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Synthesis and crystal structures of copper(II) and silver(I) complexes of a semi-rigid bipyrazolyl ligand

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Abstract A semi-rigid bipyrazolyl ligand, namely 5-*tert*-butyl-1,3-bis[(3′,5′-diethyl-1*H*-pyrazol-4′-yl) methylene]benzene, and its Ag(I) and Cu(II) complexes have been prepared and structurally characterized. X-ray analysis demonstrates that the Ag(I) complex is based on a dinuclear molecular rectangle, while the Cu(II) complex displays a mono-strand helical structure. Two different conformations, namely *cis*,*cis* and *cis*,*trans* have been observed for this bipyrazolyl ligand.

Introduction

Pyrazole is a widely used N-donating ligand in coordination chemistry. 1*H*-Pyrazole usually acts as a monodentate ligand; its deprotonated form, namely pyrazolido ion, can behave in exo-bidentate or multidentate bridging fashions with typical M···M distances of *ca* 3.3 Å [1–4]. Bipyrazolyl ligands, in which two pyrazolyl units are linked via covalent bonds, are expected to exhibit more versatile coordination patterns, and therefore be more useful in construction of complicated supramolecular architectures. It has been shown that functionalization at the pyrazolyl N^1 position results in behavior somewhat like a pyridyl group, since only one of the two N atoms of pyrazole is available for coordination in this case [5]. As might be anticipated, functionalization at the C^4 position of a pyrazole imparts less influence on its coordination behavior. Recent years have seen several reports involving metal complexes of the C^4-linked bipyrazolyl ligands. 3,3′-5,5′-Tetramethyl-4,4′-bipyrazole can act as a neutral μ_2-bridging ligand to form a wide variety of polymeric structures with transition metal ions. The silver(I) and copper(I) complexes of the deprotonated bipyrazolyl ligand exhibit rather complicated 3D metal-organic framework (MOF) structures, featuring a triangular $[M(pz)]_3$ subunit (M = Cu(I) or Ag(I); pz = pyrazolide) [6–10]. Some bipyrazolide-bridged metallomacrocycles with diplatinum or dipalladium corners were reported recently [11, 12]. We noticed that so far, only rigid bipyrazolyl ligands have been used in preparation of metal complexes, although flexible or semi-rigid bipyrazoles have been known for some time [13]. As pointed out by Steel, introducing some flexibility to the ligands can lead to structural motifs and topologies, which may be unavailable by using more rigid ligands [14]. To address this issue, we report here the synthesis and crystal structures of a semi-rigid C^4-linked bipyrazolyl ligand (H_2L, Scheme 1) and its Cu(II) and Ag(I) complexes.

Results and discussion

The bipyraozlyl ligand, 5-*tert*-butyl-1,3-bis[(3′,5′-diethyl-1*H*-pyrazol-4′-yl) methylene]benzene H_2L, was prepared according to the synthetic route shown in Scheme 1. H_2L crystallizes in space group *C2/c*. In the asymmetric unit, only half of the molecule is independent and it is related with the other half by a twofold axis. As depicted in Fig. 1a, this compound adopts a twisted *cis*,*cis*-conformation (the assignment of *cis* or *trans* conformation of each pyrazolyl ring is made by using the H atoms attached to the phenyl C^2 atom as reference, Scheme 2). The two pyrazolyl rings in each molecule are placed with a dihedral angle of 25.9°. Furthermore, the two pyrazolyl rings are skewed in order to diminish the steric repulsion caused by the 3,5-ethyl groups of the pyrazolyl ring, which can be described by the torsion

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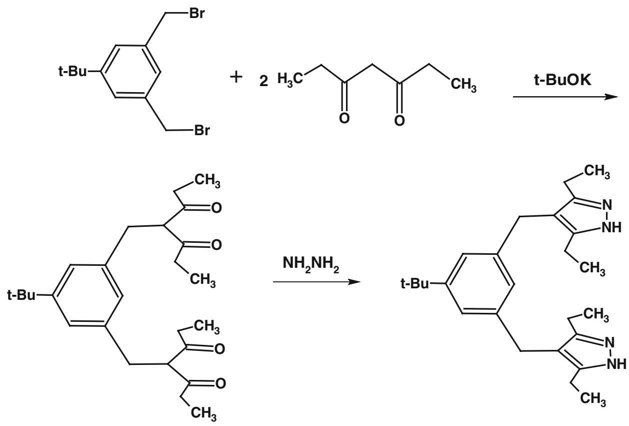


Scheme 1 Synthetic route for H_2L

angle defined by the two pyrazolyl C^4 atoms and two methylene C atoms. For H_2L, this angle (C4–C8–C8a–C4a) is 131.40°.

In the crystal of H_2L, this compound exhibits a stair-like chain structure, involving N_{pz}–H···N_{pz} and N_{pz}–H···O_w H-bonds (N2···N2^i = 2.922(4) Å, N1···O1w^{ii} = 2.827(3) Å; symmetry codes: (1) $-x + 1, y, -z + 5/2$; (2) $x + 1/2, y - 1/2, z + 1$), shown in Fig. 1b. Due to the disorder of the H atom bound to the N atom of the pyrazolyl ring, the occupancy factor for these H atoms is 0.5. Therefore, the H-bonding of N_{pz}–H···Ow···H–N_{pz} is only equivalent to one normal N_{pz}–H···Ow bond.

The complex $[Ag_2(H_2L)_2](NO_3)_2$ adopts a discrete rectangular structure. As shown in Fig. 2a and b, the Ag(I) atom is linear two-coordinate with the two coordinated pyrazolyl rings in a *trans*-fashion (Scheme 3). For bis(pyrazole) silver(I) complexes, all the three possible arrangements in Scheme 3 have been observed [15–18]. Each H_2L ligand, in *cis*,*cis*-conformation (Scheme 2), binds to two Ag(I) atoms using its pyrazolyl N^2 atoms. The intramolecular Ag···Ag distance is 5.825(3) Å. On the other hand, the intermolecular Ag···Ag distance is 3.192(3) Å, less than the sum of the van der Waals radii for the Ag atoms (3.44 Å). If this weak interaction is taken into account, the disilver complex exhibits a 1D chain structure running along the *a*-axis and linking the dimers through argentophilicity (Fig. 2c). The two pyrazolyl rings of each H_2L ligand in $[Ag_2(H_2L)_2](NO_3)_2$ are nearly parallel, with dihedral angles being 4.9 and 6.2°. The torsion angles are 36.17(57) and 37.60(64)° for C4–C8–C26–C22 and C30–C34–C52–C48, respectively, which are much less than that in free H_2L (131.40°). A few similar rectangular dimetallomacrocycles based on various metals and ligands are also known in the literature [19–23].

The complex $[Cu(H_2L)Cl_2]_n$ exhibits a chiral chain structure. The Cu(II) atom is tetrahedrally coordinated by two Cl^- ions and two pyrazolyl N^2 atoms from two adjacent ligands (Fig. 3a). The ligand adopts a *cis*,*trans*-conformation and acts as a bridge linking two Cu(II) atoms,

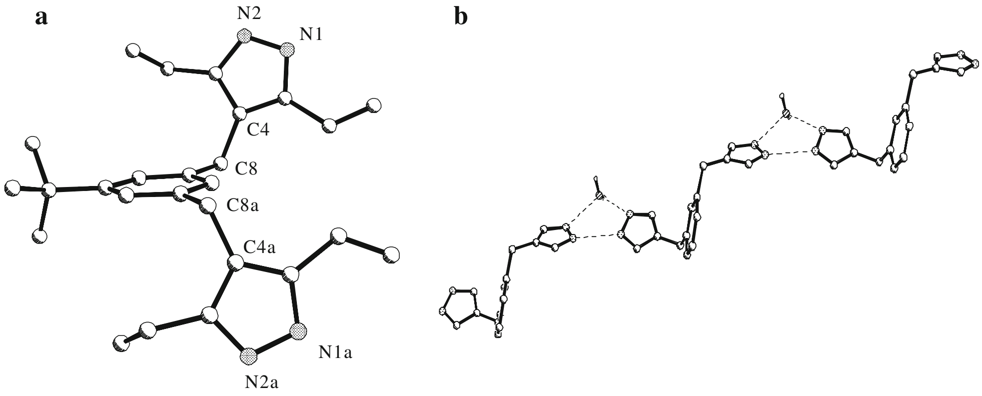
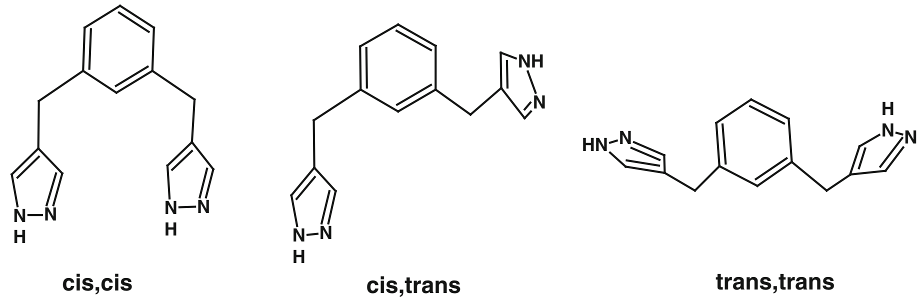


Fig. 1 **a** Ball-and-stick diagram of the bipyrazole H_2L. Hydrogen atoms are not shown for clarity. Symmetry codes: (a) $-x, y, -z + 3/2$. **b** A stair-like chain formed by linking the bipyrazole via hydrogen bonds (*dashed lines*). The t-butyl and ethyl groups have been omitted for clarity. Only H atoms of water are shown



Scheme 2 Three possible conformations of bipyrazole H_2L

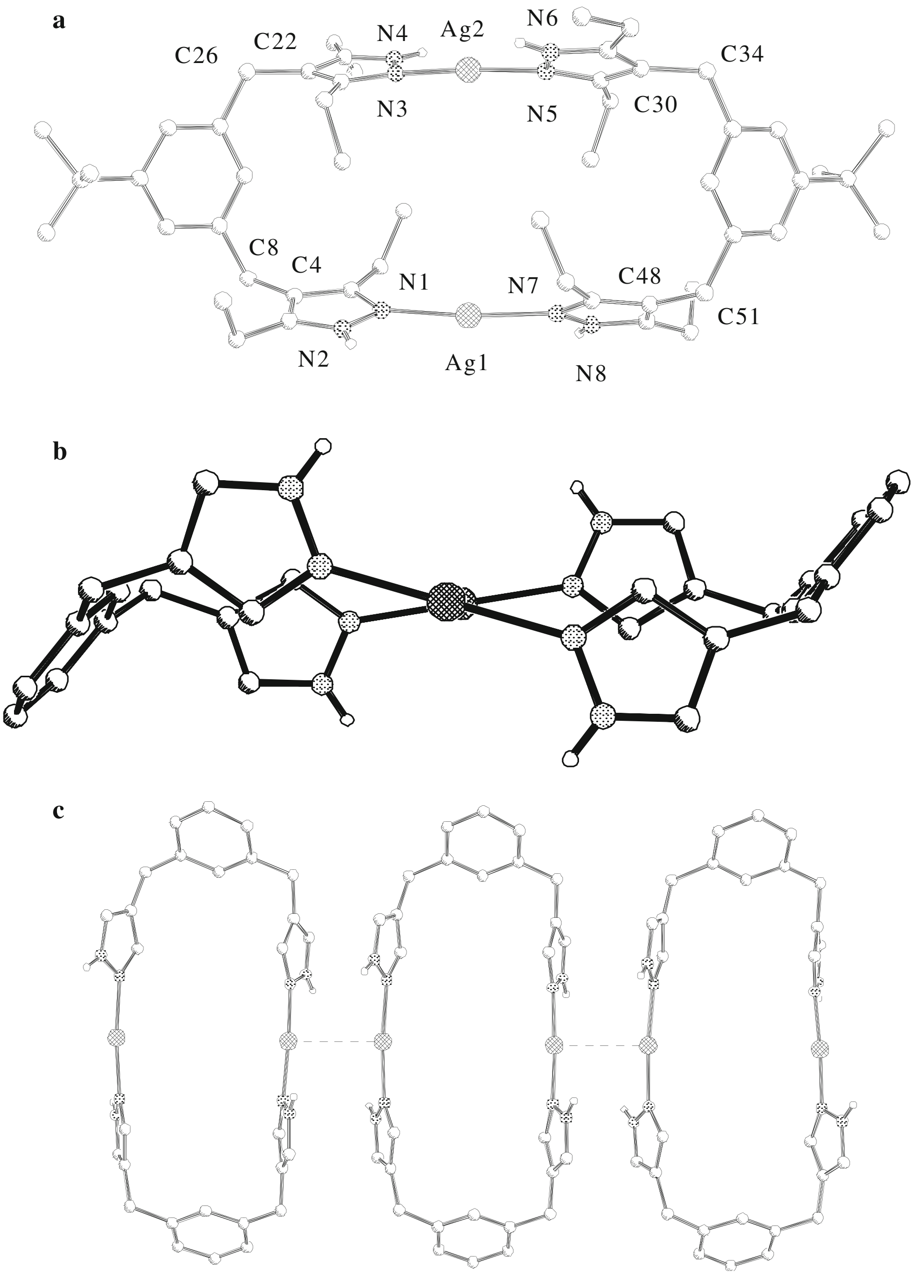
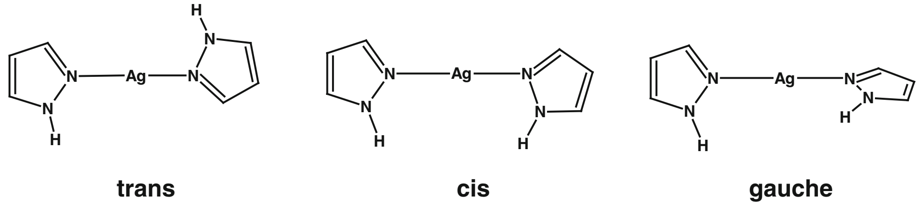


Fig. 2 **a** Ball-and-stick diagram of dimeric $[Ag_2(H_2L)_2](NO_3)_2$ with atom labels, showing the coordination environment around Ag and the *cis,cis*-conformation of the μ_2-bridging ligand. Only N-bound H atoms are shown. Selected distances (Å) and angles (°): Ag1–N7 = 2.100(5), Ag1–N1 = 2.105(6), Ag2–N3 = 2.090(5), Ag2–N5 = 2.104(5); N7–Ag1–N1 = 174.9(2), N3–Ag2–N5 = 176.8(2). **b** Top view of $[Ag_2(H_2L)_2](NO_3)_2$, noting that the two pyrazolyl rings of the ligand in the Ag complex are much less twisted than in free H_2L and the two pyrazolyl rings are *trans* about each Ag atom. The t-butyl and ethyl groups of the ligands have been omitted for clarity. **c** The dinuclear silver complexes are joined into a chain running along *a*-axis via argentophilic interactions. Ag1···Ag2^i = 3.1924(11) Å, symmetry code: (i) $x-1$, y, z



Scheme 3 Various placements of pyrazoles around linear two-coordinate Ag-atom

forming 2_1 helices along the *b*-axis with a pitch of 9.433 Å (Scheme 2 and Fig. 3b). Within the chain, N_{pz}–H···Cl H-bonds are formed, which may further consolidate the observed chiral chain structure. As shown in Fig. 2b, each helix is linked, via interstrand H-bonds, with two neighboring helices of opposite handedness to form two-dimensional nets. As a result of this kind of arrangement, the crystal as a whole is centrosymmetric. Other metal–organic

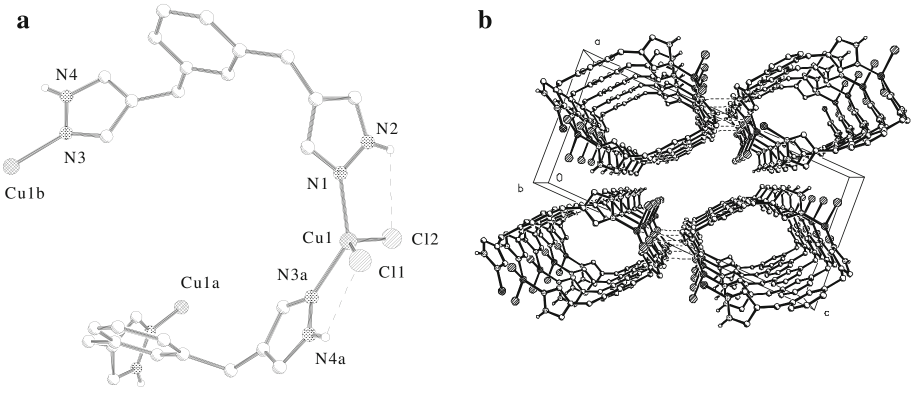


Fig. 3 **a** Ball-and-stick diagram of a fragment of 1D $[Cu(H_2L)Cl_2]_n$ with atom labels, showing the coordination environment around Cu1, the *cis,trans*-conformation of the μ_2-bridging ligand and the intra-strand hydrogen bonds (*dashed line*). The t-butyl and ethyl groups of the ligands have been omitted for clarity. Only N-bound H atoms are shown. Selected distances (Å) and angles (°): Cu1–N1 = 1.9621(17), Cu1–N3a = 1.9857(16), Cu1–Cl2 = 2.2322(7), Cu1–Cl1 = 2.2581(7), N4a···Cl1 = 3.0408(17), N2···Cl2 = 3.2116(18); N1–Cu1–N3a = 139.67(7), N1–Cu1–Cl2 = 96.51(5), N3a–Cu1–Cl2 = 100.14(5), N1–Cu1–Cl1 = 98.88(5), N3a–Cu1–Cl1 = 94.02(6), Cl2–Cu1–Cl1 = 136.17(3). Symmetry codes: (**a**) $-x + 3/2$, $y + 1/2$, $-z + 1/2$; (**b**) $-x + 3/2$, $y - 1/2$, $-z + 1/2$. **b** Packing diagram of $[Cu(H_2L)Cl_2]_n$, viewed along the *b*-axis. The dashed lines here represent the inter-strand hydrogen bonds, which join the neighboring helix of opposite handedness. N2···Cl1c = 3.4494(18) Å, symmetry code: (**c**) $-x + 1$, $-y + 2$, $-z$

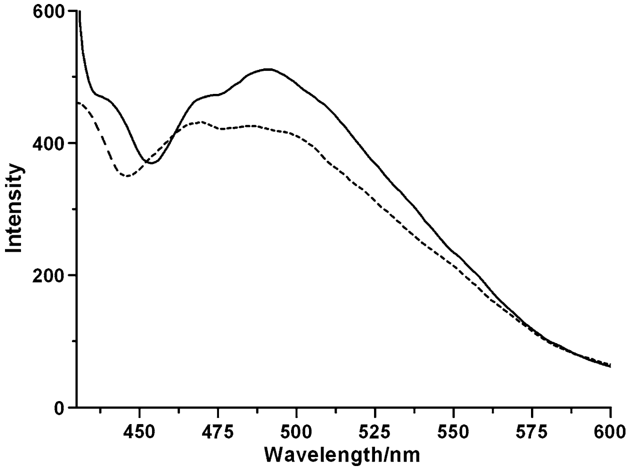


Fig. 4 Emission spectra of H_2L (*dashed line*) and $[Ag_2(H_2L)_2](NO_3)_2$ (*solid line*) in the solid state at room temperature. The excitation wavelength is 410 nm

mono-strand chiral structures have been documented in recent years [24–26].

Under UV irradiation (410 nm) at room temperature, the bipyrazolyl ligand and $[Ag_2(H_2L)_2](NO_3)_2$ give off bright green light. The emission spectra of both exhibit similar profiles with maximum emission in the range of 460–500 nm (Fig. 4). We infer that the emission of this Ag complex is probably ligand-based, with slight modification by Ag(I).

Conclusion

As far as we know, this paper is the first one dealing with metal complexes with a *semi-rigid* C^4-linked bipyrazolyl ligand. Introducing methylene group to the biprazolyl ligand provides much flexibility for metal–ligand interactions. We already observed two conformations (*cis,cis* and *cis,trans*) of the ligand upon binding to metals; a third conformation (*trans,trans*) awaits to be revealed. In the *cis,cis*-conformation, the twist of two pyrazolyl rings varies from 131.40° in free H_2L to 36.17(57) and 37.60(64)° in $[Ag_2(H_2L)_2](NO_3)_2$. The relative orientation of the two pyrazolyl rings of the ligand is the main factor to determine the structures of its metal complexes. It is expected that more complicated and interesting metal–organic structures can be formed with the deprotonated bipyrazolyl ligand, which is the subject of our future work.

Experimental section

The CHN microanalyses were carried out with an ELEMENTAR vario EL elemental analyzer. IR spectra (KBr pellets) were recorded on a Niclolet Impact 420 FT-IR spectrometer. ^1H NMR spectra were recorded on a Bruker DPX-400 spectrometer.

Preparation of 5-*tert*-butyl-1,3-bis[(3′,5′-diethyl-1*H*-pyrazol-4′-yl)methylene]benzene

Potassium (0.66 g, 17 mmol) was dissolved in *tert*-butyl alcohol (80 mL). To the solution, heptane-3,5-dione (2.5 g, 19.5 mmol), 5-*tert*-butyl-1,3-bis(bromomethyl)benzene (2.71 g, 8.5 mmol) and KI (0.34 g) were added successively. The mixture was stirred under nitrogen for 3 days and then filtered. Workup proceeded by distilling off the *tert*-butyl alcohol, taking up the residue in CH_2Cl_2, washing with

Table 1 Crystallographic data

	H_2L	$[Ag_2(H_2L)_2](NO_3)_2$	$[Cu(H_2L)Cl_2]_n$
Formula	$C_{26}H_{38}N_4{\cdot}H_2O$	$C_{52}H_{76}Ag_2N_{10}O_6$	$C_{26}H_{38}Cl_2CuN_4$
Mr	424.62	1152.97	541.04
Crystal size (mm^3)	0.30 × 0.19 × 0.12	0.49 × 0.36 × 0.23	0.44 × 0.38 × 0.18
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/n$
a (Å)	13.766(3)	9.0157(18)	11.646(2)
b (Å)	23.571(5)	13.192(3)	9.4326(19)
c (Å)	9.3333(19)	23.786(5)	25.249(5)
α (°)		78.87(3)	
β (°)	118.01(3)	89.23(3)	93.76(3)
γ (°)		88.64(3)	
V (Å^3)	2673.7(9)	2775.0(10)	2767.8(10)
Z	4	2	4
T (K)	298	298	298
D_{calcd} (Mg/m^3)	1.055	1.380	1.298
μ (mm^{-1})	0.065	0.761	1.003
F(000) (e)	928	1200	1140
hkl range	$-18 \le h \le 18$, $-31 \le k \le 30$, $-12 \le l \le 12$	$-10 \le h \le 10$, $-15 \le k \le 15$, $-28 \le l \le 28$	$-14 \le h \le 15$, $-12 \le k \le 12$, $-33 \le l \le 27$
Refl. collected	11756	18829	16619
Refl. unique	3364 ($R_{int} = 0.0548$)	9491($R_{int} = 0.0518$)	6707 ($R_{int} = 0.0428$)
Param. refined	182	645	329
Restraints	1	0	6
Final R indices	$R_1 = 0.0829$	$R_1 = 0.0811$	$R_1 = 0.0455$
$[I > 2\sigma(I)]$	$wR_2 = 0.2314$	$wR_2 = 0.2201$	$wR_2 = 0.1007$
GoF (F^2)	0.954	1.010	1.024
$\Delta\rho_{fin}$ (max,min), e Å^{-3}	0.447, −0.165	3.681, −0.887	0.536, −0.385

water, drying over $MgSO_4$, and evaporating to dryness. The obtained brown syrup was dissolved in MeOH (50 mL) and $N_2H_4{\cdot}H_2O$ (0.85 g, 17 mmol) was added. The mixture was stirred at 50 °C for 12 h and then methanol was distilled off to give a yellow liquid, which solidified upon cooling to room temperature. The crude product was recrystallized from MeOH–H_2O to afford colorless prismatic crystals of H_2L. Yield: 50%.

$C_{26}H_{38}N_4$ (406.61) Found C 76.6, H 9.7, N, 13.7; Calcd. C 76.8, H 9.4, N 13.8. IR (KBr pellet, cm^{-1}): 3430 w, 3226 m, 3129 m, 2966 s, 1712 w, 1597 m, 1474 m, 1390 w, 1045 m, 961 w, 840 w, 700 w. ^{1}HNMR (400 MHz, $CDCl_3$): $\delta = 1.15$ (t, 12H, CH_3–), 1.32 (s, 9H, ^{t}Bu), 2.42 (q, 8H, –CH_2–), 3.70 (s, 4H, Ph–CH_2–pz), 5.81 (s, 1H, Ph–H^2), 7.06 (s, 2H, Ph–H^4, H^6) ppm.

Preparation of $[Ag_2(H_2L)_2](NO_3)_2$

A solution of H_2L (0.03 mmol, 12.2 mg) in ethanol (1 mL) was layered on the surface of an aqueous solution of $AgNO_3$ (0.03 mmol, 5.1 mg) in a test tube. Colorless crystals were obtained in 60% yield within several days.

$C_{52}H_{76}N_{10}Ag_2O_6$ (1152.97) Found C 54.1, H 6.7, N 12.2; Calcd. C 54.2, H 6.7, N 12.2. IR(KBr pellet,cm^{-1}): 3445 m, 3200 s, 2966 s, 1715w, 1598 m, 1520 m, 1384 s, 1063 m, 961 w, 933 w, 763 w, 708 w. ^{1}HNMR (400 MHz, $CDCl_3$): $\delta = 1.14$ (m, 12H, CH_3–), 1.41 (s, 9H, tBu), 2.48 (m, 8H, –CH_2–), 3.75 (s, 4H, Ph–CH_2–pz), 5.63 (s, 1H, Ph–H^2), 7.20(s, 2H, Ph–H^4,H^6) ppm.

Preparation of $[Cu(H_2L)Cl_2]_n$

H_2L (8.1 mg, 0.02 mmol) and $CuCl_2$ (2.7 mg, 0.02 mmol) were mixed in ethanol (5 mL). The resulted solution was allowed to evaporate for 1 week to afford brown red crystals in 53% yield.

$C_{26}H_{38}N_4CuCl_2$ (541.04) Found C 57.7, H 7.1, N 10.4; Calcd. C 57.7, H 7.1, N 10.4. IR(KBr pellet, cm^{-1}): 3455 m, 3318 s, 2964 s, 1648 w, 1599 m, 1516 m, 1440 m, 1174 m, 1055 m, 687 m, 614 m.

X-ray crystallography

Diffraction intensities were collected on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo-Kα radiation (0.71073 Å). Absorption corrections were applied using the multiscan program [27]. The structures were solved by direct methods and refined by least squares techniques using the SHELXS-97 and SHELXL-97 programs [28]. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were generated geometrically. Since the disordered tert-butyl group of H_2L is located on a two-fold axis, three half-occupied C-atoms, located from Fourier map, were used to model it. The H atoms of the NH group could not be definitely assigned, so a half-occupied H atom was allowed to ride on each N atom in H_2L. The crystallographic data are summarized in Table 1.

CCDC 758937–758939 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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