

Crystal structures of $[M(N_3)_2(phen)_2]$ compounds, $M = Mn, Co$ or Cu and $phen = 1,10$ -phenanthroline

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Abstract: Crystal structures of the title compounds, $[Mn(N_3)_2(phen)_2]$ (**1**), $[Co(N_3)_2(phen)_2]$ (**2**) and $[Cu(N_3)_2(phen)_2] \cdot 1.5 H_2O$ (**3**), have been determined at 100 K. Central atoms of the above-mentioned compounds are coordinated by four pyridine nitrogen donor atoms from two 1,10-phenanthroline molecules and two nitrogen donor atoms of terminally coordinated azide anions, which resulted in a distorted $\{MN_6\}$ octahedral geometry. The π - π stacking interactions, as well as weak $C-H \cdots N$ hydrogen bonds, were observed in all three compounds. Moreover, complex **3** revealed also supramolecular chains of the complex and water molecules linked together through $O-H \cdots N$ hydrogen bonds.

Keywords: azide anions, crystal structures, hydrogen bonds, 1,10-phenanthroline, π - π stacking interactions

Introduction

Many compounds of the transition metals Mn, Co and Cu play essential role in biological living systems. Manganese is present in the oxygen evolving complex which is part of the photosystem(II) (Umena et al., 2011), as well as in superoxide dismutase SOD (Law et al., 1998), arginase (Costanzo et al., 2007), glutamine synthetase (Takeda, 2003) and many other enzymes. Although the main biological importance of cobalt is its role in vitamin B12 – cobalamin, and its complexes as it can mimic this metalloenzyme, cobalt compounds are also well-known as DNA binding and photo-induced DNA cleaving agents (Tabasum et al., 2016; Peng et al., 2007). The copper atom can be found in cytochrome c oxidase, superoxide dismutase (Yim et al., 1993), hemocyanin (Festa et al., 2011) and others. Copper compounds containing 1,10-phenanthroline or its derivatives also exhibit SOD mimetic activity (Devereux et al., 2007; Bijloo et al., 1990).

The first chosen ligand, 1,10-phenanthroline (phen), is a strong field bidentate ligand that can form stable chelates with most first row transition metals and many of its compounds exhibit antimicrobial properties (Coyle et al., 2003; Kani et al., 2016). Nitrogen-containing heterocycles, such as 1,10-phenanthroline, are electron-deficient aromatic systems and are predetermined for π - π stacking formation as π -acceptors (Janiak et al., 2000), therefore, compounds of this type are interesting also from the supramolecular chemistry point of view (Sun & Xu, 2010).

The second used ligand, azide, can act as a monodentate as well as a bridging ligand, adopting the end-on or end-to-end modes to form complexes with different crystal structures varying from

mononuclear to three-dimensional ones (Escuer et al., 1998). Coordination mode of the azido ligand depends on the nature and oxidation state of the central metal ion, as well as on the nature of the other coordinated ligands and on the synthesis way of the complex (He et al., 2004; Cheng et al., 2014; Miao et al., 2006; Liu et al., 2007). The azide anion is often used to study mechanisms of SODs actions and compounds that mimic SODs activity as an analogue of the superoxide radical anion due to the same charge possession and similar frontier orbitals (Gutman et al., 2013).

Herein, we report the preparation and crystal structures of three compounds: $[Mn(N_3)_2(phen)_2]$ (**1**), $[Co(N_3)_2(phen)_2]$ (**2**) and $[Cu(N_3)_2(phen)_2] \cdot 1.5 H_2O$ (**3**). Molecules of 1,10-phenanthroline and terminal azide anions are placed in the *cis* configuration. The central atoms Mn(II), Co(II) and Cu(II) are in the $\{MN_6\}$ coordination environment.

Experimental

Synthesis

Compounds $[Mn(N_3)_2(phen)_2]$ (**1**), $[Co(N_3)_2(phen)_2]$ (**2**) and $[Cu(N_3)_2(phen)_2] \cdot 1.5 H_2O$ (**3**) were prepared in a similar way, following a well-established method. Manganese(II) acetate tetrahydrate (for complex **1**, 0.25 g, 1 mmol), cobalt(II) acetate tetrahydrate (for compound **2**, 0.25 g, 1 mmol) or copper(II) acetate monohydrate (for compound **3**, 0.20 g, 1 mmol) was dissolved in 40 cm³ of methanol (compounds **1** and **2**) or in 40 cm³ of distilled water (compound **3**) and mixed together with 1,10-phenanthroline (0.36 g, 2 mmol) in the ratio of 1:2 and heated at 333 K for 10 minutes. In the next step, this mixture was treated with sodium azide (0.13 g, 2 mmol), and the solution was then heated to the boiling point,

cooled down to room temperature and filtered. The resulting solution was left to slowly evaporate at room temperature. After a couple of days, yellow (compound **1**), red (compound **2**) or green (compound **3**) single-crystals suitable for X-ray diffraction analysis were obtained.

X-ray crystallography

Crystal data and conditions of data collection and refinement are reported in Table 1. Data collection and cell refinement were carried out using a Stoe StadiVari diffractometer equipped with a Pilatus 300K HPAD detector and a microfocused source Xenocs FOX3D (CuK α radiation) at 100 K. The structures were solved by direct or charge-flipping methods using SHELXT (Sheldrick, 2015a) or SuperFlip (Palatinus & Chapuis, 2007) and refined by the full-matrix least-squares procedure with SHELXL (ver. 2016/4, Sheldrick, 2015b) or Olex2.refine (Bourhis et al., 2015). Positions of hydrogen atoms were placed geometrically using OLEX2 (Dolomanov et al., 2009). Geometrical analyses were performed with SHELXL or Olex2.refine and the structures were drawn with OLEX2 (Dolomanov et al., 2009).

Results and discussion

The principle structure features of [Mn(N₃)₂(phen)₂] (**1**), [Co(N₃)₂(phen)₂] (**2**) and [Cu(N₃)₂(phen)₂] · 1.5H₂O (**3**) are illustrated in Figs. 1–3, the main information about crystal structures (crystal systems, space groups, unit cell parameters, experimental details etc.) are shown in Table 1, and the selected bond distances are given in Table 2. Compound [Mn(N₃)₂(phen)₂] (**1**) crystallizes in the orthorhombic system (space group Pbcn), compounds [Co(N₃)₂(phen)₂] (**2**) and [Cu(N₃)₂(phen)₂] · 1.5 H₂O (**3**) crystallize in the triclinic system (space group P-1). The Mn1 atom of **1** lies on a two-fold axis, and only half of the compound molecule is placed in the independent part of the cell. On the other hand, the full complex molecules of **2** and **3** are located in the independent parts of the cells. Central atoms are coordinated by four pyridine nitrogen donor atoms from two 1,10-phenanthroline ligands and two nitrogen donor atoms of azide anions. Molecules of 1,10-phenanthroline are positioned in the *cis* configuration, azide anions act as monodentate terminal ligands. The coordination polyhedra around Mn1 and Co1 atoms are of slightly distorted octahedral shape with the

Tab. 1. Experimental details.

| | 1 | 2 | 3 |
|---|---|---|--|
| Chemical formula | C ₂₄ H ₁₆ MnN ₁₀ | C ₂₄ H ₁₆ CoN ₁₀ | C ₂₄ H ₁₉ CuN ₁₀ O _{1.5} |
| M_r | 499.41 | 503.40 | 535.03 |
| Crystal system, space group | Orthorhombic <i>Pbcn</i> | Triclinic <i>P-1</i> | Triclinic <i>P-1</i> |
| Temperature (K) | 100 | 100 | 100 |
| a, b, c (Å) | 13.7078(6) 9.2655(7) 16.7649(8) | 8.0199(2) 10.9439(3) 12.4635(4) | 8.1782(5) 11.9098(7) 12.0905(7) |
| α, β, γ (°) | 90 90 90 | 82.786(2) 82.783(2) 73.647(2) | 85.957(5) 85.246(5) 75.478(5) |
| V (Å ³) | 2129.3(2) | 1036.65(5) | 1134.57(12) |
| Z | 4 | 2 | 2 |
| Radiation type | Cu $K\alpha$ | Cu $K\alpha$ | Cu $K\alpha$ |
| α (mm ⁻¹) | 5.354 | 6.810 | 1.732 |
| μ_{calc} (g cm ⁻¹) | 1.558 | 1.613 | 1.566 |
| $F(000)$ | 1020.0 | 514.0 | 545.6 |
| Crystal size (mm) | 0.19 × 0.18 × 0.06 | 0.21 × 0.09 × 0.04 | 0.28 × 0.21 × 0.07 |
| 2 θ range for data collection (°) | 10.55 to 140.93 | 7.18 to 140.90 | 7.34 to 140.78 |
| Reflections collected | 13314 | 20985 | 23558 |
| Independent reflections | 2003 | 3857 | 4218 |
| Restraints/parameters | 0/159 | 0/316 | 0/343 |
| R_{int} | 0.0485 | 0.0253 | 0.0420 |
| $R[F^2 > 2\sigma(F^2)], wR(F^2)$, | 0.0376, 0.1089 | 0.0255, 0.0674 | 0.0398, 0.1097 |
| S | 1.029 | 1.053 | 1.021 |
| $\Delta_{\text{max}}, \Delta_{\text{min}}$ (e Å ⁻³) | 0.69, -0.79 | 0.23, -0.32 | 0.50, -0.79 |
| CCDC | 15000274 | 1500275 | 1500276 |

{MN₆} coordination chromophore. The Mn1—N and Co1—N bond distances are in the ranges of 2.145(2)–2.318(1) Å, and 2.068(1)–2.176(1) Å, respectively (Table 2). The coordination polyhedron around the Cu1 atom can be better described as a highly asymmetric distorted tetragonal bipyramid, where one of the azido ligands is disordered in two positions with different Cu1—N8 distances (Table 2). The equatorial bond distances in the equatorial plane (Cu1—N_{eq}) are in the range of 1.958(2)–2.043(2) Å (Table 2) and the axial bond distances (Cu1—N_{ax}) from one nitrogen donor atom of the 1,10-phenanthroline ligand, and one azide nitrogen atom are exactly 2.304(2) or 2.982(2) Å, respectively (Table 2).

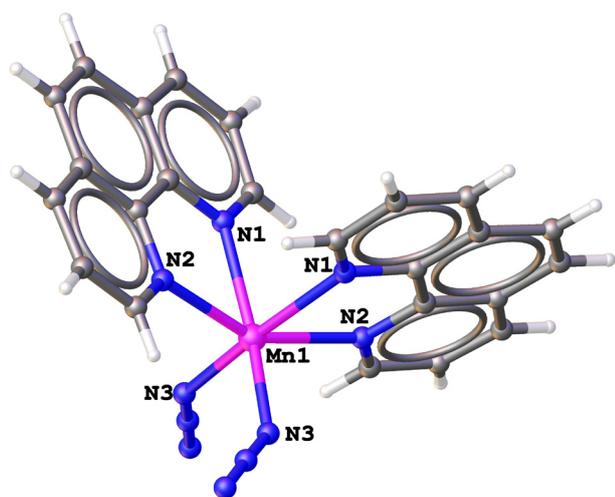


Fig. 1. Perspective view of 1, with the atom numbering scheme.

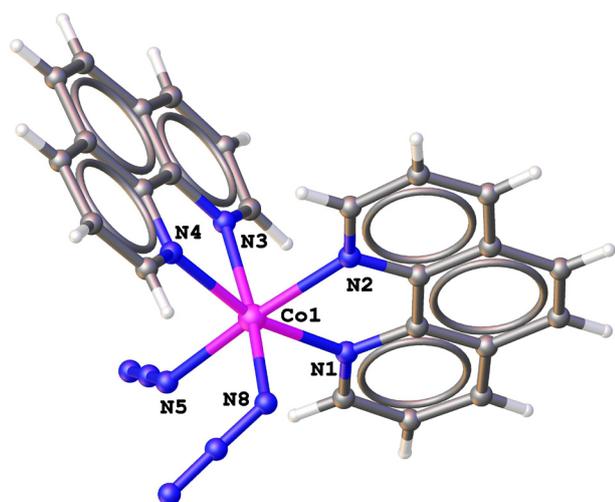


Fig. 2. Perspective view of 2, with the atom numbering scheme.

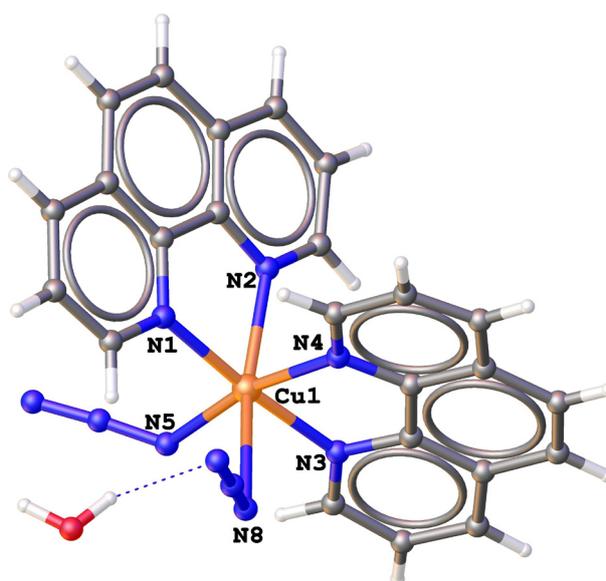


Fig. 3. Perspective view of 3, with the atom numbering scheme.

Tab. 2. Selected geometric parameters (Å).

| | | | |
|---------------------|----------|---------------------|----------|
| 1 | | | |
| Mn1—N1 | 2.318(2) | Mn1—N1 ⁱ | 2.318(2) |
| Mn1—N2 | 2.268(1) | Mn1—N2 ⁱ | 2.268(1) |
| Mn1—N3 | 2.145(1) | Mn1—N3 ⁱ | 2.145(1) |
| 2 | | | |
| Co1—N1 | 2.137(1) | Co1—N2 | 2.167(1) |
| Co1—N3 | 2.176(1) | Co1—N4 | 2.134(1) |
| Co1—N5 | 2.117(1) | Co1—N8 | 2.068(1) |
| 3 | | | |
| Cu1—N1 | 2.019(2) | Cu1—N2 | 2.304(2) |
| Cu1—N3 | 2.010(2) | Cu1—N4 | 2.043(2) |
| Cu1—N5 | 1.958(2) | Cu1—N8 | 2.982(1) |
| Cu1—N8 ⁱ | 2.725(1) | | |

Symmetry code: (i) 1 - x, y, 1/2 - z.

Crystal packing of **1** is shown in Fig. 4. Complex molecules of **1** are connected through C—H···N hydrogen bonds between carbon atoms of the 1,10-phenanthroline ligands and azide nitrogen atoms of the neighboring complex molecules [C8—H8···N3ⁱⁱ, and C10—H10···N4ⁱⁱⁱ (symmetry codes: (i) -x + 2, -y + 1, -z; (ii) x + 1, y, z; (iii) -x + 1, -y, -z) with C···N distances of 3.248(2), and 3.295(3) Å, respectively] (Table 3) into 1-D supramolecular chains in the *a* axes (Figure 4). In the crystal structure of **1**, also π ··· π stacking interactions (Janiak, 2000) between aromatic rings of both 1,10-phenanthroline ligands can be observed.

Complex molecules of **2** are linked to the 2-D supramolecular framework through C—H···N

hydrogen bonds between carbon atoms of the 1,10-phenanthroline ligands and azide nitrogen atoms of the neighboring complex molecules [C1—H1...N7^{iv}, C13—H13...N8^v, C18—H18...N7^{vi} and C19—H19...N10^{vii} (symmetry codes: (iv) $1 - x + 1, 2 - y, -z$; (v) $1 - x, 1 - y, -z$; (vi) $1 + x, -1 + y, z$; (vii) $1 - x, 1 - y, 1 - z$) with C...N distances in the range of 3.342(2)–3.375(2) Å] (Table 3) in the *bc* plane (Figure 5). The $\pi \cdots \pi$ stacking

interactions (Janiak, 2000) can be observed only between the aromatic rings of both 1,10-phenanthroline ligands.

Crystal structure of **3** contains complex molecules and uncoordinated water molecules. One of the water molecules, O2W, lies around special position and the occupancy factor is exactly 0.5. The complex molecules and the uncoordinated water molecules are linked together via O—H...N hydrogen bonds

Tab. 3. Hydrogen-bonds geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H (Å) | H... <i>A</i> (Å) | <i>D</i> ... <i>A</i> (Å) | <i>D</i> —H... <i>A</i> (°) |
|--------------------------------|-----------------|-------------------|---------------------------|-----------------------------|
| 1 | | | | |
| C8—H8...N3 ⁱⁱ | 0.95 | 2.38 | 3.248(2) | 153 |
| C10—H10...N4 ⁱⁱⁱ | 0.95 | 2.47 | 3.295(3) | 145 |
| 2 | | | | |
| C1—H1...N7 ^{iv} | 0.95 | 2.60 | 3.392(2) | 141 |
| C13—H13...N8 ^v | 0.95 | 2.48 | 3.343(2) | 151 |
| C18—H18...N7 ^{vi} | 0.95 | 2.49 | 3.369(2) | 141 |
| C19—H19...N10 ^{vii} | 0.95 | 2.66 | 3.375(2) | 133 |
| 3 | | | | |
| O1W—H1WA...N10 | 0.87 | 1.99 | 2.853(9) | 171 |
| O1W—H1WA...N10 ⁱ | 0.87 | 2.01 | 2.877(7) | 172 |
| O1W—H1WB...N10 ^{viii} | 0.87 | 2.18 | 3.047(9) | 172 |
| O1W—H1WB...N10 ^{ix} | 0.87 | 2.08 | 2.929(7) | 166 |
| O2W—H2WA...N10 ^{ix} | 0.87 | 2.06 | 2.892(9) | 159 |
| O2W—H2WA...N10 ⁱ | 0.87 | 2.38 | 3.154(7) | 148 |
| O2W—H2WB...N10 | 0.87 | 1.53 | 2.838(7) | 153 |
| O2W—H2WB...N10 ⁱ | 0.87 | 2.00 | 3.392(2) | 162 |
| C3—H3...N7 ^x | 0.95 | 2.60 | 3.467(3) | 152 |
| C20—H20...N8 ^{xi} | 0.95 | 2.45 | 3.394(19) | 171 |
| C20—H20...N8 ^{ix} | 0.95 | 2.40 | 3.315(15) | 161 |

Symmetry codes: (ii) $1/2 - x, -1/2 + y, z$; (iii) $1 - x, y, 1/2 - z$; (iv) $1 - x, 2 - y, -z$; (v) $1 - x, 1 - y, -z$; (vi) $1 + x, -1 + y, z$; (vii) $1 - x, 1 - y, 1 - z$; (viii) $2 - x, -y, -z$; (ix) $1 - x, -y, -z$; (x) $1 - x, -y, 1 - z$; (xi) $1 + x, y, z$.

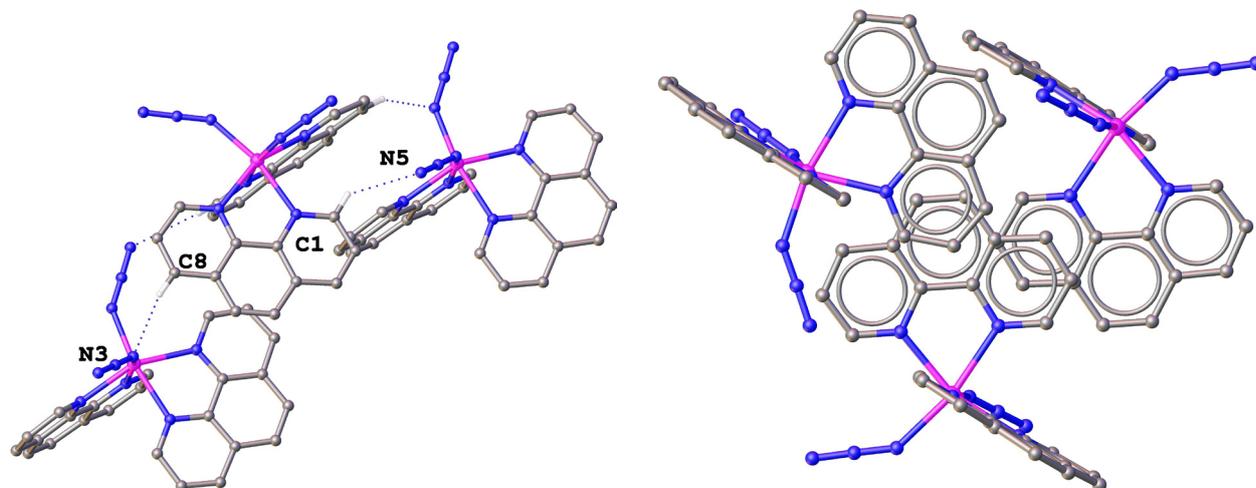


Fig. 4. C—H...N hydrogen bonds (top) and $\pi \cdots \pi$ stacking interactions (bottom) in the crystal packing of **1**.

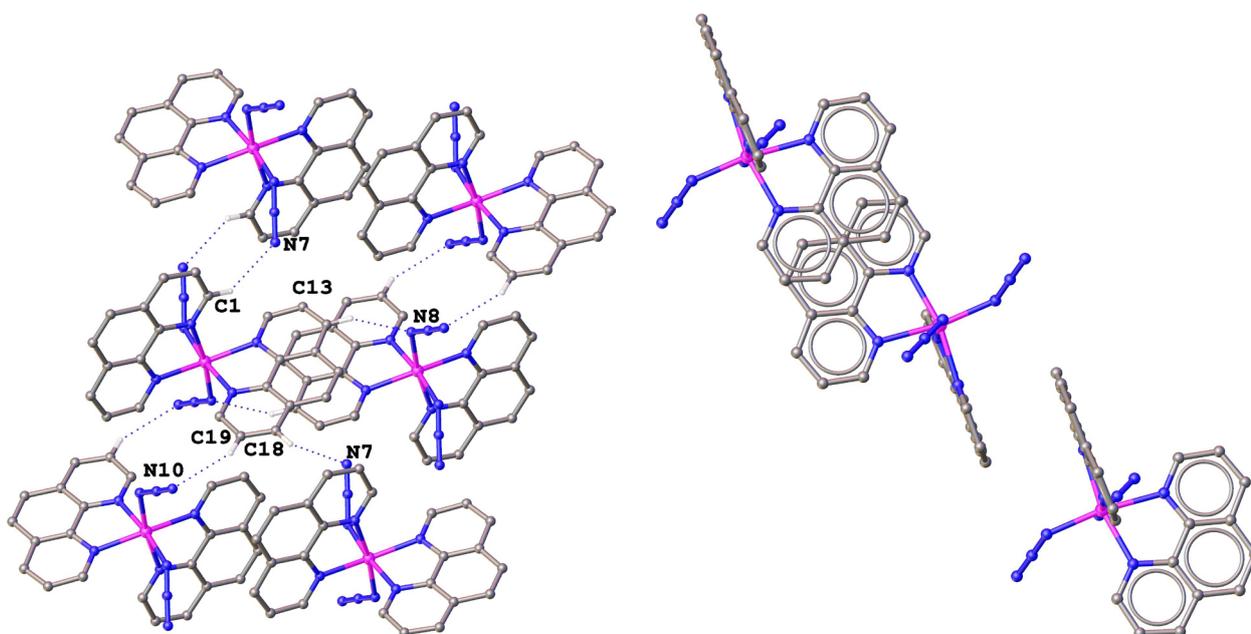


Fig. 5. C—H···N hydrogen bonds (top) and π ··· π stacking interactions (bottom) in the crystal packing of **2**.

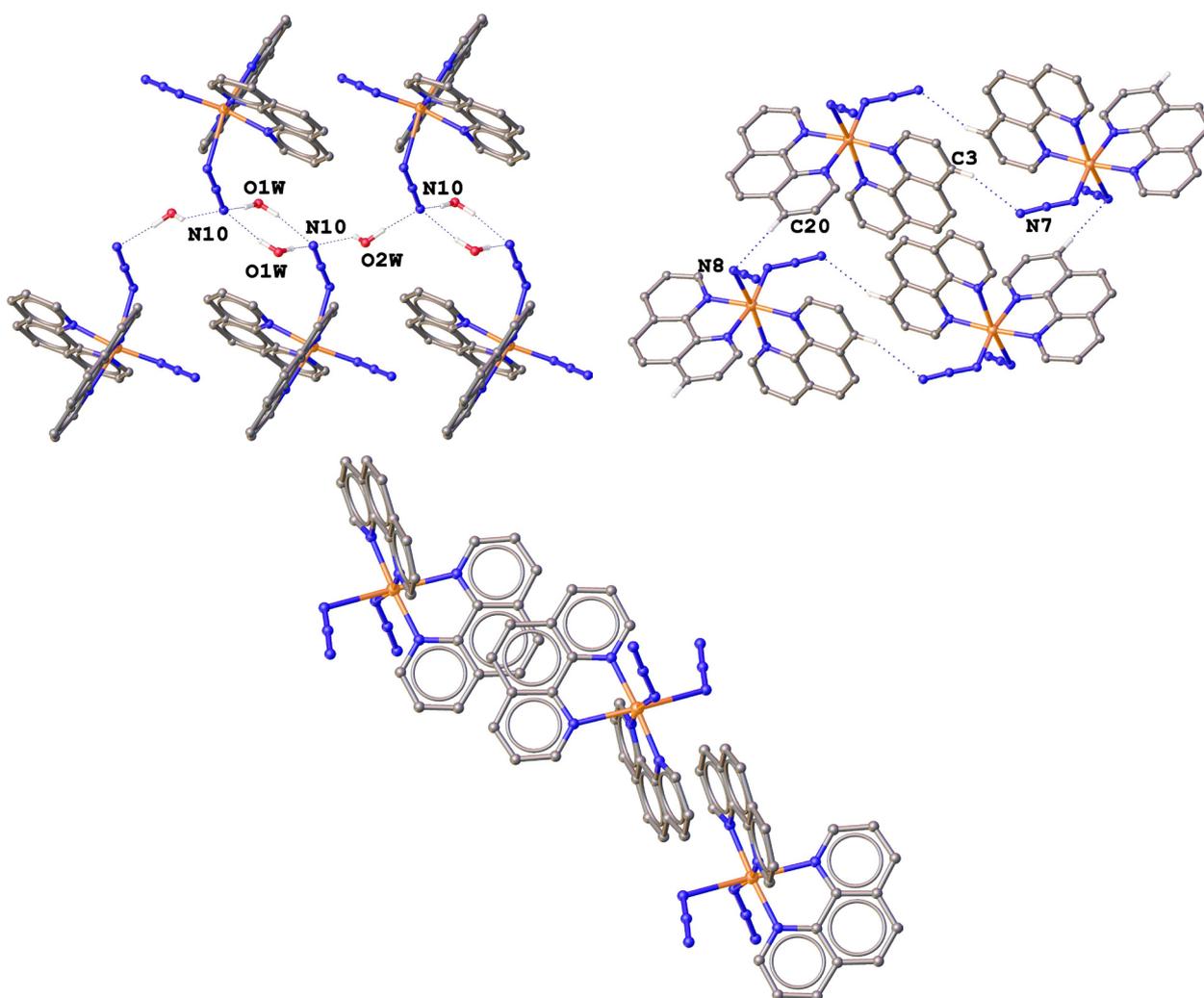


Fig. 6. C—H···N and O—H···N hydrogen bonds (top), and π ··· π stacking interactions (bottom) in the crystal packing of **3**.

into 1-D supramolecular chains (Figure 6) between uncoordinated water molecules (O1W or O2W) and azide nitrogen atoms (N10) with the O...N distance in the range of 2.838(7)–3.154(7) Å (Table 3). The complex molecules are also connected through C—H...N hydrogen bonds between carbon atoms of the 1,10-phenanthroline ligands and azide nitrogen atoms of the neighboring complex molecules [C3—H3...N7^x, C20—H20...N8^{xi} or C20—H20...N8^{i^{xi}} (symmetry codes: (x) 1 - x, -y, 1 - z; (xi) 1 + x, y, z with C...N distances in the range of 3.315(15)–3.394(19) Å] (Table 3) in the *ac* plane (Figure 6). The $\pi \cdots \pi$ stacking interactions (Janiak, 2000) can be observed only between the aromatic rings of both 1,10-phenanthroline ligands.

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