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Anion-directed Assembly of Helical Copper(II) Complexes Based on a Bispyridylpyrrole Ligand: Synthesis, Structural and Magnetic Properties

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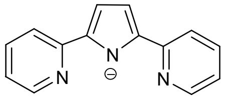
Helical copper(II) complexes based on a bispyridylpyrrole ligand, namely helical polymer $\{[Cu_2(PDP_H)_2(N_3)_2]\}_n$ (**1**) (where $HPDP_H$ = 2,5-bis(2'-pyridyl)pyrrolide) containing an one-dimensional double-helical chain, a discrete double-helical complex $[Cu_2(PDP_H)_2(NO_3)_2]$ (**2**) and triple-helical complex $[Cu_2(PDP_H)_3](OTf)$ (**3·OTf**) (where OTf^- = triflato) were synthesized by displacement of Cl^- in $[Cu(PDP_H)Cl]$ by the anion N_3^-, NO_3^- and OTf^-, respectively. Structures of these complexes directly correlate with the coordination abilities of the ligands. The N_3^- anion is found to favor the formation of polymeric helical structures. The helical chain in **1** is built-up by $[Cu_2(PDP_H)_2]$ units linked by double $\mu_{1,3}$–azido bridges. In **2**, the anion NO_3^- acting as a monodentate oxygen ligand binds to each copper center, resulting in the formation of the double helical structure, while the non-coordinating OTf^- ligand leaves space for three PDP_H^- ligands, leading to formation of the triple-helical dicopper complex **3·OTf**. Magnetic susceptibility data of **1**, measued from 1.8 to 300K, show alternating ferro- and antiferromagnetic interactions through the bridging PDP_H^- and $\mu_{1,3}$-azido pathway, respectively.

Introduction

Transition metal helicates have a wide range of interesting applications including catalysis, probing DNA structures, optical and magnetic materials [1-7]. Numerous examples of metal helicate have been described in the literature so far. They can be single-, double- and triple-helical. The flexible multidentate ligand play a crucial role for the specific formation of versatile helical structure. Preorganized linear oligonitrogen donors, linear oligooxygen donors, mixed oxygen/nitrogen donors and ligands possessing sulfur, carbon or phosphorous donors are effective in producing helicates.[8-12] Anion-directed assembly is common strategy for the synthesis of coordination polymer complexes. [13-16] Anion can directly influence the structure by coordinating to the metal ions or by acting as templates to induce the self-assembly. However, to our knowledge, the examples of metal helicates depending on the anion present during self-assembly process are relative rare.[17-20] For example, a family of circular double helicates from the reaction of tris-bipy ligand and iron(II) salts were obtained under the exact same conditions, the only difference residing in the anion present during the helicate formation.[17,18]

We have a long-standing interest in the metal complexes based on mono-anionic tridentate 2,5-bis(2'-pyridyl)pyrrolide (PDP_H^-) ligand (Scheme 1). Not only this N3 ligand has the π-backbonding capability, but also pyrrolate donor with flexible π-properties can behave as bridging ligand due to its versatile π-donor and π-acceptor responding to the metal site π-bonding properties [21-24]. PDP_H^- ligand is usually recognized as an analogue of the neutral terpyridine ligand (tpy). A number of helical Cu(I) complexes with tpy or its derivatives are reported. It inspired us to pursue new helical copper complexes with anionic bispyridylpyrrole ligand. In our previous studies, a hetero-sodium/copper(I) complex with PDP_H^- ligand in a helical arrangement around the copper(I) has been characterized.[24] Obviously, PDP_H^- is a suitable candidate for synthesis of helical metal complexes.

Thus, we will describe the preparation, crystal structures of a series of copper(II) helicates based on bispyridylpyrrole ligand. They are $\{[Cu_2(PDP_H)_2(N_3)_2]\}_n$ (**1**) with one-dimensional double-helical chain, discrete double-helical $[Cu_2(PDP_H)_2(NO_3)_2]$ (**2**) and triple-helical $[Cu_2(PDP_H)_3](OTf)$ (**3·OTf**) obtained from the reactions of $[Cu(PDP_H)Cl]_2$ with NaN_3, $NaNO_3$ and AgOTf (where OTf = triflato), respectively. Primary magnetic result of **1** is also presented.



Scheme 1 Structure of anionic PDP_H^- ligand

Experimental Sectoins

General Considerations

All manipulations were carried out under nitrogen by standard Schlenk techniques unless otherwise stated. Solvents were purified, distilled and degassed prior to use. Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by a PE240C elemental analyzer. The magnetic susceptibility data were prefromed on a Quantum Design MPMS-XL7 SQUID magnetometer. The starting 2,5-bis(2'-pyridyl)pyrrolide ($HPDP_H$) [25] and $[Cu(PDP_H)Cl]$ [26] were prepared according to literature methods. All of other chemicals were obtained from J&K Scientific Ltd.

Synthesis of $\{[Cu_2(PDP_H)_2(N_3)_2]\}_n$ (1)

A mixture of $[Cu(PDP_H)Cl]$ (64 mg, 0.2 mmol) and NaN_3 (13 mg, 0.2 mmol) in THF was stirred overnight and filtered. The filtrate was layered with hexane to give green needle crystals which were suitable for X-ray diffraction study. Yield: 54 mg (83 %). IR (KBr, cm^{-1}): 3069(w), 3022(w), 2052(vs), 1600(s), 1552(m), 1516(m), 1449(m), 1436(s), 1377(w), 1337(s), 1260(m), 1144(m), 1121(w), 1051(m), 1004(m), 955(w), 743(s), 708(w), 690(w), 645(w). Anal. Calcd for $C_{28}H_{20}Cu_2N_{12}\cdot1.2(thf)$: C, 53.50; H, 4.11; N, 22.55. Found: C, 53.98; H, 4.03; N, 22.89.

Synthesis of $[Cu_2(PDP_H)_2(NO_3)_2]$ (2)

A mixture of $[Cu(PDP_H)Cl]$ (64mg, 0.2 mmol) and $NaNO_3$ (17 mg, 0.2 mmol) in THF was stirred overnight and filtered. The filtrate was layered with hexane to give green block crystals which were suitable for X-ray diffraction study. Yield: 60 mg (87 %). IR (KBr, cm^{-1}): 3083(w), 3056(w), 1602(s), 1558(w), 1532(m), 1508(m), 1486(s), 1449(s), 1436(s), 1376(w), 1340(m), 1287(s), 1264(s), 1152(m), 1122(w), 1082(w), 1043(m), 1010(s), 954(w), 756(s), 710(w), 686(w), 647(w). Anal. Calcd for $C_{28}H_{20}Cu_2N_8O_6\cdot0.3(thf)$: C, 49.17; H, 3.17; N, 15.71. Found: C, 49.12; H, 3.05; N, 15.89.

Synthesis of $[Cu_2(PDP_H)_3]\cdot$OTf (3·OTf)

A mixture of $[Cu(PDP_H)Cl]$ (128mg, 0.4 mmol) and AgOTf (104 mg, 0.4 mmol) in THF was stirred overnight and filtered. The filtrate was layered with hexane to give green block crystals which were suitable for X-ray diffraction study. Yield: 78 mg (62 %). IR (KBr, cm^{-1}): 3089(w), 3031(w), 1602(s), 1558(m), 1506(s), 1453(m), 1434(s), 1389(w), 1332(s), 1259(s), 1223(m), 1147(s), 1100(w), 1052(m), 1030(s), 953(w), 785(m), 753(s), 712(m), 638(m). Anal. Calcd for $C_{43}H_{30}Cu_2F_3N_9O_3S$: C, 55.12; H, 3.23; N, 13.45. Found: C, 55.32; H, 3.45; N, 13.51.

X-ray crystallography

Diffraction data of **1**-**3·OTf** were recorded on a Bruker CCD diffractometer with monochromatized Mo-K_α radiation (λ□= 0.71073Å). The collected frames were processed with the software SAINT. The absorption correction was treated with SADABS [27]. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [28]. Atomic positions of non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were introduced at their geometric positions and refined as riding atoms. In complex **1**, one tetrahydrofuran molecule is co-crystallized.

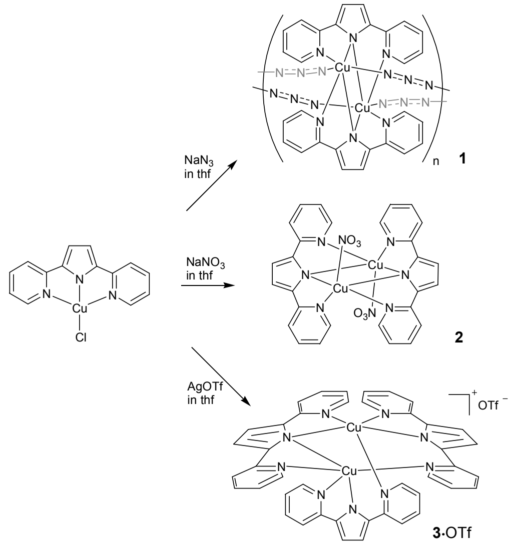
Results and Discussion

Synthesis and characterization Replacements of Cl^- ligand in $[Cu(PDP_H)Cl]$ by N_3^-, NO_3^- and OTf^- give helical polymer $\{[Cu_2(PDP_H)_2(N_3)_2]\}_n$ (**1**), descrete double-helical $[Cu_2(PDP_H)_2(NO_3)_2]$ (**2**) and triple-helical $[Cu_2(PDP_H)_3](OTf)$ (**3·OTf**) in good yields and excellent purity,

Table 1 Crystallographic data and experimental details for complexes **1** - **3·OTf**

	1·thf	**2**	**3·OTf**
formula	$C_{32}H_{28}Cu_2N_{12}O$	$C_{14}H_{10}CuN_4O_3$	$C_{43}H_{30}Cu_2F_3N_9O_3S$
fw	723.74	345.80	936.90
crystal system	Orthorhombic	Monoclinic	Orthorhombic
space group	Pbcn	C2/c	Pca2(1)
a, Å	8.22470(10)	17.6233(3)	18.6566(9)
b, Å	33.0397(5)	12.3436(2)	11.8775(6)
c, Å	11.3562(2)	15.2939(3)	19.2374(10)
β, deg		123.0260(10)	
V, $Å^3$	3085.95(8)	2789.40(9)	4262.9(4)
Z	4	8	4
ρ_{calc}, g cm^{-3}	1.558	1.647	1.460
T, K	293(2)	293(2)	293(2)
μ, mm^{-1}	1.428	1.584	1.110
no. of refln.	16889	20205	30751
no. of indep. refln.	3583	3199	9179
R_{int}	0.0246	0.0146	0.0581
GoF [a]	1.081	1.085	1.013
R_1, [b] wR_2 [c] [I > 2σ(I)]	0.0358, 0.0827	0.0205, 0.0645	0.0647, 0.1546
R_1, wR_2 (all data)	0.0522, 0.0976	0.0215, 0.0654	0.1053, 0.1685

[a] GoF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{½}$. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] wR_2 $[(\Sigma w|F_o| - |F_c|)^2/\Sigma w^2|F_o|^2]^{½}$.



Scheme 2 Syntheses of complexes **1-3·OTf**

respectively (Scheme 2). **1-3·OTf** are readily soluble in common organic solvents, such as CH_2Cl_2, THF and DMSO, yet not soluble in water and nonpolar solvents such as diethyl ether and hexane. These complexes are air-stable in solid state and in solution. Recrystallization of the crude products from tetrahydrofuran by diffusion of hexane afford crystals which are suitable for X-ray diffraction study. The IR spectra of **1-3·OTf** indicate that the PDP_H^- ligand has several distinctive signals, including weak aromatic C-H stretching at about 3022-3089 cm^{-1}, and moderately strong streching bands at 1340-1600 cm^{-1} corresponding to the in-plane vibrations of C=C and C=N bonds, which are well comparable with those in the coinage metal complexes with PDP_H^- ligand [24]. A strong stretching band at 2052 cm^{-1} in **1** due to azido groups, as well as strong signals at 1010 and 1030 cm^{-1} attributed to nitrato and triflato ligands in complexes **2** and **3·OTf**, respectively, are observed.

Strucutre description The structures of **1-3·OTf** are confirmed by single crystal X-ray diffraction method. A summary of crystallographic data and experimental details for these complexes are given in Table 1. The ORTEP diagrams for **1-3**$^+$ with ellipsoids and their space-filling representation are shown in Figure 1-3, respectively.

Known from our previous studies,[26] starting material $[Cu(PDP_H)Cl]$ is mononuclear. Its structure is analogous with that of known bispyridylpyrrolide metal complexes, such as $[M(PDP_H)Cl]$ (M = Pd, Pt).[22] The total bond angels around Cu is 359.42 °, which is close approximately to 360 °, indicating of a planar structure. Three interplanar angles among two side rings and the pyrrole ring are close to zero. The bond distance of Cu-Cl is 2.2216(11) Å. Its $Cu\text{-}N_{pyridine}$ distance (2.141(3) Å and 2.148(3) Å) is longer than that of $Cu\text{-}N_{pyrrole}$ (1.862(3) Å).

As shown in Fig 1a, the structural feature of complex **1** is one dimensional double-helical chain.Two PDP_H^- ligands are twisted around Cu···Cu axis to form $[Cu_2(PDP_H)_2]^{2+}$ building block. Two μ-1,3 N_3^- ligands bridge the $[Cu_2(PDP_H)_2]^{2+}$ building block to generate nutural 1D helical coordination polymer. The analogous polymieric helical chains containing copper(I) terpyridine units $[Cu_2(terpy)_2]^{2+}$ (where terpy = 2,2':6'2"-terpyridine) [29] was reported, where $[Cu_2(terpy)_2]^{2+}$ building block is linked through weak Cu(I)-Cu(I) d^{10}-d^{10} secondary bonds.

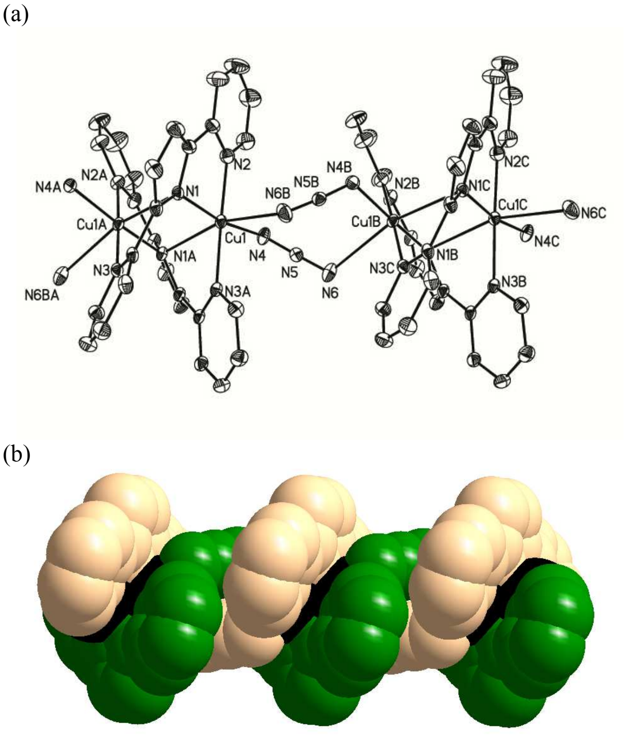


Fig. 1 (a) ORTEP diagram of building block of $[Cu_2(PDP_H)_2(\mu\text{-}N_3)_2]$ in **1** with ellipsoids shown at the 50% probability level; (b) Space-filling representation showing the helical chain of **1**. The hydrogen atoms are omitted for clarity. Selected bond distances(Å): Cu1–N1 2.002(2), Cu1–N2 2.037(2), Cu1–N3A 2.0555(19), Cu1–N4 1.977(2), Cu1–N1A 2.534, Cu1–N6B 2.624, Cu1–Cu1A 3.062; Selected bond angles(º): N1–Cu1–N2 80.35(8), N1–Cu1–N3A 100.31(8), N1–Cu1–N4 169.18(8), N2–Cu1–N3A 178.24(9), N4–Cu1–N2 89.03(9), N4–Cu1–N3A 90.24(8). Symmetry transformations used to generate equivalent atoms: A -x, y, -z+3/2

In the $[Cu_2(PDP_H)_2]^{2+}$ building block of **1**, each Cu atom locates in the center of elongated octahedron geometry. Two long axial sites are provided by N1A from equivalent PDP_H^- and N6B from the azido ligand with distances of 2.534(3) and 2.624(3) Å, respectively. The bond angle of N1A-Cu1-N6B is 161.1(8) °. The basal plane is defined by the N2, N1, N3A from two PDP_H^- ligands and N4 from azido ligand. The Cu1-N1, Cu1-N2, Cu1-N3A and Cu1-N4 bond distances are 2.002(2), 2.037(2), 2.0555(19) and 1.977(2) Å. To be notable, the central N atom of each N_3^- ligand lies close to a Cu(II) with a distance of 2.768(2) Å, comparable with that of a weak Cu(II)-N bond. The Cu1-Cu1A seperation (3.062(6) Å) is longer than Cu1-Cu1B (5.163(6) Å). The angle of Cu1-N1-Cu1A is 84.1(3) °.

Complex **2** is a discrete double-helicate. Each copper(II) in **2** is in an irregular five–coordinate environment to form distorted trigonal dipyramidal geometry with four short contacts to one oxygen atom from NO_3^- (Cu1–O2 2.0104(10) Å), two nitrogen atom from a "monopyridylpyrrole" fragment of one PDP_H^- ligand (Cu1-N2A 1.9878(12) Å; Cu1–N3A 2.0035(11) Å) and one nitrogen atom from a terminal pyridine of the other PDP_H^- ligand (Cu1–N1 2.0194(10) Å). The coordination sphere is completed by a long contact to the pyrrole of the second PDP_H^- ligand

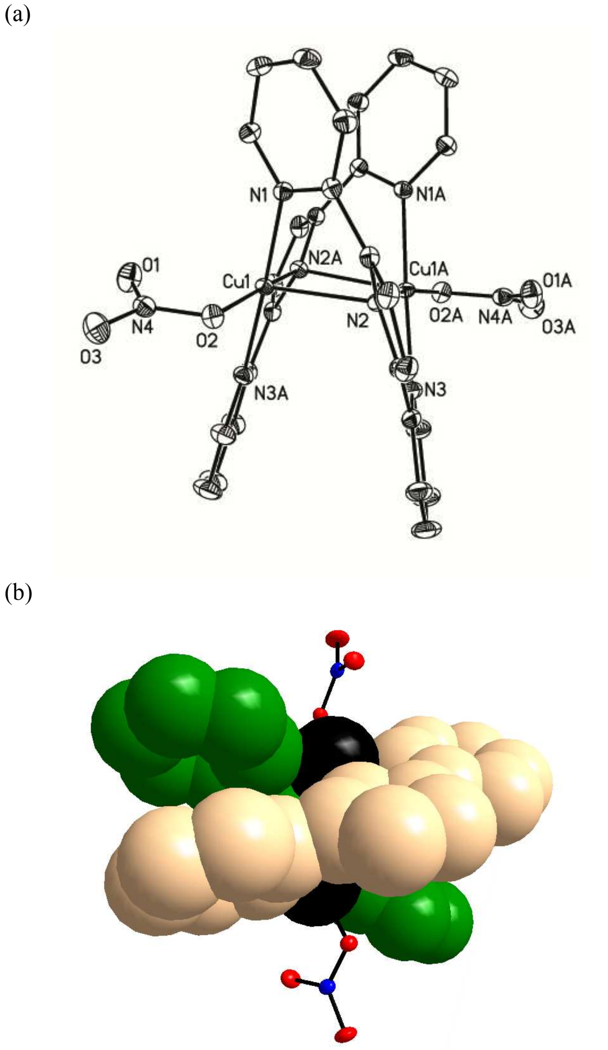


Fig. 2 (a) ORTEP diagram of dinuclear complex **2** with ellipsoids shown at the 50% probability level; (b) Space-filling representation showing the helical structure of **2**. The hydrogen atoms are omitted for clarity. Selected bond distances(Å): Cu1–N1 2.0194(10), Cu1–N2 2.3712(12), Cu1–N2A 1.9878(12), Cu1–N3A 2.0035(11), Cu1–O2 2.0104(10), Cu1–Cu1A 2.9234(3); Selected bond angles(º): N1–Cu1–N2 77.07(4), N1–Cu1–O2 88.76(4), N1–Cu1–N2A 99.30(4), N1–Cu1–N3A 177.85(4), N2–Cu1–O2 91.26(4), N2–Cu1–N2A 96.15(4), N2–Cu1–N3A 104.92(4), N2A–Cu1–O2 170.08(4), N2A–Cu1–N3A 81.35(4), N3A–Cu1–O2 90.40(4). Symmetry transformations used to generate equivalent atoms: A -x+2, y, -z +1/2

(Cu1–N2 2.3712(12) Å). The copper-copper distance is 2.9234(3) Å. It is interesting to be notable that the metal ions in the helicates commonly are four-, six- or eight-coordinate, but cases of helicate with metal maintaining a trigonal dipyramidal geometry as **2** are very rare. Only known example is a helical oligopridine palladium complex.[11]

The crystal structure determination shows **3·OTf** is composed of $[Cu_2(PDP_H)_3]^+$ ($\mathbf{3}^+$) cation and an uncoordinated trifalto anion. $\mathbf{3}^+$ displays an unusual triple-helical structure in which three PDP_H^- ligands wrap in a helical arrangement around two copper atoms. Each Cu atom is also penta-coordinate by five nitrogen atoms from three dipyridinepyrrole ligands to form trigonal dipyramidal geometry. N3, N5, N9 around Cu1 as well as N1, N5, N7 around Cu2 atoms form the basal plane, and N4, N8 and N2, N6 atoms occupy their respective axial direction. The average distances of Cu-N on the basal plane (av. 2.151 Å) is longer than that of Cu–N on the axis (av. 1.969 Å). The N4–Cu1–N8 and N2–Cu2–N6 on the axis are nearly linear with bond angles of 176.1(2) ° and 170.8(2) °, respectively. The Cu···Cu seperation of 2.8147(10) Å in $\mathbf{3}^+$ are significantly shorter than that found that in **1** and **2**, perhaps due to one more PDP_H^- ligand chelating two copper atoms.

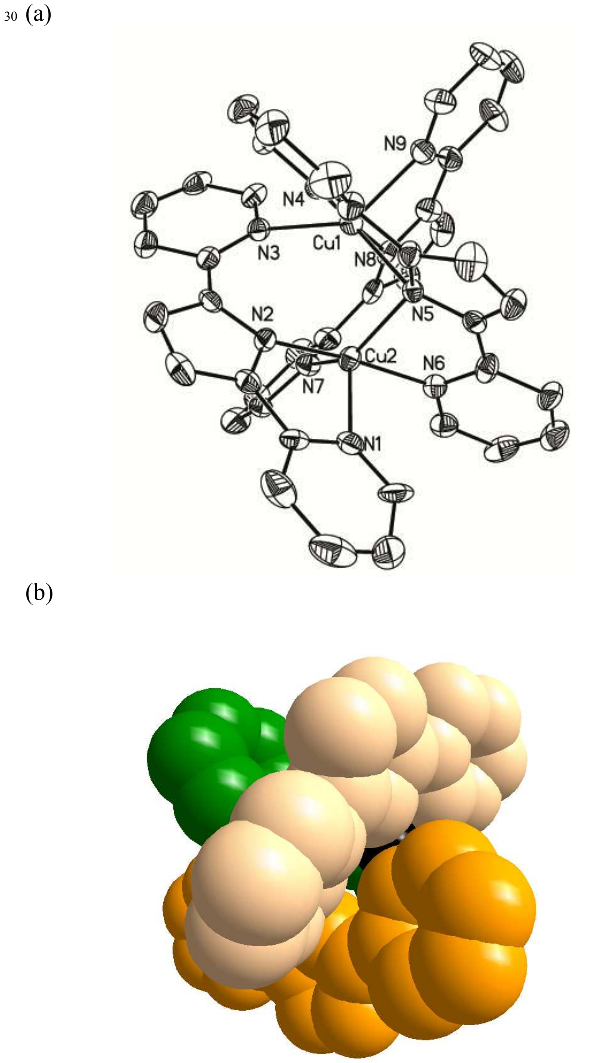


Fig. 3 (a) ORTEP diagram of dinuclear $\mathbf{3}^+$ with ellipsoids shown at the 30% probability level. (b) Space-filling representation showing the helical structure of $\mathbf{3}^+$. The hydrogen atoms and OTf^- anion are omitted for clarity. Selected bond distances(Å): Cu1–N3 2.066(5), Cu2–N1 2.199(6), Cu1–N4 1.988(6), Cu2–N2 1.954(5), Cu1–N5 2.341(5), Cu2–N5 2.155(5), Cu1–N8 1.950(6), Cu2–N6 1.982(5), Cu1–N9 2.094(5), Cu2–N7 2.051(6), Cu1–Cu2 2.8147(10); Selected bond angles(º): N3–Cu1–N4 89.9(2), N1–Cu2–N2 80.7(2), N3–Cu1–N5 131.2(2), N1–Cu2–N5 96.8(2), N3–Cu1–N8 93.9(2), N1–Cu2–N6 90.4(2), N3–Cu1–N9 133.5(2), N1–Cu2–N7 123.3(2), N4–Cu1–N5 79.8(2), N2–Cu2–N5 97.6(2), N4–Cu1–N8 176.1(2), N2–Cu2–N6 170.8(2), N4–Cu1–N9 93.9(2), N2–Cu2–N7 93.2(2), N5–Cu1–N8 98.2(2), N5–Cu2–N6 81.0(2), N5–Cu1–N9 94.9(2), N5–Cu2–N7 139.7(2), N8–Cu1–N9 82.8(3), N6–Cu2–N7 93.6(2).

Structural invesitgations of complexes **1**-$\mathbf{3}^+$ reveal that the bispyridylpyrrole ligand is flexible and is capable of acting as chelating and bridging ligand to bound to Cu(II) atom in bonding mode of μ_2-(κ_2-N, N'),(κ_2-N', N'') and/or μ_2-(κ_2-N, N'), N''. The PDP_H^- ligand in these complexes are twisted. Three interplanar angles with the central ring are in the range of 4.0(1)-35.8(1)°, well comparable with those found in the coinage metal terpyridine and pyridylpyrrole complexes [24, 30-31].

Magnetic properties of complex 1 Variable-temperature magnetic susceptibility measurement was performed on crystalline **1** in the range of 1.8-300 K at 1000 G. The χ_MT *versus* T plots and 1/χ_M *versus* T plots are shown in Fig. 4. The effective magnetic moment (2.828 μ_B per Cu2) at 300 K is well consistant with the theoretical value (2.828 μ_B) expected for a two uncoupled S = 1/2 spin system. The χ_MT value continuously increases and reaches 1.41 cm^3 K mol^{-1} at 3.0 K on cooling from room temperature, indicating of ferromagnetic interaction between the Cu(II) ions. The ferromagnetic coupling is further confirmed by a positive Weiss constant (θ = 1.42 K), determining in the temperature range 3-300 K. By lowering the temperature further, χ_MT drops down sharply, reaching the minimum value of 1.33 cm^3 K mol^{-1} at 1.8 K. This could be due to zero-field splitting and/or inter-chains antiferromagnetic interaction.

Taking into consideration of structural features of **1** analogous with those of the alternating $\mu_{1,1}$-azido and $\mu_{1,3}$-azido one dimensional coordination polymers, **1** may exhibit alternating ferro- and antiferro-magnetic interaction mediated by bridging PDP_H^- and $\mu_{1,3}$-azido ligands, respectively.[32-33] The magnetic data are fitted as chains using the one-dimensional S= 1/2 expression based on the Hamiltonian

$$H = -J_1\sum S_{2i}S_{2i+1} - J_2\sum S_{2i+1}S_{2i+2} \qquad (1)$$

Where J_1 is the magnetic coupling constant between the Cu(II) ions *via* PDP_H^- bridges, and J_2 that between the Cu(II) ions *vis* $\mu_{1,3}$-azido ligands. The expression of the molar susceptibility is derived as:

$$\chi_{chain} = \frac{Ng^2\beta^2}{3kT}\frac{1+u_1+u_2+u_1u_2}{1-u_1u_2}S(S+1) \qquad (2)$$

where

$$u_1 = \coth(J_1S(S+1)/kT) - kT/J_1S(S+1)$$
$$u_2 = \coth(J_2S(S+1)/kT) - kT/J_2S(S+1)$$

Considering the weak magnetic interactions between the Cu(II) ions in the adjacent chains, the mean field approximation, *zJ′*, is introduced. The total magnetic susceptibility is:

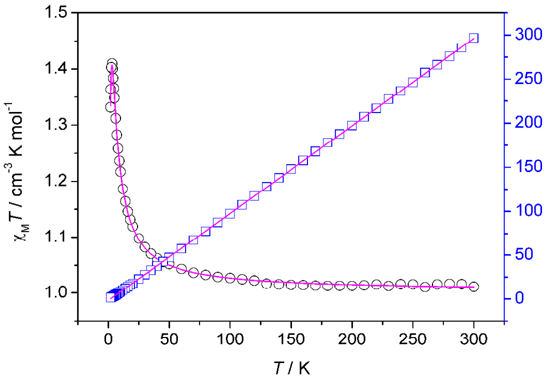


Fig. 4 Plot of χ_MT *versus* T , 1/χ_M *versus* T for **1**. The solid line corresponds to the best theoretical fit.

$$\chi = \frac{\chi_{chain}}{1-(2zJ/Ng^2\beta^2)\chi_{chain}} \qquad (3)$$

The best-fit parameters are g = 2.09, J_1 = 7.36 cm^{-1}, J_2 = -0.75 cm^{-1}, *zJ′* = -0.017 cm^{-1}. The fitting results show that the magnetic interaction between the Cu(II) ions *via* PDP_H^- bridges, and between the Cu(II) ions *vis* $\mu_{1,3}$-azido ligand are ferromagnetic and antiferromagnetic, respectively. The small negative *zJ′* value indicates the magnetic coupling between the Cu(II) ions in the adjacent chains is very weakly antiferromagnetic.

Conclusions

In summary, we have synthesized helical complexes **1-3·OTf** by displacements of Cl^- in [Cu(PDP_H)Cl] by the anion N_3^-, NO_3^- and OTf^-, respectively. These complexes are isolated and structureally characterised. The results indicated that the counter anions are crucial factors for formation of the different helical structures. $\mu_{1,3}$-azido bridge lead to helical polymer. Weakly coordinating nitrate occupies on coordination site on a Cu center, leading to the double helix structure. No coordinating triflate leaves space for three PDP_H^- ligands and result in formation of triple helicate. Flexible bispyridylpyrrole backbones accompanying with anions with varied coordination abilities can ligate metal centres in different orientations, and finally give helical structures. Magnetic analyses for **1** reveal that alternating ferro- and antiferromagnetic interactions are operative through the alternating PDP_H^- and $\mu_{1,3}$-azido bridges, respectively.

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Notes and references

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† Electronic supplementary information (ESI) available: Crystallographic data in CIF format. CCDC reference numbers 1015413 to 1015415 for complexes **1** - **3·OTf**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

1 (a) Y. Sawada, S. Furumi, A. Takai, M. Takeuchi, K. Noguchi, K. Tanaka, *J. Am. Chem. Soc.*, 2012, **134**, 4080-4083. (b) T. Yamamoto, T. Yamada, Y. Nagata, M. Suginome, *J. Am. Chem. Soc.*, 2010, **132**, 7899-7901.
2 K. L. Haas and K. Franz, *Chem. Rev.*, 2009, **109**, 4921-4960.

3 (a) S**.** Ye, Y. Wu, W. Zhang, N. Li, B. Tang, *Chem. Commun.,* 2014, DOI: 10.1039/C4CC03988B. (b) C. Jobbágy, M. Molnár, P. Baranyai, A. Deák, *Dalton Trans*., 2014, DOI: 10.1039/c4dt01214c.

4 M. J. Hannon, V. Moreno, M. J. Prieto, E. Moldrheim, E. Sletten, I. Meistermann, C. J. Isaac, K. J. Sanders, A. Rodger, *Angew. Chem. Int. Ed*., 2001, **40**, 879-884.

5 (a) P. Cucos, F. Tuna, L. Sorace, I. Matei, C. Maxim, S. Shova, R. Gheorghe, A. Caneschi, M. Hillebrand and M. Andruh, *Inorg. Chem.*, 2014, DOI: 10.1021/ic501051q. (b) M. M. Szostak, H. Chojnacki, K. Piela, U. Okwieka-Lupa, E. Bidzińska and K. Dyrek, *J. Phys. Chem. A*., 2011, **115**, 7448-7455.

6 (a) C. Jobbágy, M. Molnár, P. Baranyai, A. Hamza, G. Pálinkás, A. Deák, *CrystEngComm*., 2014, **16**, 3192-3202. (b) A. El-ghayoury, L. Douce, A. Skoulios, R. Ziessel, *Angew. Chem. Int. Ed*., 1998, **37**, 2205-2208.

7 C. J. Matthews, S. T. Onions, G. Morata, L. J. Davis, S. L. Heath and D. J. Price, *Angew. Chem. Int. Ed*., 2003, **42**, 3166-3169.

8 (a) J. Keegan, P. E. Kruger, M. Nieuwenhuyzen and N. Martin, *Cryst. Growth Des*., 2002, **2**, 329-332. (b) J. R. Nitschke, D. Schultz, G. Bernardinelli and D. Gérald, *J. Am. Chem. Soc*., 2004, **126**, 16538-16543.

9 (a) C. J. Baylies, J. C. Jeffery, T. A. Miller, R. Moon, C. R. Rice and T. Riis-Johannessen, *Chem. Commun*., 2005, 4158-4160. (b) F. G. Gelalcha, M. Schulz, R. Kluge and J. Sieler, *J. Chem. Soc., Dalton Trans*., 2002, 2517-2521.

10 (a) C. Piguet, G. Bernardinelli and A. F. Williams, *Inorg. Chem*., 1989, **28**, 2920-2925. (b) K. T. Potts, M. Keshavarz-K, F. S. Tham, H. D. Abruila and C. Arana, *Inorg. Chem*., 1993, **32**, 4450-4456.

11 E. C. Constable, S. M. Elder, J. Healy and M. D. Ward, *J. Am. Chem. Soc*., 1990, **112**, 4590-4592.

12 D. B. D. Amico, F. Calderazzo, M. Curiardi, L. Labella and F. Marchetti, *Inorg. Chem*., 2004, **43**, 5459-5465.

13 (a) T. Wang and X. –P. Yan, *Chem. Eur. J*., 2010, **16**, 4639-4649. (b) D.–X. Wang, S.–X. Fa, Y. Liu, B.–Y. Hou and M.–X. Wang, *Chem. Commun*., 2012, **48**, 11458-11460.

14 (a) W. Feng, Y. Zhang, Z. Zhang, X. Lü, H. Liu, G. Shi, D. Zou, J. Song, D. Fan, W.–K. Wong and R. A. Jones, *Inorg. Chem.,* 2012, **51**, 11377-11386. (b) M. Hirotsu, Y. Shimizu, N. Kuwamura, R. Tanaka, I. Kinoshita, R. Takada, Y. Teki and H. Hashimoto, *Inorg. Chem*., 2012, **51**, 766-768.

15 (a) Y.–Q. Huang, X.–Q. Zhao, W. Shi, W.–Y. Liu, Z.–L. Chen, P. Cheng, D.–Z. Liao, S.–P. Yan, *Cryst. Growth Des.,* 2008, **8**, 3652-3660. (b) T. F. Mastropietro, N. Marino, D. Armentano, G. D. Munno, C. Yuste, F. Lloret and M. Julve, *Cryst. Growth Des*., 2013, **13**, 270-281.

16 (a) H.–J. Kim, W.–C. Zin, M. Lee, *J. Am. Chem. Soc*., 2004, **126**, 7009-7014. (b) J. Chen, S.–H. Wang, Z.–F. Liu, M.–F. Wu, Y. Xiao, F.–K. Zheng, G.–C. Guo and J.–S. Huang, *New J. Chem*., 2014, **38**, 269-276. (c) T. F. Mastropietro, N. Marino, D. Armentano, G. D. Munno, C. Yuste, F. Lloret and M. Julve, *Cryst. Growth Des*., 2013, **13**, 270-281.

17 B.Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. Van Dorsselaer, B. Kneisel, D. Fenske, *J. Am. Chem. Soc.* 1997, **119**, 10956-10962.

18 B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 1838-1840.

19 M. Albrecht, *Chem. Rev.* 2001, **101**, 3457-3498.

20 W. L. Leong, J. J. Vittal, *Chem. Rev.* 2011, **111**, 688-764.

21 J. W. Ciszek, Z. K. Keane, L. Cheng, M. P. Stewart, L. H. Yu, D. Natelson and J. M. Tour, *J. Am. Chem. Soc*., 2006, **128**, 3179-3189.

22 G. H. Imler, Z. Lu, K. A. Kistler, P. J. Carroll, B. B. Wayland and M. J. Zdilla, *Inorg. Chem*., 2012, **51**, 10122-10128.

23 F. Hein and U. Beierlein, *Pharm. Zentralhalle Dtschl*., 1957, **96**, 401-421.

24 X. H. Hu, Y. Liang, C. Li, X. Y. Yi, *Dalton Trans.,* 2014, **43**, 2458–2464.

25 (a) H. Schindlbauer, *Monatsh. Chem.,* 1968, **99**, 1799-1807. (b) R. A. Jones, M. Karatza, T. N. Voro, P. U. Civcir, A. Franck, O. Ozturk, J. P. Seaman, A. P. Whitmore and D. J. Williamson, *Tetrahedron.,* 1996*,* **52***,* 8707-8724.

26 M. Rui, X. H. Hu, X. Y. Yi, S. C. Zhang, *J. Cent. South Univ.*, 2014, accepted.

27 G. M. Sheldrick, *SADABS*, University of Göttingen, Germany, 1997.

28 G. M. Sheldrick, *SHELXTL-Plus V5.1 Software Reference Manual*; Bruker AXS Inc., Madison, Wisconsin, USA, 1997.

29 A. Messimeri, C. Papadimitriou, C. P. Raptopoulou, A. Escuer, S. P. Perlepes, A. K. Boudalis, *Inorg. Chem. Commun.,* 2007, **10**, 800-804.

30 (a) Y. Cui and C. He, *J. Am. Chem. Soc*., 2003, **125**, 16202-16203. (b) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft and T. Kulke, *Chem. Commun.,* 1998, 2659-2660. (c) E. C. Constable, T. Kulke, M. Neuburger and M. Zehnder. *Chem. Commun.* 1997, 489-490.

31 (a) Effendy, F. Marchetti, C. Pettinari, R. Pettinari, B. W. Skelton and A. H. White, *Inorg. Chim. Acta.*, 2007, **360**, 1414-1423. (b) H. Feng, X.-P. Zhou, T. Wu, D. Li, Y.-G. Yin and S. W. Ng, *Inorg. Chim.. Acta*, 2006, **359**, 4027-4035. (c) Z. Ma, Y.-P. Xing, M. Yang, M. Hu, B.-Q. Liu, M. F. C. G. da Silva and A. J. L. Pombeiro, *Inorg. Chim. Acta*, 2009, **362**, 2921-2926. (d) M. J. Hannon, C. L. Painting, E. A. Plummer, L. J. Childs and N. W. Alcock, *Chem. Eur. J*., 2002, **8**, 2225-2238.

32 E. Q. Ago, S. Q. Bai, Y. F. Yue, Z. M. Wang, C. H. Yan, *Inorg. Chem.* 2003, **42**, 3642-3649.

33 R. Cortés, M. Drillon, X. Solans, L. Lezama, T. Rojo, *Inorg. Chem.* 1997, **36**, 677-683.

Table of Contents Entry

Anion-directed Assembly of Helical Copper(II) Complexes Based on Bispyridylpyrrole Ligand: Synthesis, Structural and Magnetic Properties

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