Synthesis and crystal structure of a novel multimodal ligand, 6,6'-bis(2-(di(pyridin-2-yl)methylene)-1-methylhydrazinyl)-2,2'-bipyridine, and its copper(I) complex, $\{[Cu_3L_2](PF_6)_3 \cdot 3H_2O\}$ (1)

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The single crystal X-ray structure of the novel multimodal ligand 6,6'-bis(2-(di(pyridin-2-yl)methylene)-1-methylhydrazinyl)-2,2'-bipyridine, $C_{34}H_{28}N_{10}$ (**L**), was determined at 120 (2) K. The ligand possesses a centre of symmetry that generates a planar bipyridyl core with the hydrazone substituents in a trans-geometry. The di-2-pyridyl moieties at either terminus of the molecule twist out of the plane (52.90 and 56.32 Å). The crystal structure comprises 2-dimensional ribbons that stack about each other so as to optimise van der Waals interactions and packing efficiency. Studies of the coordination properties of the novel multimodal ligand with copper(I) show that 2 ligand strands wrapped around the copper(I) having a preference for tetrahedral geometry to furnish a supramolecular self-assembled of a double-stranded tri-nuclear helical complex, $\{[Cu_3\mathbf{L}_2](PF_6)_3 \cdot 3H_2O\}$ (**1**), as revealed by the ESI-MS, and further characterised by ^{1}H-NMR, UV-Vis, and FT-IR spectra.

Key Words: Bipyridine derivatives; hydrazone; dipyridyl ketone; metal complexes; N-donor ligands

Introduction

Hydrazones and their metal compounds are of interest for their physical properties, reactivity patterns, and applications in many important chemical processes. These include non-linear optics,[1] sensors,[2] medicine,[3] and analysis and separation.[4]

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Our interest in this ligand system was stimulated by the medicinal reactivity patterns of hydrazone derivatives. The well-established coordination ability of the 2,2'-bipyridyl ligand system[5] suggests that bulky substituents at the 6,6'-positions repel each other and prevent the ligand adopting a planar conformation. This facilitates the self-assembly of mono-, double-, or triple-stranded helical metal complexes in a variety of coordination geometries.[6] On the other hand, the di-2-pyridyl ketone (dpk) and its oxime, hydrazone, and thiosemicarbazone derivatives, and their complexes have recently attracted attention due to their reactivity, physical properties, and applications.[7,8] Recently, structurally related di-2-pyridyl imine ligands derived from 2,2'-dipyridyl ketone and 2,4,6-trimethylaniline and also 2,6-di-isopropylaniline were successfully employed in the Suzuki coupling reaction of p-bromoanisole and phenylboronic acid.[9] There is no other similar di-2-pyridyl ketone structure containing the 2,2'-bipyridine moiety reported in the literature.

Lehn and co-workers reported the synthesis of strands by symmetric double condensation of dihydrazinopyrimidine with pyridine-2-carboxaldehyde.[10] Due to the conformational mobility of the hydrazone unit, the strands confer flexibility to undergo folding into helical shapes. Herein, we describe the synthesis and characterisation for the novel titled ligand and its copper(I) complex.

Experimental

Apparatus

Melting point was determined with a Büchi Melting Point B-540 model digital melting point instrument. ^{1}H-NMR spectra were recorded on a Bruker DPX 400 Spectrometer, using dmso-d_6 as a solvent and TMS as an internal standard. IR spectra (ATR) were recorded on a Perkin Elmer FT-IR Spectra-100E spectrophotometer. APCI-ES Mass spectra were recorded on an Agilent 1100 MSD Mass spectrometer. Elemental analyses were performed on an Elementary Micro Vario CHNS analyser.

Synthesis of the ligand (L)

All chemicals were of reagent grade and used as received, unless otherwise stated. The precursor ligand, namely 6,6'-bis(N-methylhydrazine)-2,2'-bipyridine, was previously prepared and reported in the literature.[4] The present ligand was synthesised in high yield by condensation of 6,6'-bis(N-methylhydrazine)-2,2'-bipyridine (0.390 g; 1.6 mmol) with di-2-pyridyl ketone (0.589 g; 3.2 mmol) in methanol in the presence of a catalytic amount of glacial acetic acid under dry nitrogen atmosphere over molecular sieves (4 Å) (Scheme 1). A white precipitate was obtained after refluxing for 6 h, and collected by filtration and air-dried to give 0.78 g (85%). Block-like crystals suitable for X-ray diffraction analysis were grown by slow ether diffusion at room temperature. Mp: 145-150 °C. Anal. Calcd. for $C_{34}H_{28}N_{10}$: C, 70.82; H, 4.89; N, 24.29%. Found: C, 70.8; H, 4.6; N, 24.4. APCI-ES MS (m/z): 576.6 M$^+$.

Synthesis of double-stranded tri-nuclear copper(I) complex $[Cu_3L_2]^{3+}$ (1)

To the ligand (0.127 mmol) in acetonitrile (25 mL) was added an equivalent amount of $[Cu(MeCN)_4]PF_6$ under dry nitrogen atmosphere. The homogeneous solution was degassed with dry nitrogen gas for 30 min via a 2-end

needle connected to the nitrogen tube. After degassing, the solution was kept at 50 °C with continuous stirring under an inert atmosphere for 3 days. The solution was concentrated to half of its volume under vacuum, and underwent ether diffusion in an isolated flask to yield red-brown powder (Scheme 2). Recrystallisation from dichloromethane-acetonitrile (1:1) failed to give any suitable crystal for X-ray analysis.
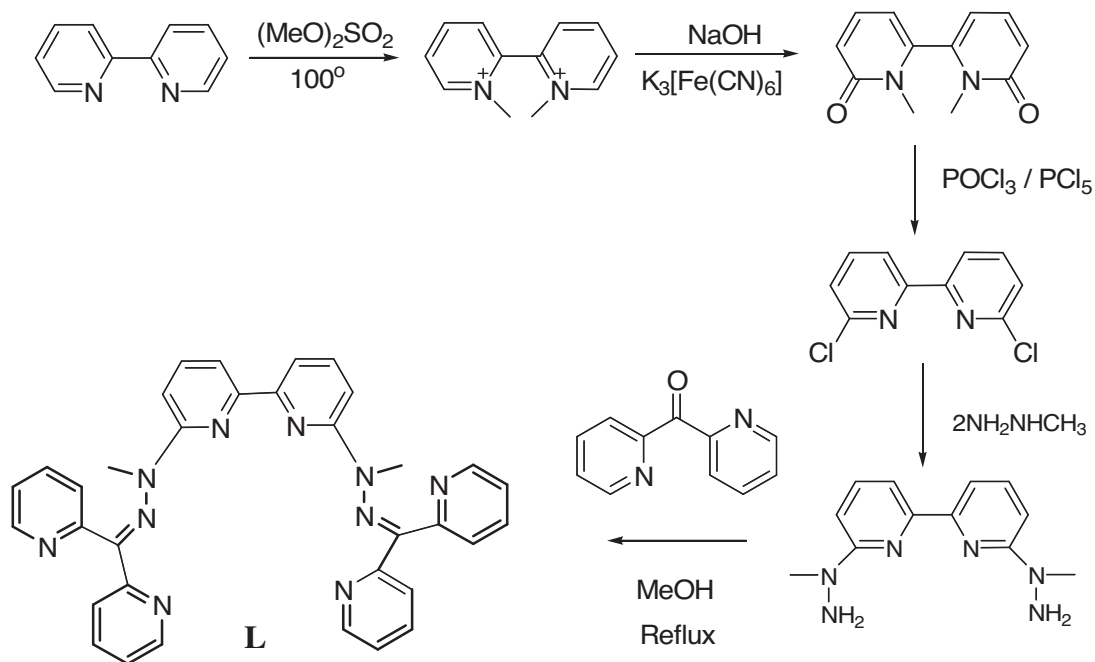
Scheme 1

IR (ATR, ν cm^{-1}): (H_2O) 3270, (CH_{ar}) 3113, ($CH_{al.}$) 2916, (CH) 2850, (C=N) 1651, (H–O–H) 1608, (C=C) 1570, (C=C + C=N) 1469 and 1433, (py ring) 1283, (py ring) 1269, (N–N) 1070, (PF_6) 840, δ (CH) 789. ^{1}H-NMR (dmso-d_6, δ_{ppm}): δ 8.5-6.5 (m, 24H, 6xPy), 3.4 (s, 6H, 2 × CH_3). UV-Vis (DMF, λ_{max}/nm): 348, 269. APCI-ES (m/z): 496.0 $[Cu_3(\mathbf{L})_2PF_6]^{3+}$ (calculated (m/z): 497.1) and 465.7 $[Cu_3(\mathbf{L})_2(H_2O)_3]^{3+}$ (Calculated m/z = 466.79).

X-ray crystallography of L

Data were collected on a Bruker-Nonius APEX2 area detector diffractometer[11] situated at the window of a rotating anode (λ MoK$_\alpha$ = 0.71073 Å). The structure was solved by direct methods, SHELXS-97, and refined using SHELXL-97.[12] The data were corrected for absorption effects using the multi-scan technique of the program SADABS V2.10.[13] Data reduction was performed with DENZO,[14] and the software used to prepare material for publication was PLATON.[15] Full-matrix least squares refinement was based on F^2. Hydrogen atoms were included in the refinement in geometrically idealised positions with isotropic thermal parameters related to those of the parent atom where $U_{iso}(H) = 1.2$ or 1.5 $U_{eq}(C)$.

All e.s.d.'s (except the e.s.d. in the dihedral angle between 2 l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles, and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by

crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes. The structure is centrosymmetric with an inversion centre between atoms C16 and C16a in the molecule.

Refinement on F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2; conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R-$factors (gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Crystal data and details of the structural determinations for **L** are given in Table 1, whilst selected bond lengths and angles (Table 2) and details of hydrogen bonding geometries (Table 3) are also given. There are no significant C-H $\cdots \pi$ interactions and no significant $\pi \ldots \pi$ interactions (<4.775 Å) in the crystal structure. Atomic coordinates are given in Table 4, whilst anisotropic displacement parameters are included in Table 5.

Results and discussion

Single block-like crystals of **L** were obtained by slow ether diffusion into methanol solution at room temperature. The CHN analysis and the ES-MS confirm the structure (Figure 1). The spectroscopic studies, such as FT-IR and ^{1}H-NMR, were only performed for the copper(I) complex (**1**), due to lack of sufficient ligand for the preparation of the complex compound. However, it is very well known that a free ligand and its corresponding metal complexes usually show almost identical infrared and NMR spectra with the observation of slightly shielding or deshielding in NMR, and shifting to lower wave numbers in infrared spectra for the complexes, but the peaks patterns and positions usually remain unaltered.
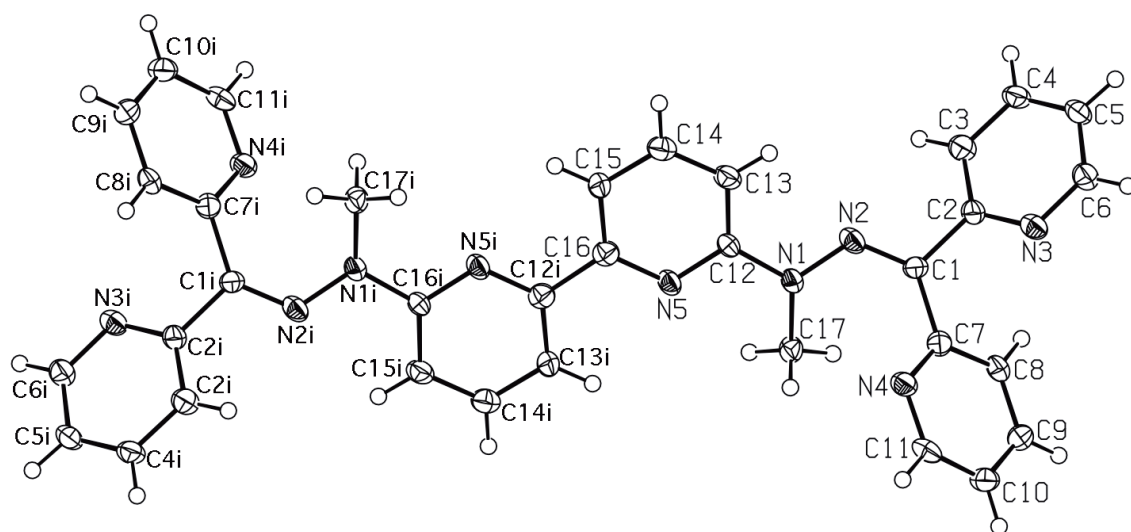

Figure 1. The molecular structure of **L**, showing the atom labelling scheme, and with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radius and symmetry related atoms (labelled i) are generated by the operation 1-x, -y, 1-z.

Table 1. Crystallographic data and details of the structure refinement of **L**.

Empirical formula	$C_{34}H_{28}N_{10}$
Formula weight	576.66
Temperature	120 K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P$\bar{1}$
Unit cell dimensions	$a = 4.2037$ (3) Å $b = 9.5547$ (6) Å $c = 17.3998$ (13) Å $\alpha = 92.811(4)°$ $\beta = 90.040$ (4)° $\gamma = 92.898$ (4)°
V	697.13 (8) Å^3
Z	1
Density (calculated)	1.374 g/cm^3
$F(000)$	302
Crystal	Plate, colourless
Crystal size (mm)	$0.2 \times 0.1 \times 0.01$
θ range for data collection	2.9-27.5°
Index ranges	$-5 \leq h \leq 5$ $-12 \leq k \leq 12$ $-22 \leq l \leq 22$
R indices (all data)	$R_1 = 0.130$, $wR_2 = 0.376$
Final R indices $[I > 2\sigma(I)]$	$R_{int} = 0.129$, $wR_2 = 0.376$
GOF on F^2	1.06
T_{min} and T_{max}	0.983 and 0.999
μ (mm^{-1})	0.087
Largest difference in peak and hole	0.50 and -0.49 eÅ^{-3}
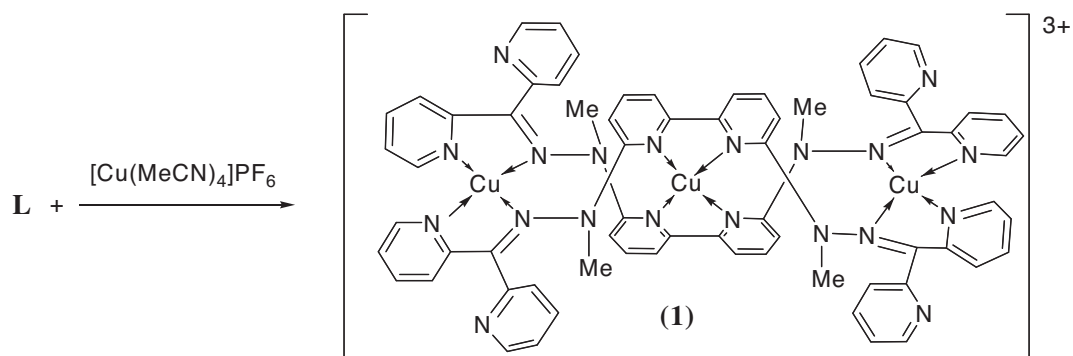
Scheme 2

Crystal structure of L

The structure is centrosymmetric with an inversion centre between atoms C16 and C16i in the molecule (i = -x+1,-y,-z+1). The bond distances and angles (Table 2) are similar to those reported for di-2-pyridylketone-2-aminobenzoylhydrazone, di-2-pyridylketone-2-pyridyl hydrazone, and other related structures.[16] For example, the C–N–N=C hydrazone moiety has bond lengths of 1.395, 1.368, and 1.290 Å; 1.365, 1.368, and 1.294 Å; and 1.388, 1.348, and 1.294 Å for **L**, di-2-pyridylketone-2-aminobenzoylhydrazone, and di-2-pyridyl ketone *p*-nitrophenylhydrazone, respectively.

Table 2. Selected bond lengths (Å) and angles (°) for (**L**).

C16- C16^i	1.491 (10)	C11-N4	1.334 (7)
C16- C15	1.405 (8)	C16^i-C16- C15	117.2 (6)
C15- C14	1.395 (8)	C15-C16-N5	122.3 (5)
C13- C12	1.412 (8)	N5-C12-C13	122.5 (5)
N5- C12	1.339 (7)	C12-N1-N2	115.0 (4)
N5- C16	1.338 (7)	C12-N1-C17	120.2 (4)
C12-N1	1.395 (7)	N1-N2-C1	123.0 (5)
N1- C17	1.471 (7)	C2-C1-N2	113.0 (5)
N1-N2	1.368 (6)	C2-C1-C7	116.4 (5)
N2-C1	1.290 (7)	C7-N4-C11	117.0 (5)
C1-C7	1.502 (7)	N4-C7-C8	122.6 (5)
C1-C2	1.503 (7)	C11-C10-C9	118.6 (5)
C2-N3	1.335 (7)	C2-N3-C6	118.0 (5)
N3-C6	1.354 (7)	N3-C2-C3	122.0 (5)
C7-N4	1.347 (7)	C3-C4-C5	118.5 (5)

^{i} = -x+1,-y,-z+1

Table 3. Hydrogen bond geometries in the crystal structure of **L**.

Hydrogen bond	D···A length/Å	D–H·A angle/°
C(8)–H(8)···N(3)	3.440(7)	149.2(4)
C(17)–H(17B)···N(4)	2.904(7)	106.3(4)
C(17)–H(17C)···N(4)	3.357(7)	144.2(4)

The hydrazone linkages and the bipyridine rings are planar; however, the dipyridyl ketone pyridine rings are twisted out of plane by 52.90 (3)° and 56.32(3)° (for C2 > C6, N3 and C7 > C11, N4 respectively). The di-pyridyl hydrazone units adopt a *transoid* configuration to minimise unfavourable electronic interactions between the lone pairs of the pyridine nitrogen and the hydrazone nitrogen atoms as shown in Figure 1.

A weak C–H···N interaction (C4–H4···N5) of 2.635(6) Å causes the formation of a ribbon motif that propagates in an offset fashion along the *b* axis as depicted in Figure 2. These ribbons stack in a zig-zag manner and layer on top of each other. Adjacent ribbons form a sheet, with a separation between discrete units

of 2.730(5) Å. The contact distances between potential interacting functions in the molecule are rather long and therefore it is assumed that the structure is formed by the most efficient packing motif and minimisation of electrostatic interactions.
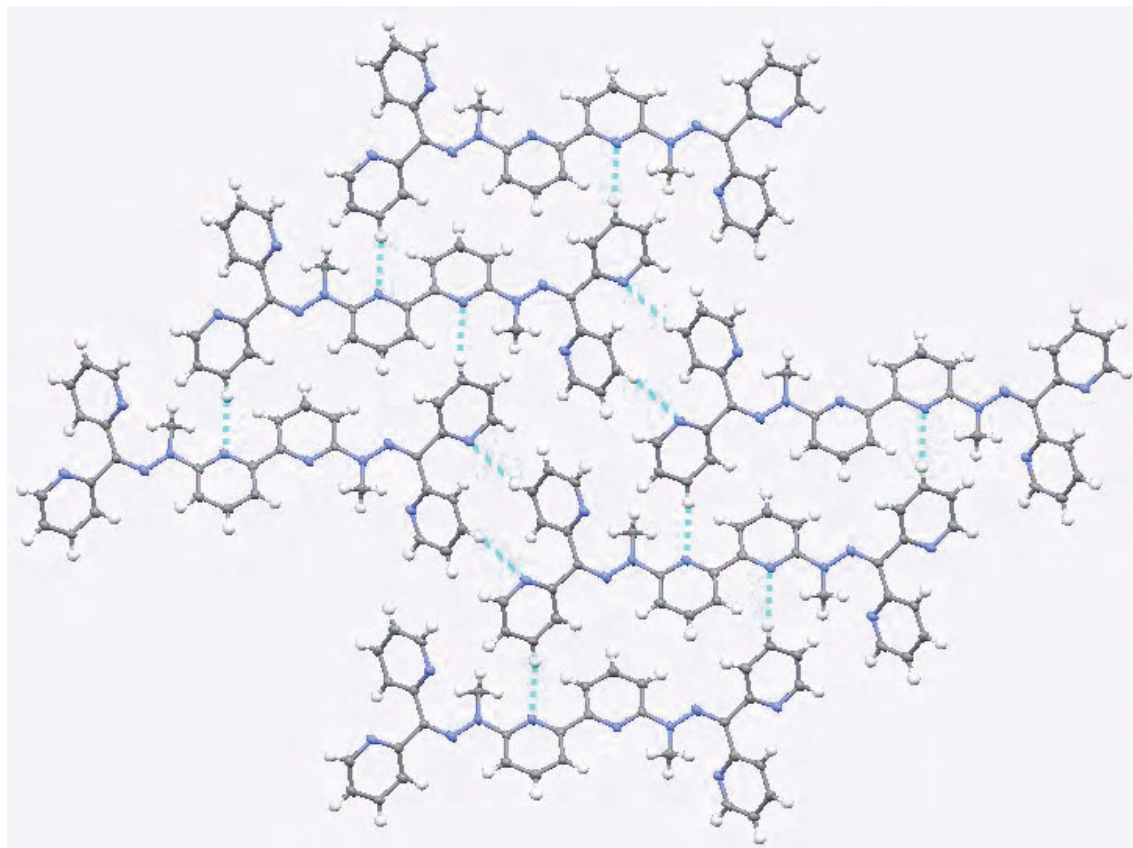

Figure 2. Crystal packing of **L** as projected on a-axis showing the intermolecular contacts between the adjacent units.

Synthesis and characterisation of 1

The synthesis of the complex is depicted in Scheme 2. Several attempts to obtain a single crystal by recrystallisation in a variety of solvent systems have met with failure. However, the ESI-MS analysis is consistent with the formulation of $\{[Cu_3 L_2](PF_6)_3 \cdot 3H_2O\}$. The peak at m/z 496 corresponds to the cationic fragment $[Cu_3 (L)_2 PF_6]^{3+}$. The very small peak (1.3%) at m/z 745.15 is attributable to doubly charged ion $[Cu_3 L_2 (PF_6)]^{2+}$. In the ionisation processes, the tri-cationic complex is stable enough to yield the parent peak. All these assignments are ensured by good agreement between the observed and calculated isotopic distributions. This also shows that the complex **1** is very stable in solution and ESI-MS condition. The counter ion plays a role in the degree of ionisation, and can interact with the metal centre.[17] The secondary peak observed at m/z 465.7 is attributable to a cationic fragment of $[Cu_3 (L)_2 (H_2O)_3]^{3+}$ in solution, and is identical with the calculated value at m/z 466.79 for the triply charged ion. The ligand can act as a tris(binucleating) ligand (Scheme 2) by coordinating to the metal centre through 1 N atom of the dipyridyl ketone and the hydrazone spacers at 6,6'-positions of the bipyridine and through 2 N atoms of the main bipyridine body. As shown in Figure 1,

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **L**.

	x	y	z	U(eq)
C(1)	6194(13)	4432(5)	2343(3)	23(1)
C(2)	6912(14)	5981(5)	2291(3)	25(1)
C(3)	6092(14)	6911(6)	2887(4)	30(1)
C(4)	6826(14)	8348(5)	2827(3)	27(1)
C(5)	8332(13)	8780(6)	2185(3)	27(1)
C(6)	9117(14)	7804(6)	1615(4)	28(1)
C(7)	5693(12)	3599(5)	1595(3)	23(1)
C(8)	3933(13)	4116(5)	1000(3)	26(1)
C(9)	3624(14)	3357(6)	307(3)	28(1)
C(10)	5157(14)	2104(6)	222(3)	29(1)
C(11)	6859(13)	1660(5)	846(4)	28(1)
C(12)	6172(13)	2358(5)	3973(3)	22(1)
C(13)	8283(14)	3228(6)	4439(3)	28(1)
C(14)	9015(14)	2770(6)	5148(4)	31(1)
C(15)	7771(14)	1489(5)	5396(3)	26(1)
C(16)	5727(12)	687(5)	4888(3)	23(1)
C(17)	2913(13)	1820(6)	2794(3)	25(1)
N(1)	5305(11)	2705(4)	3235(3)	24(1)
N(2)	6274(11)	4029(4)	3040(3)	25(1)
N(3)	8396(11)	6414(4)	1660(3)	25(1)
N(4)	7171(11)	2381(5)	1520(3)	26(1)
N(5)	4990(10)	1112(4)	4191(3)	23(1)

the ligand is sterically hindered and the di-2-pyrdiyl fragments mutually twisted such that there is a substantial dihedral angle between them and a tetrahedrally distorted geometry is therefore imposed on the metal, as has been observed in the case of similar tetrahedrally enforcing ligand strands that generate a double helix with Cu(I) and Ag(I) ions.[18−20] In addition, the reactions of the 2- or 3-binucleating ligands with cations favouring tetrahedral coordination leading to double-stranded helical complexes are very well established.[21] Thus, ES mass spectrometry can be a good spectrophotometric technique to study the stability and the behaviours of metal complexes in solution. ESI-MS measurements have been widely used to identify the species in solution as a very soft technique reducing demetallation processes in mass condition.[4] Since the copper(I) ion adopts a tetrahedral geometry, the ligand twists around the single bonds between the pyridine rings and the flexible hydrazone spacers due to N–N bonds to most favourably afford a tri-nuclear double-stranded helical copper(I) complex. One should bear in mind that ESI-MS gives only the molecular entity of the species in the solution; thus, in order to study the self-assembly processes and to be ascertain about the double-helical structure found in the solid state and in solution, the classical UV-Vis spectrophotometric titration experiment and single crystal X-ray analysis have to be performed.

Table 5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **L**.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	28(3)	18(3)	20(3)	-2(2)	-4(2)	2(2)
C(2)	34(3)	18(3)	24(3)	3(2)	-8(2)	4(2)
C(3)	34(3)	23(3)	31(3)	1(2)	-5(3)	1(2)
C(4)	35(3)	18(3)	29(3)	-4(2)	-5(2)	3(2)
C(5)	31(3)	17(3)	33(3)	2(2)	-5(2)	-1(2)
C(6)	32(3)	21(3)	32(3)	3(2)	-3(2)	0(2)
C(7)	20(2)	23(3)	24(3)	3(2)	-3(2)	-1(2)
C(8)	30(3)	17(3)	30(3)	3(2)	-1(2)	3(2)
C(9)	35(3)	27(3)	22(3)	2(2)	-9(2)	-3(2)
C(10)	32(3)	24(3)	29(3)	-3(2)	-3(2)	-3(2)
C(11)	29(3)	15(2)	39(3)	-4(2)	-2(2)	1(2)
C(12)	29(3)	13(2)	26(3)	2(2)	0(2)	5(2)
C(13)	35(3)	19(3)	30(3)	-2(2)	-7(3)	3(2)
C(14)	37(3)	24(3)	30(3)	-1(2)	-7(3)	-2(2)
C(15)	36(3)	18(3)	23(3)	3(2)	-2(2)	2(2)
C(16)	24(3)	21(3)	23(3)	-1(2)	1(2)	5(2)
C(17)	25(3)	23(3)	26(3)	5(2)	-7(2)	-1(2)
N(1)	32(3)	17(2)	23(2)	5(2)	-5(2)	-1(2)
N(2)	25(2)	16(2)	34(3)	3(2)	-5(2)	1(2)
N(3)	27(2)	18(2)	31(3)	0(2)	-3(2)	2(2)
N(4)	30(2)	18(2)	29(3)	0(2)	-6(2)	2(2)
N(5)	25(2)	16(2)	27(3)	3(2)	-2(2)	2(2)

The UV-Vis spectrum of **1** in DMF displays 2 absorption maxima at 269 and 348 nm, which correspond mainly to a $\pi-\pi$ transition characteristic of the conjugate C=N groups (hydrazones) and $\pi-\pi^*$ transitions of the pyridine rings[10] or an intra-ligand transition and MLCT band, respectively.[22] Upon coordination to copper(I), the colour became red-brown, indicating the formation of tetrahedral complex.

The ATR-IR spectrum of **1** agrees well with the structure. The crystal lattice water absorbs at 3500-3200 cm^{-1} (antisymmetric and symmetric O–H stretching modes) and at 1608 cm^{-1} (H–O–H bending mode).[23] The absorption band arising from aromatic C–H stretching vibration is observed at 3113 cm^{-1} with asymmetric CH_3 at 2956 and 2916 cm^{-1} and symmetric stretching mode at 2850 cm^{-1}.[10,24] The absorption bands between 1650 and 1570 cm^{-1}, and 1570 and 1433 cm^{-1}, respectively, correspond to the stretching vibration of the C=N hydrazone bond and to the pyridine-ring stretching vibrations (skeletal bands). The strong absorption band at 1070 cm^{-1} is assigned to in-plane CH bending vibration, and also arises due to in bridging mode of the N–N bond,[25] because, if the hydrazine is attached to a conjugate system, then ν(N–N) increases up to 980-1000 cm^{-1}.[25] The stretching vibration of PF_6 is observed at 840 cm^{-1}. The Cu–N stretching vibrations fall beyond of the measurement scale of the instruments.[26]

The ^{1}H-NMR spectrum of **1** is not very well resolved. This may be due to partial oxidation of the metal centre in the solution to give a paramagnetic d^9 copper(II) ion. However, the integration of the peaks in the aromatic and the aliphatic regions is easily recognisable. In the aromatic region, a very broad multiplet at 8.5-6.5 ppm with the integration of 22 protons corresponds to 4 pyridine rings from di-2-pyridyl ketone moieties and 1 bipyridine main body, and a very sharp singlet at 3.4 ppm in the aliphatic region corresponds to 6 protons of N-CH$_3$ on the hydrazone linkages.

Acknowledgements

Supplementary data

CCDC 763332 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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