Symmetry in Recognition of Supramolecular Synthons—Competition between Hydrogen Bonding and Coordination Bond in Multinuclear Cu^{II}–4f Complexes with Bicompartamental Schiff Base Ligand

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Received: 9 March 2019; Accepted: 27 March 2019; Published: 2 April 2019

Abstract: Classic Cu–O coordination bonds in 1 or elongated semi-coordination ones in 2 and 3 were applied to construct Cu^{II}–4f complexes composed of trinuclear subunits linked through μ-NO$_3^-$ ions with formulae given as [Cu$_2$Tm(H$_2$tehy)$_2$(NO$_3$)$_6$H$_2$O, (1), [Cu$_2$Ho(H$_2$tehy)$_2$(NO$_3$)$_2$][Cu$_2$Ho(H$_2$tehy)$_2$(H$_2$O)$_2$](NO$_3$)$_4$ 2H$_2$O, (2), and [Cu$_2$Er(H$_2$tehy)$_2$(H$_2$O)$_2$][Cu$_2$Er(H$_2$tehy)$_2$(NO$_3$)$_2$](NO$_3$)$_10$ 2H$_2$O-4CH$_3$OH, (3), where H$_2$tehy = C$_{19}$H$_{20}$N$_2$O$_4$ is a tetrahydroxy Schiff base ligand. Topological analysis showed that the same characteristic motif of coordination accompanied by hydrogen bonds involving the uncoordinated nitrate oxygen atom and ligand’s phenoxy O atoms is responsible for linking trinuclear subunits into a hexanuclear one as well as for bridging the hexanuclear coordination units in 3 into a 1D supramolecular polymer, with the Cu–O distance being 3.19(1) Å, much longer than the limit of a semi-coordination bond (3.07 Å). The Cambridge Structural Database was used to discuss issues of crystallographic criteria (distance and angular preferences) for the assessment of the stabilizing or destabilizing effect of hydrogen bonding on coordination. The presented results show that the symmetrically repeated arrangement of molecules may provide a useful tool for identifying higher order non-covalently bonded supramolecular aggregates. The complexes 1–3 have been characterized by X-ray diffraction, FTIR, and thermal analysis. The magnetic studies indicated the ferromagnetic interaction between Cu^{II} and Ho^{III} ions.

Keywords: semi-coordination bond; Schiff base; 3d–4f complex; Jahn-Teller distortion; hydrogen bond assisted coordination bond

1. Introduction

Symmetry and asymmetry are the fundamental features of matter in solids and liquids that help in the understanding of many physical phenomena and chemical reactions. Symmetry is often a useful clue for the recognition of supramolecular synthons.

The application of non-covalent interactions in crystal engineering is a thoroughly studied research area, among them hydrogen bonds [1–7], halogen bonds [8–10], dipole⋯dipole [11–14], and stacking [15–20] interactions should be mentioned. Such non-covalent interactions provide directional and stabilizing contacts that can be used successfully in the design of coordination compounds [21]. Additionally, there are also reports showing that hydrogen bonding can act as a pathway for magnetic interaction between metal ions [1, 22–26].
The coordination sphere plasticity for hexacoordinated copper(II) ions is known as the Jahn–Teller effect. This distortion from ideal symmetry usually exhibits as an elongation of two axial bonds in the tetragonal bipyramid polyhedron of the complex. The Jahn–Teller deformations are believed to be stabilized in the solid state by, e.g., hydrogen bonds. The observed crystal elongation has led to the introduction of a term of a “semi-coordination bond” by Brown et al. in 1967 [27]. The theoretical studies performed by Valach et al. resulted in the calculation of the limit of a semi-coordination bond being of 3.07 or 3.04 Å for the Cu–O bond located at the elongated out-of-plane axis [28,29]. Valach also found that transition from the bonded to non-bonded state in the elongated metal–ligand direction occurs discontinuously [28].

There are some interesting reports on semi-coordinated bonds found in crystal structures of CuII cations staying within this Cu–O distance limits [33–32]. The strength of metal–ligand bonds depends on the bond length [33]. However, Nelyubina et al. proved that even very long and weak interatomic contacts (Cu···O 3.6 Å, 0.5 kcal/mol) may mediate magnetic super-exchange pathways [34]. On the other hand, non-covalent interactions have proved to be effective in the design of supramolecular polymers of exceptional properties [35–38].

The nitrate anion is often used in crystal engineering as a counterion since it has three oxygen atoms ready to form both coordinative and/or hydrogen bonds. However, the NO$_3^−$ anion generally links the neighboring copper centers by two oxygen donors independently [24]. The hydrogen bonds are usually formed with the non-coordinated nitrate oxygen. A recurrent structural motif based on nitrate ions being the interplay between a coordination or semi-coordination bond and bifurcated hydrogen bonds has been found in the presented structures 1–3 ([Cu$_2$Tm(H$_2$tehy)$_2$]$_2$(NO$_3$)$_6$H$_2$O, (1), ([Cu$_2$Ho(H$_2$tehy)$_2$](NO$_3$)$_2$][Cu$_2$Ho(H$_2$tehy)$_2$H$_2$O$_2$])(NO$_3$)$_4$·2H$_2$O, (2), and ([Cu$_2$Er(H$_2$tehy)$_2$](H$_2$O)$_2$][(Cu$_2$Er(H$_2$tehy)$_2$](NO$_3$)$_2$](NO$_3$)$_{10}$·2H$_2$O·4CH$_3$OH, (3), where H$_2$tehy = C$_{19}$H$_{20}$N$_2$O$_4$ is a doubly deprotonated tetrahydroxy Schiff base ligand and in previously reported ones [39,40] (Scheme 1). The topologically analogous supramolecular arrangement has been found in 3, but this time linking not only the trinuclear subunits into hexanuclear ones but also the hexanuclear ones into a linear supramolecular aggregate, with a much longer Cu···O$_{nitrate}$ distance (3.19(1) Å) which is above the limit of a semi-coordination bond (3.07 Å) [28] but still shorter than the distance where a very weak interaction has been reported by Nelyubina et al. (3.6 Å) [34].

![Scheme 1. (a) Structure of H$_4$tehy ligand and (b) a building motif found in 1–3; green dotted lines—out-of-plane Cu–O semi-coordination bonds at the apical positions; blue dashed lines—hydrogen bonds.](image)

The series of Cu$^{II}$–4f complexes presented here formed by a tetrahydroxy compartmental Schiff base ligand H$_4$tehy (where H$_4$tehy = C$_{19}$H$_{22}$N$_2$O$_4$) and nitrate anions offers an interesting object to study the influence of hydrogen bonding on the coordination and formation of a supramolecular network.

We present here the synthesis, crystal structure, FTIR spectra, and thermal and magnetic properties of complexes 1–3 where topological similarities are discussed in terms of crystallographic distance limit of a Cu–O semi-coordination bond and the cooperative or competitive nature of coexisting coordination and hydrogen bonds.
2. Materials and Methods

2.1. Materials

Starting materials: 2,3-dihydroxybenzaldehyde, 2,2-dimethyl-1,3-propanediamine, Cu(CH$_3$COO)$_2$·H$_2$O, Ho(NO$_3$)$_3$·5H$_2$O, Er(NO$_3$)$_3$·5H$_2$O, Tm(NO$_3$)$_3$·5H$_2$O, and CH$_3$OH were purchased from commercially available sources (Sigma Aldrich) and were used without further purification. The Schiff base ligand 3-[[(2,3-dihydroxyphenyl)methylideneamino]-2,2-dimethylpropyl]iminomethyl] benzene-1,2-diyl (H$_2$tehy); C$_{15}$H$_{22}$N$_2$O$_4$ was prepared as described in the literature [41,42].

2.2. Synthesis of Complexes

The heteronuclear compounds 1–3 were synthesized as follows: To 30 mL of methanolic solution of 0.1368 g Schiff base ligand (0.4 mmol) was added dropwise 10 mL of methanolic solution of 0.0799 g Cu(CH$_3$COO)$_2$·H$_2$O (0.4 mmol) giving a green mixture. After 30 min the freshly prepared solution (5 ml) of Ho(NO$_3$)$_3$·5H$_2$O (0.2 mmol, 0.0882 g), Er(NO$_3$)$_3$·5H$_2$O (0.2 mmol, 0.0887 g) or Tm(NO$_3$)$_3$·5H$_2$O (0.2 mmol, 0.0890 g) was slowly added to the constantly stirred suspension. The resulting deep green solution was stirred for another 30 min. A small amount of precipitate was filtered off, and the reaction mixture was left undisturbed at 4 °C. Slow evaporation yielded green crystals suitable for X-ray crystal structure analysis.

\[\text{[Cu}_2\text{TM}(\text{H}_2\text{tehy})]_2(\text{NO}_3)_4·\text{H}_2\text{O} (1): \text{empirical formula} \text{C}_{76}\text{H}_{82}\text{N}_{14}\text{O}_{35}\text{Cu}_4\text{Tm}_2, \text{molecular weight} 2343.57 \text{~g/mol}. \text{Yield} 42%. \text{Analytical data} (\%), \text{Calcd:} \text{C}, 38.95; \text{H}, 3.53; \text{N}, 8.37; \text{Cu}, 10.85; \text{Tm}, 14.42. \text{Found:} \text{C}, 38.50; \text{H}, 3.20; \text{N}, 8.40; \text{Cu}, 10.40; \text{Tm}, 14.00.\]

\[\text{[Cu}_2\text{Ho}(\text{H}_2\text{tehy})]_2(\text{NO}_3)_4·\text{H}_2\text{O} (2): \text{empirical formula} \text{C}_{76}\text{H}_{82}\text{N}_{14}\text{O}_{35}\text{Cu}_4\text{Ho}_2, \text{molecular weight} 2389.62 \text{~g/mol}. \text{Yield} 38%. \text{Analytical data} (\%), \text{Calcd:} \text{C}, 38.20; \text{H}, 3.71; \text{N}, 8.21; \text{Cu}, 10.64; \text{Ho}, 13.80. \text{Found:} \text{C}, 38.00; \text{H}, 3.50; \text{N}, 8.00; \text{Cu}, 10.30; \text{Ho}, 13.50.\]

\[\text{[Cu}_2\text{Er}(\text{H}_2\text{tehy})]_2(\text{H}_2\text{O})_2][\text{Cu}_2\text{Er}(\text{H}_2\text{tehy})_2(\text{NO}_3)_3]_2(\text{NO}_3)_{10}·2\text{H}_2\text{O}·4\text{CH}_3\text{OH} (3): \text{empirical formula} \text{C}_{156}\text{H}_{184}\text{Cu}_8\text{Er}_4\text{N}_{28}\text{O}_{76}, \text{molecular weight} 4844.66 \text{~g/mol}. \text{Yield} 30%. \text{Analytical data} (\%), \text{Calcd:} \text{C}, 38.67; \text{H}, 3.83; \text{N}, 8.10; \text{Cu}, 10.49; \text{Er}, 13.81. \text{Found:} \text{C}, 39.00; \text{H}, 3.20; \text{N}, 8.40; \text{Cu}, 10.00; \text{Er}, 13.40.\]

2.3. Methods

The elemental CHN analysis was performed using a CHN 2400 Perkin Elmer analyser. The contents of metals (copper, holmium, erbium, and thulium have been determined using ED XRF spectrophotometer (Cannberra –Packard). The FTIR spectra of compounds in KBr pellets were recorded in the range of 4000 to 400 cm$^{-1}$ on the M–80 spectrophotometer (Carl Zeiss Jena). Thermal analyses of 1–3 and H$_2$tehy were conducted under air flow in the temperature range of 20 to 1000°C (1–3) and 20 to 700°C (H$_2$tehy) at a heating rate of 10 °C·min$^{-1}$ by the thermogravimetric (TG) and differential scanning calorimetry (DSC) methods with the use of the SETSYS 16/18 analyser (Setaram). The samples of 7.72 mg (1), 7.88 mg (2), 5.76 mg (3) were heated in Al$_2$O$_3$ crucibles. The XRD powder diffractograms of the decomposition products were collected at room temperature on an Empyrean PANalytical automated powder diffractometer (CuKa radiation $\lambda = 1.54187$ Å) in the 2θ range of 20 to 90°. The magnetic susceptibility for finely ground crystalline samples was measured over the temperature range of 1.8 to 300 K at magnetic field 0.1 T using a Quantum Design SQUID-VSM magnetometer. The field dependences of magnetization were investigated at 2 K in the applied field up to 5 T and were corrected by subtracting the sample–holder signal and contribution $\chi$D estimated from Pascal’s constants [43].

Diffraction intensities for 1–3 were measured on SuperNova X-ray diffractometer (with Atlas S2 CCD detector and the mirror-monochromatized CuKa radiation ($\lambda = 1.54184$ Å) at 294 K for 1 and at 120 K for 2–3, using the $\omega$ scan technique. The CrysAlis CCD and CrysAlis Red programs [44] have been applied for data collection, cell refinement, and data reduction. The molecular models were found by direct methods using SHELXS-97 and refined on $F^2$ by the full-matrix least-squares using the SHELXL-97 implemented in OLEX2 [45,46]. Non-hydrogen atoms (except the disordered part of
the ligand molecule in 3 and selected nitrate and water molecules in 1–3) were refined anisotropically. The 2,2-dimethylpropyl bridge in 3 is disordered over two positions with site occupation factors (sof’s) of the major part being of 0.6. The structure of 3 has been refined in a noncentrosymmetric space group as a two-component twin with the following twin law (−1 0 0, 0 1 0, 0 0 −1) (two-fold rotation about b axis with inversion twinning). The refined twin population parameter BASF (fractional contribution of twin domain calculated on batch scale factors) was 0.42. The conditions for the data collection and the crystal structure refinement parameters are shown in Table 1. The drawings were made in Mercury and Diamond software [47,48]. The experimental details and final atomic parameters for 1–3 were deposited with the Cambridge Crystallographic Data Centre as supplementary material (CCDC ID 1901698–1901700). Copies of the data can be obtained free of charge on request via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk.

3. Results and Discussion

3.1. Molecular and Crystal Structure of Complexes 1–3

Compounds 1–3 were obtained by the same method of synthesis giving, however, crystal structures of different symmetry. The complexes show subtle differences in the coordination architecture and in the degree of Jahn–Teller distortion of CuII ions.

3.2. Hexanuclear Complex of 1

Compound 1 form crystals in the monoclinic space group (C2/c) with half of the coordination unit being symmetrically independent (Table 1). The asymmetric part consists of a trinuclear CuII–TmIII–CuII core linked by a bridging nitrate anion (lying on the two-fold axis) to the other half resulting in a hexanuclear coordination entity with the Cu2–O10 coordination bond length being 2.594(5) Å (Figures 1 and 2; Tables 2 and 3). This characteristic motif is supplemented by two O4–H4···O9 hydrogen bonds with a bifurcated acceptor O atom (Table 4). A similar characteristic arrangement of two trinuclear subunits linked by a bridging NO3− ion and hydrogen bonds has been discussed in structures of 2 and 3.

![Figure 1](image-url)  
Figure 1. View at the asymmetric unit in 1 (left) and view at the hexanuclear unit repeated by a two-fold axis (right) linked by semi-coordination bond Cu2–O10 and hydrogen bonds (marked with dashed lines).
Figure 2. Scheme of coordination unit in complex 1 with Cu–O and O⋯O distances in angstrom (Å), the position of two-fold axis is marked, the two halves are related by a two-fold axis, green dotted lines—semi-coordination Cu–O bonds at the apical positions, red dash–dotted lines—contact behind the limit of a semi-coordination bond but topologically important, blue dashed lines—hydrogen bonds, * nitrate anion disordered other three positions (sof’s 0.33), ** disorder of water and nitrate anion (sof’s 0.5).

Table 1. Crystal data and structure refinement details for 1–3.

| Identification Code | 1 | 2 | 3 |
|---------------------|---|---|---|
| Empirical formula   | C$_7$H$_4$C$_2$O$_3$Cu$_4$Tm$_2$ | C$_7$H$_8$N$_1$O$_3$Cu$_4$H$_2$O | C$_{15}$H$_{34}$N$_2$O$_7$Cu$_8$E$_{24}$ |
| Formula weight      | 2343.57 | 2389.62 | 4844.66 |
| Temperature/K       | 294.1(3) | 120.0(0) | 120.0(1) |
| Crystal system      | monoclinic | monoclinic | orthorhombic |
| Space group         | C2/c | P2_1/c | Pn2 |
| b/Å                 | 26.043(1) | 26.134(1) | 16.8980(4) |
| c/Å                 | 22.7584(9) | 21.515(1) | 15.5493(3) |
| α/°                 | 90 | 90 | 90 |
| β/°                 | 90 | 90 | 90 |
| Volume/Å³           | 8744.9(5) | 8712.5(7) | 8709.6(3) |
| Z                   | 4 | 4 | 2 |
| ρ calc, g/cm³       | 1.780 | 1.822 | 1.847 |
| μ/μm³               | 5.080 | 5.149 | 5.342 |
| F(000)              | 4680.0 | 4784.0 | 4856.0 |
| Crystal size/mm³    | 0.22 × 0.2 × 0.15 | 0.2 × 0.1 × 0.05 | 0.25 × 0.08 × 0.02 |
| Radiation           | CuKa (λ = 1.54184) | CuKa (λ = 1.54184) | CuKa (λ = 1.54184) |
| 2Θ range for data collection/° | 6.814 to 135.366 | 6.622 to 135.364 | 7.472 to 153.146 |
| Index ranges        | -31 ≤ h ≤ 25, -17 ≤ k ≤ 26 | -31 ≤ h ≤ 31, -18 ≤ k ≤ 26 | -21 ≤ h ≤ 18, -30 ≤ k ≤ 26 |
| ≤ 18, -27 ≤ l ≤ 26 | -14, -25 ≤ l ≤ 25 | ≤ 41, -19 ≤ l ≤ 18 |
| Reflections collected | 7897 | 15748 | 17487 |
| Independent reflections | R$_{int}$ = 0.0434, | R$_{int}$ = 0.1026, | R$_{int}$ = 0.0537, |
| R$_{sym}$ = 0.0366 | | R$_{sym}$ = 0.0951 | R$_{sym}$ = 0.0509 |
| Data/restraints/parameters | 7897/40/586 | 15748/36/1218 | 17487/37/1220 |
| Goodness-of-fit on F² | 1.058 | 0.984 | 1.033 |
| Final R indexes [F > 2σ (I)] | R$_1$ = 0.0596, | R$_1$ = 0.0599, | R$_1$ = 0.0425, |
| wR$_2$ = 0.1696 | wR$_2$ = 0.1498 | wR$_2$ = 0.1076 |
| R$_{int}$ = 0.0727 | R$_{int}$ = 0.0978 | R$_{int}$ = 0.0529 |
| Final R indexes [all data] | wR$_2$ = 0.1922 | wR$_2$ = 0.1788 | wR$_2$ = 0.1333 |
| Largest diff. peak/hole/e Å⁻³ | 1.33/–1.13 | 1.36/–1.33 | 1.12/–1.32 |
| Flack parameter     | – | – | 0.001(5) |
| CCDC No.            | 1901698 | 1901699 | 1901700 |
Table 2. Selected bond lengths and Cu⋯O contacts in angstrom (Å) for crystals 1–3.

|        | 1          | 2          | 3          |
|--------|------------|------------|------------|
| Tm1–Cu1 | 3.463(1)   | Ho1–Cu1    | Er1–Cu1    |
| Tm1–Cu2 | 3.4636(9)  | Ho1–Cu2    | Er1–Cu2    |
| Tm1–O1  | 2.280(5)   | Ho1–O1     | Er1–O1     |
| Tm1–O2  | 2.317(4)   | Ho1–O2     | Er1–O2     |
| Tm1–O3  | 2.289(5)   | Ho1–O3     | Er1–O3     |
| Tm1–O4  | 2.377(5)   | Ho1–O4     | Er1–O4     |
| Tm1–O5  | 2.291(5)   | Ho1–O5     | Er1–O5     |
| Tm1–O6  | 2.306(4)   | Ho1–O6     | Er1–O6     |
| Tm1–O7  | 2.326(6)   | Ho1–O7     | Er1–O7     |
| Tm1–O8  | 2.368(5)   | Ho1–O8     | Er1–O8     |
| Cu1–O1  | 1.934(5)   | Ho2–Cu3    | Er2–Cu3    |
| Cu1–O2  | 1.941(4)   | Ho2–Cu4    | Er2–Cu4    |
| Cu1–O3  | 1.977(5)   | Ho2–O38A   | Cu1–O1     |
| Cu1–O4  | 1.959(8)   | Ho2–O38    | Cu1–O2     |
| Cu1–O5  | 1.933(5)   | Ho2–O5     | Cu1–O30    |
| Cu1–O6  | 1.959(7)   | Ho2–O6     | Cu1–O32    |
| Cu1–O7  | 1.967(6)   | Ho2–N3     | Cu2–O5     |
| Cu1–O8  | 1.933(5)   | Ho2–O9     | Cu2–O6     |
| Cu1–N1  | 1.99(1)    | Er2–O9     | Cu2–O7     |
| Cu1–N2  | 1.987(6)   | Er2–O10    | Cu2–O8     |
| Cu1–O17 | 2.57(2)    | Er2–O11    | Cu2–O9     |
| Cu1–O16 | 3.35(2)    | Ho2–O12    | Cu2–O10    |
| Cu1–O16A| 2.93(2)    | Ho2–O13    | Cu2–O11    |
| Cu1–O16B| 2.66(1)    | Ho2–O14    | Cu2–O12    |
| Cu1–O17 | 2.57(2)    | Ho2–O15    | Cu2–O13    |
| Cu2–O5  | 1.930(5)   | Ho2–O16    | Cu2–O14    |
| Cu2–O6  | 1.935(4)   | Ho2–O38A   | Cu2–O15    |
| Cu2–N3  | 1.977(5)   | Ho2–O38    | Cu2–O16    |
| Cu2–N4  | 1.975(5)   | Cu1–O1     | Cu2–O17    |
| Cu2–O10 | 2.594(5)   | Cu1–O2     | Cu2–O18    |
| Cu2–O11 | 3.28(2)    | Cu1–N1     | Cu3–O7     |
| Cu1–O30 | 2.83(1)    | Cu1–N2     | Cu3–O8     |
| Cu1–O32 | 2.947(6)   | Cu1–N30    | Cu3–O9     |
| Cu1⋯O35 | 3.89(1)    | Cu1–O32    | Cu3–O10    |
| Cu2–O5  | 1.933(5)   | Cu2–O6     | Cu3–O11    |
| Cu2–O6  | 1.939(5)   | Cu2–O7     | Cu3–O12    |
| Cu2–O7  | 1.967(6)   | Cu2–O8     | Cu3–O13    |
| Cu2–O8  | 1.965(6)   | Cu2–O9     | Cu3–O14    |
| Cu2–O9  | 2.488(9)   | Cu2–O10    | Cu3–O15    |
| Cu2⋯O26 | 3.356(7)   | Cu2–O11    | Cu3–O16    |
| Cu3–O9  | 1.933(5)   | Cu3–O21    | Cu3–O17    |
| Cu3–O10 | 1.960(5)   | Cu3–O22    | Cu3–O18    |
| Cu3–N5  | 1.989(6)   | Cu3–O23    | Cu3–O19    |
| Cu3–N6  | 1.972(6)   | Cu3–O24    | Cu3–O20    |
| Cu3–N7  | 1.972(6)   | Cu3–O25    | Cu3–O21    |
| Cu3–N8  | 1.972(6)   | Cu3–O26    | Cu3–O22    |
| Cu3–N9  | 1.989(6)   | Cu3–O27    | Cu4–O13    |
| Cu4–O13 | 1.993(5)   | Cu4–O14    | Cu4–O15    |
| Cu4–O14 | 1.936(5)   | Cu4–O15    | Cu4–O16    |
| Cu4–N7  | 1.972(6)   | Cu4–O16    | Cu4–O17    |
| Cu4–N8  | 1.972(6)   | Cu4–O17    | Cu4–O18    |
| Cu4–O18 | 2.565(6)   | Cu4–O18    | Cu4–O20    |
| Cu4–O22 | 2.603(5)   | Cu4–O22    | Cu4–O23    |

* distance above the limit of 3.07 Å for semi-coordination bond but recognized as a semi-coordinative assisted by hydrogen bonding.

Table 3. Selected bond angles in degrees for 1–3.

|        | 1          | 2          | 3          |
|--------|------------|------------|------------|
| Cu1–O1–Tm1 | 110.3(2)   | Cu1–O1–Ho1 | Er1–Cu1    |
| Cu1–O2–Tm1 | 108.5(2)   | Cu1–O2–Ho1 | Er1–O1     |
| Cu2–O5–Tm1 | 110.0(2)   | Cu2–O5–Ho1 | Er1–O2     |
| Cu2–O6–Tm1 | 109.2(2)   | Cu2–O6–Ho1 | Er2–O2     |
| Cu1–Tm1–Cu2 | 175.6(1)   | Cu3–O9–Ho2 | Cu4–O13    |
| Cu3–O10–Ho2 | 110.0(2)   | Cu3–O10–Er2| Cu4–O14    |
| Cu4–O13–Ho2 | 107.7(2)   | Cu4–O13–Er2| Cu4–O15    |
| Cu4–O14–Ho2 | 109.3(2)   | Cu4–O14–Er2| Cu4–O16    |
| Cu1–Ho1–Cu2 | 170.5(1)   | Cu1–Er1–Cu2| Cu4–O17    |
| Cu3–Ho2–Cu4 | 177.1(1)   | Cu3–Er2–Cu4| Cu4–O18    |
The smaller N₂O₂ compartments are occupied by Cu²⁺ cations. Cu1 ion has the coordination number of five or six because one of the monodentate NO₃⁻ anions is disordered over three positions. The Cu1···O16/O16A/O16B distance varies from 2.66(1) to 3.57(1) Å (Table 2), which differentiates the character of the interatomic contact (semi-coordination or non-bonding). The nitrate ion may be bonded directly to Cu1 cation by a coordinative bond, or it can act as a hydrogen bond acceptor in O8···H8···O14 interaction (Figures 1 and 2; Table 4). Cu2 cation is penta-coordinated. The apical position of the polyhedron is occupied by a bridging nitrato ion with Cu2–O10 bonds being of 2.594(5) Å. The Cu2 ion has also a long contact, above the limit of a semi-coordination bond (Cu2···O11 3.28(2) Å), to a nitrate anion hydrogen bonded through the same O11 atom to the phenoxy group (O3···H3···O11 interaction). The Tm³⁺ ion is octa-coordinated by two O₄ cavities of the perpendicularly oriented Schiff base ligands. In the crystal structure, there is only one uncoordinated solvent molecule—water linked strongly by a hydrogen bond to the H₂tehy ligand (Table 4).

| Crystal | D–H···A | D–H | H···A | D···A | θD–H···A |
|---------|---------|------|-------|-------|---------|
| 1       | O3···H3···O11 | 0.87 | 1.76  | 2.55(2) | 150     |
|         | O4···H4···O9  | 0.87 | 1.88  | 2.614(6) | 143    |
|         | O7···H7···O17 | 0.87 | 2.26  | 2.87(2) | 128    |
|         | O7···H7···O19 | 0.87 | 2.26  | 3.00(1) | 144    |
|         | O7···H7···O20 | 0.87 | 1.80  | 2.64(2) | 165    |
|         | O8···H8···O14 | 0.87 | 1.61  | 2.54(2) | 161    |
|         | O8···H8···O14A | 0.87 | 2.02  | 2.89(2) | 150    |
|         | O8···H8···O16B | 0.87 | 1.67  | 2.59(2) | 157    |
| 2       | O3···H3···O23 | 0.86 | 1.79  | 2.628(7) | 167    |
|         | O4···H4···O26 | 0.86 | 1.69  | 2.535(8) | 167    |
|         | O7···H7···O32 | 0.86 | 1.75  | 2.545(8) | 154    |
|         | O8···H8···O35 | 0.86 | 1.74  | 2.544(9) | 158    |
|         | O35···H35A···O36 | 0.86 | 2.22  | 2.819(16) | 127    |
|         | O11···H11···O20 | 0.86 | 1.76  | 2.592(9) | 167    |
|         | O12···H12···O17 | 0.86 | 1.76  | 2.587(8) | 166    |
|         | O15···H15···O29 | 0.86 | 1.80  | 2.621(10) | 163    |
|         | O16···H16···O23 | 0.86 | 1.97  | 2.723(8) | 148    |
|         | O38A···H38A···O37 | 0.89 | 2.23  | 3.04(1) | 152    |
|         | O38···H38C···O22 | 0.89 | 2.64  | 3.14(1) | 118    |
|         | O37···H37A···O29 | 0.85 | 2.04  | 2.719(15) | 135    |
|         | O37···H37B···O30 | 0.85 | 2.03  | 2.825(15) | 154    |
|         | O36···H36B···O35 | 0.89 | 2.49  | 2.819(16) | 103    |
|         | O35···H35A···O26 | 0.85 | 2.018 | 2.83(1) | 159.6  |
| 3       | O3···H3···O19 | 0.86 | 1.78  | 2.61(1) | 162    |
|         | O4···H4···O37 | 0.86 | 1.73  | 2.55(1) | 158    |
|         | O7···H7···O17 | 0.86 | 1.85  | 2.66(1) | 134    |
|         | O8···H8···O29 | 0.86 | 1.81  | 2.641(8) | 164    |
|         | O11···H11···O19 | 0.86 | 2.50  | 3.10(1) | 127    |
|         | O11···H11···O20 | 0.86 | 1.79  | 2.60(1) | 159    |
|         | O12···H12···O28 | 0.86 | 1.79  | 2.617(9) | 160    |
|         | O15···H15···O38 | 0.86 | 1.79  | 2.66(1) | 163    |
|         | O16···H16···O23 | 0.86 | 1.91  | 2.72(1) | 158    |
|         | O17A···H17A···O38 | 0.86 | 1.95  | 2.76(1) | 156    |
|         | O39···H39A···O18 | 0.86 | 2.31  | 2.96(1) | 131    |
|         | O37···H37···O34 | 0.84 | 1.80  | 2.63(1) | 171    |

Symmetry codes: i x, 1.5 − y, −0.5 + z; ii 1 − x, −y, −z; iii 2 − x, −y, 1 − z; iv x, 0.5 − y, 0.5 + z.

### 3.3. Dimer of Trinuclear Cores Linked by a Semi-Coordination Bond in 2

The coordination unit in the monoclinic crystal 2 (P2₁/c) is built of two symmetrically independent trinuclear Cu²⁺···Ho³⁺···Cu²⁺ coordination moieties linked by a bidentate nitrate ligand into one hexanuclear entity (Figures 3 and 4). However, the distances between the O nitrate atom and Cu²⁺ centers are different: 2.488(5) and 3.031(5) Å for Cu2–O24 and Cu3–O25 pairs of atoms, respectively. The first distance may be regarded as a classic coordination bond, whereas, the other one is very
long but still within the limit of a semi-coordination bond (3.07 Å). Additionally, the coordination motif is again accompanied by two bifurcated hydrogen bonds O3–H3···O23 and O16–H16···O23 to the non-coordinated nitrate O atom, similar to 1. The hydrogen bonding seems to compete with the coordination bond causing the elongation of the Cu3–O25 distance above the conventional coordinative bond limit, but it seems to stabilize the whole motif. Because of the topological similarities between structures 1 and 2, the Cu3–O25 bond has been recognized as a semi-coordinative one, and the structure of 2 as a hexanuclear one.

Figure 3. Coordination polyhedra and selected hydrogen bonds (dashed lines) in 2.

Figure 4. Scheme of coordination in complex 2 with Cu–O and O···O distances in angstrom (Å), green bold lines—coordination bonds Cu–O at the apical positions, green dotted lines—Cu–O semi-coordination bonds at the apical positions, red dash–dotted lines—contacts behind the limit of a semi-coordination bond but topologically important, blue dashed lines—hydrogen bonds, * nitrate anion disordered over two positions (sof’s 0.5); ** water molecule disordered other two positions (sof’s 0.6:0.4).

The CuII ions occupy the N2O2 cavities of the doubly deprotonated H2tehy ligand. Cu1 and Cu2 cations have a coordination number (CN) of five. The apical position of tetragonal pyramids occupies NO3− ions. The contacts between atoms Cu1···O35 (3.89(1) Å) and Cu2···O26 (3.356(7) Å) are much longer than coordinative ones. Additionally, the same nitrate O atom is involved in hydrogen bonding (Figure 4, Table 4). Cu2 is linked by the nitrate bridge to Cu3 ion. The non-bonding nitrate O23 atom accepts two bifurcated hydrogen bonds closing the characteristic building motif. Cu3 (CN = 6) supplements its coordination sphere with a water molecule (Cu3–O37 2.475(8) Å). Cu4 (CN = 6) coordinates two monodentate NO3− ions. The Ho1 ion has the same coordination environment as Tm1 in 1, whereas, Ho2 is nona-coordinated. Except for two perpendicularly located H2tehy ligands,
there are two other positions which are disordered water molecules. This results in the change in conformation of the Schiff base ligands, which adopt a bent conformation instead of nearly planar as in 1. The remaining uncoordinated nitrate anions and water molecules interact through many hydrogen bonds (Table 4).

3.4. Supramolecular Polymer Built of Hexanuclear Monomers in 3

Compound 3 crystallizes in the orthorhombic Pnmc2 space group with two types of symmetrically independent hexanuclear coordination units composed of trinuclear subunits A and B linked by the NO$_3$$^-$ ions into AA and BB entities (Figures 5 and 6).

![Figure 5. Hexanuclear coordination units composed of trinuclear subunits A and B in 3 (top) and the suggested supramolecular polymeric chain AA–BB–AA–BB in 3 (bottom); symmetry codes: ’ −x, 1 − y, z; “ 1 − x, 1 − y, z.](image-url)
In a topological sense, compound 3 may be regarded as a 1D supramolecular polymer AA–BB–AA–BB running as a folded chain along the a axis with hexanuclear entities AA and BB linked by an elongated semi-coordinative bond (Cu4–O20 3.01(1) Å) and by a long contact of the same topology but probably of a different nature of interaction (Cu2–O18 3.19(1) Å). Each of these semi-coordination bonds or contacts is accompanied by a specific array of hydrogen bonds forming the characteristic motif found in 1 and 2 (Figure 6).

The assumption of an attractive character of this long contact is based on topological similarities of the recurrent supramolecular motif found in 1–3 and on the results of studies performed by Nelyubina et al. [34]. The stabilizing effect is provided by the accompanying hydrogen bonds O3–H3···O19, O11–H11···O19, and O11–H11···O20 (Table 4), wherein it is important that the hydrogen bonding occurs through the non-coordinated O nitrate atoms. The Er III cation is octa-coordinated as Tm III in 1. Cu1 (CN = 6) has H2O molecule in the apical position and μ-NO3⁻ ion at the other apex of a tetragonal bipyramid. The nitrate anion links by a semi-coordination bond (Cu1–O30 2.83(1) Å) two related by a two-fold rotation Cu1 ions into a hexanuclear unit. The apical ligands of Cu2 ion (CN = 6) are one methanol molecule and one NO3⁻ anion with a very long Cu2–O18 contact distance (3.19(1) Å) bridging to Cu4 cation. The Cu4 (CN = 6) is linked further to a repeated by a two-fold axis to another Cu4 ion. Cu3 (CN = 5) ion coordinates one monodentate nitrate ion. The Cu3···O38 (3.613(8) Å) contact was not identified as a coordinative because of the long distance and a competitive influence of O15–H15···O38 hydrogen bond (interaction to the same O nitrate atom).
3.5. The Geometric Criteria for a Semi-Coordination Bond on the Base of CSD Search

For the search of Cambridge Structural Database (CSD, ver. 5.40 Nov. 2018) the Conquest software (ver. 2.0.0.) was used, the restrictions were as follows R values <5%, no disorder, no powder structures [47]. The search for Cu···O–NO₂ distances up to 4 Å without determining the type of bonding or contact gave 1068 results. The number of occurrences of a given Cu–O distance (Figure 7) clearly confirm the Jahn–Teller distortion: 1) the first sharp peak with the maximum at ca. 1.9 Å corresponds to the shorter in-plane coordination bonds, 2) the next population of longer Cu–O distances has a wider range with a lower maximum at ca. 2.5 Å (Cu–O distance to the out-of-plane ligands). Next, the number of occurrence of Cu···O contacts seems to be nearly constant from three until ca. 3.5 Å, where it starts to grow with a small increase at ca. 3.1 Å. From the crystallographic point of view, this plot does not indicate any sharp border between coordination and semi-coordination bonding nor the sharp border of the second one.

![Figure 7. Distribution of Cu···O distance values up to 4 Å found in Cambridge Structural Database (CSD).](image)

The plot of Cu···O–N(O₂) angle shows three maxima at ca. 7, 75, and 115° (Figure 8). The highest maximum at ca. 115° corresponds to the optimal orientation of oxygen lobes toward the positive charge of the Cu center in coordination bonding, the peaks at ca. 7 and 75° are related to the angles between Cu and the non-interacting nitrate oxygen atoms.

![Figure 8. Distribution of Cu···O–N(O₂) angle values (ANG1 in °) found in CSD.](image)

It shows a clear directional preference in the orientation of nitrate ions toward the Cu metal centers (semi-coordination Cu···O–N(O₂) angle in the range of ca. 100 to 140°). It is even more pronounced at the scatter plot of Cu···O–N(O₂) angle vs Cu···O distance values (Figure 9). The directionality is sustained until ca. 3.65 Å and only above this distance limit does the distribution of Cu···O–N(O₂) valence angles start to be more random.

![Diagram](image)
directionality is sustained until ca. 3.65 Å and only above this distance limit does the distribution of Cu···O–N(O₂) valence angles start to be more random.

**Figure 9.** Scatter plot of Cu···O–N(O₂) angle (ANG1 in °) vs Cu···O distance (CUO in Å) up to 4 Å with marked six regions described in the text.

At the scatter plot (Figure 9) six groups of data can be distinguished: (1) the group of classic coordination bond to the in-plane ligands with short Cu···O distance (up to ca. 2.2 Å) and Cu···O–N(O₂) angle being in the range of 90 to 130°; (2) and (3) are clearly distinctive groups with low valence angles 5 to 10° and 60 to 90° and ranges of Cu···O distances above 3.65 Å and 2.3–3.7 Å, respectively. They correspond to the non-bonding contacts to the neighborly located oxygen atoms within the same coordinated NO₃⁻ molecule; (4) the elongated coordination or semi-coordination bond to the out-of-plane ligands (Cu–O bond ca. 2.3–3 Å, Cu···O–N(O₂) angle ca. 110–140°); (5) the extended area for very long interactions of a different character but still with a high degree of directionality (Cu···O distance ca. 3–3.65 Å, Cu···O–N(O₂) angle ca. 100–150°), could be probably hydrogen bond assisted coordination bonds. Additionally, in this group, if the regarded Cu···O–N(O₂) contact was not included as a coordination, nearly all of the copper(II) centers were tetra- or penta-coordinated and the nitrate anion was located at the “free” non-coordinated side of the central ion closing, at least in a topological sense, the coordination sphere of copper; 6) Group of contacts above 3.65 Å showing no specific directional preferences. A similar distribution of Cu–O distances and Cu–O–X(O₂) angles was observed in the group of other oxo complexes, where X was C or N; 7226 data, Figure S1 in Supplementary Materials).

### 3.6. Infrared Spectra

The obtained Cu^{II}-4f complexes show similar FTIR spectral features (Figure 10 and Figures S2–S4). A strong band at 1620 cm⁻¹ from ν(C=Nimine) is red-shifted by 20 cm⁻¹ in comparison to the free H₄teleh ligand indicating a decrease of the C=N bond order because of the formation of the coordination bond to the copper(II). The broad band with a maximum at ca. 3400 cm⁻¹ comes from
ν(O–H) stretching vibrations of coordinated and/or solvated water/methanol molecules and from the undeprotonated hydroxyl groups of the H₂tehy ligand. The strong phenolic ν(C–O) stretching vibration band was observed at 1240 cm⁻¹ for free H₂tehy ligand, whereas, in complexes there was a doublet with peaks at 1252 and 1220 cm⁻¹, confirming the coordination through these groups [49–53].

![FTIR spectra of the ligand H₄tehy and its complexes 1–3.](image)

3.7. Thermal Properties

The TG, DTG, and DSC curves of 1–3 (Figure 11 and Figures S5–S7) show that the Cu^{II}–4f compounds are stable at room temperature. During heating to ca. 100 °C the complexes 1–3 desolvate with a mass loss found 1.20% (1), 2.00% (2), 3.60% (3); calculated 0.80% (1), 1.50% (2), 3.40% (3).
Figure 11. Thermogravimetric (TG) curves of complexes 1–3 in air.

The DSC curves indicate a small endothermic effect. The decomposition process of the Cu$^{II}$–4f compounds was intricate, and the intermediate solid products were hard to distinguish. The final decomposition products of 1–3 were mixtures of metal oxides CuO and Ho$_2$O$_3$/Er$_2$O$_3$/Tm$_2$O$_3$ (calculated from TG curves and verified experimentally by powder XRD patterns (Figure S8). The calculated TG curves percentages (29.40% (1), 31.00% (2), 31.50% (3)) coincided with the theoretical values 30.00% (1), 28.90% (2), 30.00% (3).

3.8. Magnetic Properties

The plots of temperature-dependent molar susceptibility ($\chi_M T$ versus $T$) were shown in Figure 12, where $\chi_M$ is the molar magnetic susceptibility, and $T$ is the absolute temperature. The magnetic properties of the complexes result from the interplay between three factors: the Cu$^{II}$···Cu$^{II}$ and Cu$^{II}$–Ln$^{III}$ interactions, as well as the thermal population of the Stark components of the lanthanide(III) ions. The $\chi_M T$ values of the complexes studied at room temperature were calculated theoretically by the Equation (1) assuming four Cu$^{II}$ and two magnetically isolated Ln$^{III}$ ions.

$$\chi_M T = \left( N \beta^2 / 3k \right) \left[ 4g_{Cu}^2 S_{Cu} (S_{Cu} + 1) + 2g_{Ln}^2 J_{Ln} (J_{Ln} + 1) \right]$$  \hspace{1cm} (1)

where $N$ is Avogadro constant, $\beta$ is the Bohr magneton, and $k$ is Boltzman’s constant. In this equation $g_{Ln}$ is the $g$ factor of the ground $J$ terms of Ln$^{III}$ and is expressed as in Equation (2):

$$g_{Ln} = \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2(J + 1)}$$  \hspace{1cm} (2)
In Cu$^{II}_{4}$–Tm$^{III}_{2}$ (1) complex the $\chi M T$ value of 14.85 cm$^3$Kmol$^{-1}$ observed at 300 K corresponds to the value of 15.80 cm$^3$Kmol$^{-1}$ expected for two Tm$^{III}$ ($^3H_6$, $S = 1$, $L = 5$, $J = 6$, $g = 3/2$) and four Cu$^{II}$ ($S = 1/2$, $g = 2$) magnetically isolated ions. This value steadily decreased as $T$ was lowered to reach 6.99 cm$^3$Kmol$^{-1}$ at 1.8 K. For Cu$^{II}_{4}$–Ho$^{III}_{2}$ (2) the $\chi M T$ value experimentally determined at 300 K (28.04 cm$^3$Kmol$^{-1}$) is slightly lower than the value of 29.63 cm$^3$Kmol$^{-1}$ expected for two Ho$^{III}$ ($^5I_6$, $J = 8$, $L = 6$, $S = 2$, $g = 5/4$) and four Cu$^{II}$ ($S = 1/2$, $g = 2$) noninteracting metal ions. With the lowering of the temperature the $\chi M T$ remained constant until 120 K, then it decreased to 27.00 cm$^3$Kmol$^{-1}$ at 19 K and next increased to reach a value of 28.48 cm$^3$Kmol$^{-1}$ at 6.6 K. Finally, it showed a small decrease to 22.07 cm$^3$Kmol$^{-1}$ at 1.8 K. For the compound Cu$^{II}_{4}$–Er$^{III}_{2}$ (3) the experimental value of $\chi M T$ at room temperature was equal to ca. 24.83 cm$^3$Kmol$^{-1}$ corresponding to the calculated value of 24.45 cm$^3$Kmol$^{-1}$ for two uncoupled Er$^{III}$ ($^4I_{15/2}$, $S = 3/2$, $L = 6$, $J = 15/2$, $g = 6/5$) and four uncoupled Cu$^{II}$ ions ($S = 1/2$, $g = 2$). As shown in Figure 12, this value decreased with the lowering of the temperature to 13.93 cm$^3$Kmol$^{-1}$ at 1.8 K.

The lowering of $\chi M T$ at low temperature in 1 and 3, is caused most probably by the crystal field splitting of Ln$^{III}$ ion, and/or a combination of the contribution of the overall antiferromagnetic interactions of metal ions. The profile of the $\chi M T$ vs $T$ curve in 2 strongly suggests the existence of two competitive phenomena. The decrease of $\chi M T$ on temperature lowering was most probably caused by the depopulation of the Ho Stark sublevels, or the presence of magnetic anisotropy, or the antiferromagnetic coupling between ions, whereas, the increase of the $\chi M T$ at lower temperatures may arise because of the ferromagnetic Cu$^{II}$–Ho$^{III}$ interaction.

4. Conclusions

The nuclearity of the presented complexes 1–3 was tuned by the interplay between coordination and hydrogen bonds involving nitrate anions. The recurrent array of coordination or semi-coordination bonds and hydrogen bonding presented here can be added to the crystal engineering library as a building motif. The coordination bond may be weakened and elongated until it transforms into a non-covalent interaction when a competitive influence of hydrogen bonding will occur. It is worth to underline that even at long distances (above the limit of semi-coordination bond 3.07 Å) the directionality of the Cu···O–NO$_2$ contact (100–150°) may be sustained up to ca. 3.65 Å, which also correlates well with the reports of Nelyubina et al. about weak but still attractive in nature interactions (Cu···O 3.6 Å, 0.5 kcal/mol), which was involved in the magnetic super-exchange [34]. These may be regarded as crystallographic criteria for the searching of elongated semi-coordination bonds when
assisted by hydrogen bonding. On the basis of these results, the following conclusions can be drawn:

That depending on the supramolecular topology and symmetry of the analyzed system, the hydrogen bonding can stabilize the coordination, or it can disrupt it. It seems that the stabilizing effect on semi-coordination bonding is observed when the accompanying hydrogen bond is directed to the non-coordinated O nitrate atom (see sets of contacts in crystal 3: O3–H3⋯O19 and Cu2⋯O18; bifurcated O11–H11⋯O19/O20 and Cu4⋯O20). The destabilizing effect occurs when coordination and hydrogen bonding compete for the same O atom (see the pairs of contacts in 1: O13–H13⋯O11 and Cu2⋯O11; in 2: O8–H8⋯O35 and Cu1⋯O35; O4–H4⋯O26 and Cu2⋯O26). Additionally, the border of 3.07 Å for a semi-coordination bond can be probably extended when the “hydrogen bond assisted” coordination occurs, but additional angular preference factor must be considered.

The presented results show that hydrogen bonding has a significant influence on the coordination bonds being responsible for the weakening and the elongation of the axial out of plane bonds in structures disturbed by the Jahn–Teller effect. Irrespective of the semi-coordination bond distance limit, topological analysis of crystal structures should always be performed since even minor structural features may help in better understanding of physicochemical properties of coordination compounds, as well as in designing of self-assemblying materials or in protein–ligand docking methods.

Supplementary Materials: The following are available online: http://www.mdpi.com/2073-8994/11/4/460/s1, Figure S1. Scatter plot of Cu⋯O–X(O2) angle where X = C or N (ANG1 in °) vs Cu⋯O distance (CUO in Å) up to 4 Å with marked six regions described in the text; Figure S2. FTIR spectra of the H4tehy ligand and complex 1; Figure S3. FTIR spectra of the H4tehy ligand and complex 2; Figure S4. FTIR spectra of the H4tehy ligand and complex 3; Figure S5. TG and DSC curves of 1 in air; Figure S6. TG and DSC curves of 2 in air; Figure S7. TG and DSC curves of 3 in air; Figure S8. The powder XRD diffractograms of the final products of decomposition in air of complexes 1–3.

Author Contributions: Conceptualization, B.M.; funding acquisition, B.M.; investigation, B.M., D.O., B.C., H.G.; methodology, B.M., B.C.; software, B.M.; visualization, B.M., D.O., B.C.; writing—original draft preparation, B.M., B.C.; writing—review and editing, B.M., B.C.

Funding: The research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Operational Program Development of Eastern Poland 2007–2013 (Contract No. PO PW.01.03.00-06-009/11-00, equipping the laboratories of the Faculties of Biology and Biotechnology, Mathematics, Physics and Informatics, and Chemistry for studies of biologically active substances and environmental samples).

Acknowledgments: We kindly thank Prof. Keiji Hirose for the invitation to participate in this special issue on Symmetry and Asymmetry in Host-Guest Chemistry and Supramolecular Chemistry.

Conflicts of Interest: The authors declare no conflict of interest.

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