solution of catalyst 2, an increase in the absorption band of the 3,5-DTBQ product is observed (Figure 6). Similar dependences for catalyst 1 and copper(II) acetate (control experiment) and a mixture composed of copper(II) acetate with PTA=O are given in Supporting Information (Figures S7–S9). Maximum initial reaction rate (V_{max}) and Michaelis-Menten constant (K_M) were determined from the Michaelis-Menten plots (Figures 7 and S10 for 2, S11, S12 and S13 for 1, for copper acetate, and a mixture of copper acetate and PTA=O, respectively). The obtained values of maximum initial reaction rates for 1 and 2 are 3.24×10^{-3} and 5.26×10^{-3} M·min⁻¹, respectively (Table 1). The catalyst turnover frequencies (k_{cat}) were measured as a ratio of V_{max} /[catalyst] and attain values of 49.62 and 80.92 min⁻¹ for 1 and 2, respectively. Resembling kinetic parameters were observed for 1 and a catalyst formed *in situ* from copper(II) acetate and PTA=O in 1:1 molar ratio, showing similar nature of active species. It is important to highlight that these turnover frequencies are two- or fourfold superior than the value of 20.88 min⁻¹ determined herein for copper(II) acetate as well as in comparison with other catalysts.⁷⁰⁻⁷² Hence, compounds 1 and 2 can be considered as very promising bioinspired catalysts for the oxidation of catechols.



Scheme 2. Schematic representation of the oxidation of 3,5-DTBC to 3,5-DTBQ.



Figure 6. Time sequences showing an increase in the absorption band at 390 nm of 3,5-DTBQ in the oxidation of 3,5-DTBC (1.33×10^{-2} M, 2.0 mL MeOH) catalyzed by **2** (6.50×10^{-5} M, 1.0 mL MeOH); 25 °C, in air.



Figure 7. Catecholase activity of 2: Michaelis-Menten plot.

Table 1. Kinetic parameters for the aerobic oxidation of 3,5-DTBC to 3,5-DTBQ catalyzed by **1**, **2**, Cu(MeCOO)₂ and Cu(MeCOO)₂ + PTA=O (molar ratio 1:1) in MeOH.

| Catalyst | V_{\max}^{a} [M min ⁻¹] | $K_{\rm M}^{a}$ [M] | $R^{2 a}$ | $k_{\text{cat}} [\min^{-1}]$ |
|----------|---------------------------------------|---------------------|-----------|------------------------------|
| | | | | |

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| Cu(MeCOO) ₂ * | 1.42×10 ⁻³ | 8.24×10 ⁻⁵ | 0.91179 | 20.88 |
|-------------------------------|-----------------------|-----------------------|---------|-------|
| Cu(MeCOO) ₂ +PTA=O | 2.63×10 ⁻³ | 1.14×10 ⁻⁴ | 0.88345 | 42.22 |
| 1 | 3.24×10 ⁻³ | 1.28×10 ⁻⁴ | 0.93948 | 49.62 |
| 2 | 5.26×10 ⁻³ | 1.83×10 ⁻³ | 0.97177 | 80.92 |

^aValue for Michaelis-Menten plot, ^{*}calculated for monomeric copper(II) acetate.

Conclusions

In the present work, we further explored a still very limited usage of aqua-soluble cage-like aminophosphine PTA and its *P*-oxide derivative toward the self-assembly generation of unusual coordination polymers. In fact, a slight variation of reaction conditions and modification of principal building block (PTA=O vs. PTA) resulted in the assembly of three distinct products 1–3, which all bear dicopper(II) paddle-wheel tetraacetate units. However, the compounds 1–3 reveal different dimensionality and structural and topological features, as well as magnetic properties. Topological analysis has disclosed a decorated uninodal 3-connected framework with the **ths** topology in **2** and a uninodal 2-connected chain with the decorated **2C1** topology in **3**.

Despite revealing different structural features, compounds 1–3 show similar magnetic and EPR spectroscopic properties owing to the presence of dicopper(II) paddle-wheel tetraacetate $[Cu_2(\mu-MeCOO)_4]$ blocks. Magnetic properties were investigated and modelled, disclosing a strong antiferromagnetic coupling between copper atoms within the Cu₂ blocks that can be rationalized by the Bleaney-Bowers expression. The nature and magnitude of the magnetic couplings were discussed on the basis of structural parameters.

Furthermore, the obtained compounds 1 and 2 were applied as powerful bioinspired catalysts for the aerobic oxidation of 3,5-di-*tert*-butyl-catechol to 3,5-di-*tert*-butyl-obenzoquinone, resulting in catalyst turnover frequency values of up to 81 min⁻¹.

The present study also extended a still very limited family of Cu-PTA=O and Cu-PTA coordination polymers to novel and rather unique examples. In fact, compound **2** represents the first 3D copper-based metal-organic framework that is driven by PTA=O or any other PTA derivative, whereas compound **3** features an unusual mixed-valence copper(I/II) coordination polymer wherein PTA blocks act as both linkers and terminal ligands. Further research aiming at the application of PTA=O, PTA and related cage-like building blocks for the design of new functional coordination polymers is currently in progress.

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Supporting Information Available: additional figures (Figures S1-S22), tables (Tables S1-S4) and crystallographic files in CIF format for **1-3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Unique Copper-Organic Networks Self-Assembled from 1,3,5-Triaza-7-Phosphaadamantane and its Oxide: Synthesis, Structural Features, Magnetic and Catalytic Properties

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TOC graphic



Synopsis

New types of copper-organic networks were assembled from cage-like aminophosphine building blocks; their structural features, magnetic and oxidation catalytic properties were investigated.