A NEW 1-D HYDROGEN BOND POLYMER CONSTRUCTED FROM A TRINUCLEAR 3d-4f TECTON AND 4,4'-BIPYRIDINE- *N,N'*-DIOXIDE

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A new heteropolymetallic system, $[\{Cu(OH_2)L\}_2Pr(OH_2)_2](bpno)(NO_3)_3 \cdot 8H_2O$ **1**, was obtained by reacting the [CuL] complex with $Pr(NO_3)_3 \cdot 6H_2O$ and 4,4'-bipyridine- *N,N'*-dioxide, bpno. (L^{2-} is the dianion of the compartmental Schiff-base ligand obtained from the 2:1 condensation of 3-methoxysalicylaldehyde with 1,3-diaminopropane) The crystal structure of **1** has been solved: it crystallizes in the triclinic system, space group *P-1*; $a = 14.576(5)$ Å, $b = 15.004(8)$ Å, $c = 15.183(5)$ Å, $\alpha = 90.21(5)^o$, $\beta = 114.72(4)^o$, $\gamma = 90.45(5)^o$, $V = 3016(2)$ Å^3, $Z = 2$. The structure consists of $[\{Cu(OH_2)L\}_2Pr(OH_2)_2]^{3+}$ discrete cationic heterotrinuclear entities, uncoordinated 4,4'-bipyridine- *N,N'*-dioxide molecules and nitrate ions, as well as crystallization water molecules. The crystallographic investigation reveals a one-dimensional chain-like structure based upon hydrogen bond interactions between the aqua ligands coordinated to the praseodymium atoms and the 4,4'-bipyridine- *N,N'*-dioxide molecules. The π-π stacking interactions established between the aromatic fragments of the compartmental Schiff-base ligands and the 4,4'-bipyridine- *N,N'*-dioxide molecules also play an important role in sustaining the supramolecular solid-state architecture.

INTRODUCTION

Since the pioneering work of Robson et al., in 1990,[1] the 'node and spacer' approach became a widely employed strategy in synthesizing coordination polymers with various dimensionalities and network topologies. Symmetrical *exo*-bidentate ligands, such as pyrazine, and bis(4-pyridyl) derivatives,[2] or polycarboxylates[3] are among the most popular linkers. The resulting solid-state architectures are determined by several factors: (i) metal-to-ligand stoichiometry; (ii) the stereochemical preference (coordination algorithm) of the assembling cations; (iii) the use of ancillary ligands attached to the metal ions or of additional bridging ligands; (iv) the intervention of the non-covalent interactions (hydrogen bonds, π–π stacking interactions); (v) the role of the anions (coordinated, bridging, uncoordinated); (vi) the presence of organic guest molecules, which can act as templates.

In a series of papers we have shown that Cu^{II}-Ln^{III} oligonuclear complexes (Ln: lanthanide ion) can be successfully used as nodes in constructing novel solid-state architectures, by connecting them through a large variety of *exo*-dentate ligands (spacers).[4] Two families of linkers have been chosen in our systematic investigation: (a) *exo*-dentate ligands bearing nitrogen donor atoms; (b) *exo*-dentate ligands with oxygen donor atoms. We found that the variety of the resulting structures is due to several factors: (i) the nature of the donors atoms of the linkers; (ii) the preference of the copper(II) ion for nitrogen atoms; (iii) the oxophily of the lanthanides; (iv) the various connectivity modes exhibited by the linkers; (v) the stoichiometry of the final products, that is, the Cu^{II} : Ln^{III} : linker molar ratio. Moreover, the binuclear [CuLn] complexes are suitable starting materials in the attempt to design heterospin systems with three different spin carriers.[5]

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Another interesting linker exhibiting various coordination modes is the 4,4'-bipyridine- *N,N'*-dioxide molecule. The study of its role in designing extended structures has started fairly recently.[6] 4,4'-Bipyridine-*N,N'*-dioxide is a rigid spacer and it can act as bridging and/or terminal ligand. Its aromatic rings can also be involved in π-π stacking interactions. On the other hand, bpno has several peculiarities: (i) it can form bridges with different geometries (*cis* and *trans* coordination modes); (ii) it is a good hydrogen acceptor; (iii) because of the orientation of the lone pairs at the oxygen atoms, it presents a rich variety of connectivity modes through hydrogen bond interactions. The convolution of the coordinative, hydrogen bond, and stacking interactions leads to interesting solid-state architectures.[7]

In this paper we report on the synthesis and crystal structure of a new 1-D heteropolymetallic polymer, which is obtained by reacting [CuL] with $Pr(NO_3)_3 \cdot 6H_2O$ and 4,4'-bipyridine- *N,N'*-dioxide (L^{2-} is the dianion of the compartmental Schiff-base ligand obtained from the 2:1 condensation of 3-methoxysalicylaldehyde with 1,3-diaminopropane).

EXPERIMENTAL

Synthesis

The chemicals were purchased from commercial sources and all manipulations were performed using the materials as received. [CuL] was obtained according to ref.[8] $[\{Cu(OH_2)L\}_2Pr(OH_2)_2](bpno)(NO_3)_3 \cdot 8H_2O$ **1** was obtained as follows: an aqueous solution (10 mL) of $Pr(NO_3)_3 \cdot 6H_2O$ (0.05 mmol, 0.021 g) and 4,4'-bipyridine- *N,N'*-dioxide (0.05 mmol, 0.009 g) was added to a 1/1 acetonitrile-methanol solution (10 mL) of [LCu] (0.1 mmol, 0.04 g). The green solution was stirred for about 15 minutes. The low evaporation of the solution led after three days to green single crystals. IR data (KBr, cm^{-1}): 3387 s, 2940vw, 2850vw, 1622s, 1561vw, 1471s, 1382vs, 1294m, 1226s, 1175w, 1100vw, 1066w, 1026vw, 976vw, 946vw, 835w, 783vw, 742w, 634vw, 548vw, 440vw.

Physical measurements

IR spectra (KBr) pellets was recorded on a Bio-Rad FTS 135 spectrophotometer in the 4000 – 400 cm^{-1} region. UV-Vis spectra (diffuse reflectance technique) was recorded with a UV4 Unicam spectrophotometer.

Table 1

Crystallographic data and structure refinement

Empirical formula	$C_{48}H_{47}N_9O_{30.5}Cu_2Pr$
Formula weight	1505.94
Crystal system	triclinic
Space group	*P -1*
Temperature (K)	180(2)
a (Å)	14.576(5)
b (Å)	15.004(8)
c (Å)	15.183(5)
α (°)	90.21(5)
β (°)	114.72(4)
γ (°)	90.45(5)
V (Å^3)	3016(2)
Z	2
D_{calc} (g cm^{-3})	1.658
μ (mm^{-1})	1.592
F(000)	1518
θ range (°)	2.54 - 20.81
Reflexions collected / independent reflexions	16298 / 5987 [R_{int} = 0.0624]
Data / restraints / parameters	5987 / 0 / 824
GOF F^2	1.375
final R indices [$I>2\sigma(I)$]	0.0993, 0.2584
R indices (all data)	0.1060, 0.2611

Crystal structure determination

Measurements were performed at room temperature T = 180(2) K, on an one circle STOE Imaging Plate Detector X-Ray diffractometer system (Mo-radiation, λ = 0.71073 Å). A phi scan strategy was used for the data collection, frames were integrated

using the STOE software package X-RED,[9] the integrated frames yielded a total of 22188 reflections collected (8154 independent, R_{int} = 0.0638, R_{sig} = 0.0486) and 7544 (92.51 %) reflections were found greater than 2σ(I). The unit cell parameters were, a = 14.576(5) Å, b = 15.004(8) Å, c = 15.183(5) Å, α = 90.21(5)°, β = 114.72(4)°, γ = 90.45(5)°, V = 3016(2) Å³, Z = 2, calculated density D_c =1.658 Mg/m³. Absorption corrections were applied for all data using the DIFABS program.[10] Programs SIR92[11] and SHELXL 97[12] included in the WinGX software package[13] were respectively used for phase determination and structure refinement. Direct methods of phase determination followed by some subsequent difference Fourier map led to an electron density map from which most of the non-hydrogen atoms were found. With subsequent isotropic refinement and Fourier difference synthesis, all of the non-hydrogen atoms could be identified. Atomic coordinates, isotropic and anisotropic displacement parameters of all non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F². H-atoms were included in the refinement in calculated positions, riding on the carbon atoms with an isotropic thermal parameter fixed 20% higher than carbon atoms to which they were attached. In the case of methyl groups torsion angles were also refined. The refinement converged at: R_1 = 0.0945, w$R2$ = 0.2495 with intensity, I>2σ(I), with the largest peak/hole in the final difference map were found to be between 1.866 and -1.503 e.Å⁻³.

All calculations were carried out using the WinGX 32.[14] Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC 294461), Copies of this information may be obtained for free from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The reaction between [CuL], Pr(NO₃)₃·6H₂O and 4,4'-bipyridine- *N,N'*-dioxide in a 2:1:1 molar ratio leads to a 3d-4f heterotrimetallic complex, with the formula [{Cu(OH₂)L}₂Pr(OH₂)₂](bpno)(NO₃)₃·8H₂O **1**.

The IR spectrum of compound **1** clearly shows, apart from the characteristic bands of the organic compartmental ligand, a band coming from the nitrate anions at 1382 cm⁻¹. This sharp and strong band is characteristic for uncoordinated nitrate anions.[15a] Compared to the IR spectrum of the free bpno, the ν(NO) band is shifted by 16 cm⁻¹ to a lower wavenumber from 1242 cm⁻¹, which can be attributed to the hydrogen bonded N-O group[15a]. It also indicates that the hydrogen bonding interactions are remarkably strong and efficient. A broad absorption band for ν(OH) appears at 3397 cm⁻¹, showing the presence of water molecules in the complex.

The solid state electronic spectrum of **1** exhibits a large band located at 650 nm, that is due to the superposition of the bands assigned to the $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$, $d_{xz,yz} \rightarrow d_{x^2-y^2}$ transitions for a square pyramidal [Cu(II)N₂O₂O'] chromophore.

The structure of **1** consists of discrete cationic, [{Cu(OH₂)L}₂Pr(OH₂)₂]³⁺, neutral, bpno, and anionic, NO₃⁻, units, and crystallization water molecules, which are held together by an extensive hydrogen-bonding network (Fig. 1).

Let us discuss first the molecular structure of the complex cation [{Cu(OH₂)L}₂Pr(OH₂)₂]³⁺. Relevant bond lengths and angles of the Cu(II) and Pr(III) environments are quoted in Table 2. The copper(II) ion is hosted within the inner compartment (the N₂O₂ site) of the organic ligand. The trinuclear entity is built up by two [CuL] units, which are linked to the central praseodymium(III) ion by two pairs of oxygen atoms: the methoxy oxygen atoms at the 3-position of the L ligand [O(3), O(4), and O(7), O(8)] and the oxygen atoms of the salicylidene fragment [O(1), O(2), and O(5), O(6)], which are bridging positions between the Cu(II) and the Pr(III) ions. The structure of cation is bent, the angle Cu(1) - Pr(1) - Cu(2) being 107.2°. The four atoms involved in each Cu(O,O)Pr bridge are not coplanar [(O,O) bridging phenoxide oxygen atoms]. The dihedral angles between the (OCuO) and (OPrO) planes are equal to 19.5° and 12.7° in the Cu(1) and Cu(2) moieties, respectively. The related Cu···Pr separations, Cu(1)···Pr(1) and Pr(1)···Cu(2), are equal to 3.595(3) Å and 3.614(3) Å, respectively.

The praseodymium ion is ten-coordinated. In addition to the eight oxygen atoms afforded by two L ligands, the rare earth ion achieves its environment with two oxygen atoms coming from two molecules of water. The Pr - O bond lengths depend on the nature of the oxygen atoms; they vary from 2.446(11) to 2.796(13) Å, with mean value of 2.557 Å. The bonds issued from the phenolato oxygens are shorter than those from the water molecules, the largest ones being related to the methoxy sidearms. Each copper has a classical square pyramidal environment. The four basal donors (N₂O₂) are afforded by a L ligand, while a water molecule occupies the apical position. The apical Cu - O bonds with a mean value of 2.297 Å are longer than the equatorial ones (mean value 1.952 Å).

Table 2

Selected bond lengths (Å) and interbond angles (°)

Bond lengths (Å)

Cu(1) – N(1)	1.964(16)	Pr (1) – O(1)	2.487(10)
Cu(1) – N(2)	1.955(16)	Pr (1) – O(2)	2.446(11)
Cu(1) – O(1)	1.936(13)	Pr (1) – O(3) Me	2.631(13)
Cu(1) – O(2)	1.901(13)	Pr (1) – O(4) Me	2.650(13)
Cu(1) – O(4w)	2.34(4)	Pr (1) – O(5)	2.481(12)
Cu(2) – N(3)	2.015(16)	Pr (1) – O(6)	2.448(13)
Cu(2) – N(4)	1.931(17)	Pr (1) – O(7) Me	2.656(13)
Cu(2) – O(5)	1.989(12)	Pr (1) – O(8) Me	2.796(13)
Cu(2) – O(6)	1.926(12)	Pr (1) – O(1w)	2.473(12)
Cu(2) – O(3w)	2.255(12)	Pr (1) – O(2w)	2.507(13)

Bond angles (°)

Cu(1)-O(1)- Pr(1)	106.6(5)	Cu(2)-O(5)- Pr(1)	107.2(5)
Cu(1)-O(2)- Pr(1)	110.9(5)	Cu(1)-O(6)- Pr(1)	110.7(5)
O(4w)-Cu(1)-O(1)	85.4(12)	O(3w)-Cu(2)-O(5)	99.7(5)
O(4w)-Cu(1)-O(2)	86.1(10)	O(3w)-Cu(2)-O(6)	85.9(5)
O(4w)-Cu(1)-N(1)	106.7(12)	O(3w)-Cu(2)-N(3)	102.9(6)
O(4w)-Cu(1)-N(2)	86.3(11)	O(3w)-Cu(2)-N(4)	89.9(6)

The trinuclear entity owes its bent, butterfly - type, shape to an offset π-π intramolecular stacking interaction between the aromatic rings of the two [CuL] moieties (Fig. 2). The separations associated to these interactions are in the range of 3.20 - 3.76 Å.

The bpno species further extend the structure via hydrogen-bond interactions involving the aqua ligands coordinated to the Pr(III) ion, resulting in a chain-like supramolecular arrangement, where the nodes are the trinuclear complex $[\{Cu(OH_2)L\}_2Pr(OH_2)_2]^{3+}$ species and the bpno molecules act as linkers. One hydrogen atom from one aqua molecule coordinated to praseodymium [O(1w)] interacts with the oxygen atom from a bpno molecule: O(1w)···O(9) = 2.608 Å. The second aqua ligand from praseodymium [O(2w)] is involved in a hydrogen bond interaction with the oxygen atom from another bpno entity: O(2w)···O(9) = 2.632 Å (Fig. 3). This way, the bpno molecule acts as a *cis* - hydrogen bond acceptor.

By further analyzing the structure of this supramolecular chain, we notice that it results from the interplay of the hydrogen bonding and π-π intermolecular stacking interactions established between the aromatic rings of the compartmental L ligand and the ones belonging to the adjacent bpno molecules. For clarity, the aromatic ring coming from the Cu(2) moiety is labeled **A**, and the one belonging to the Cu(1) fragment is **B** (Fig. 4). The two aromatic rings of the bpno molecule are labeled **A'** and **B'**, according to their stacking partner arising from the trinuclear entity. **A** and **A'** interact through a graphite-like aromatic stacking (the distances associated to this interaction are in the range of 3.52 - 3.80 Å) and **B** - **B'** is an offset aromatic interaction, the intermolecular distances ranging from 3.34 to 3.79 Å.

The system described in this paper illustrates that oligonuclear Cu^{II}-Ln^{III} complexes are suitable starting materials in the attempt to design interesting solid-state architectures, not only by means of coordinative bonding between the complex connectors and the organic linkers, but also through hydrogen bond and π-π stacking interactions.

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