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The first structurally characterized 3,4′-bipyridine copper(I) coordination polymer with an approximately rectangular molecular box

Hoong-Kun Fun,*[a] S. Shanmuga Sundara Raj,[a] Ren-Gen Xiong,*[b] Jing-Lin Zuo,[b] Zhi Yu,[b] Xiao-Lei Zhu[b] and Xiao-Zeng You[b]

[a] *X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia. E-mail: hkfun@usm.my*

[b] *Coordination chemistry Institute, State key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P. R. China. E-mail: xyz@netra.nju.edu.cn*

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The first metal coordination polymer containing 3,4′-bipyridine (3,4′-bpy) was prepared by the hydrothermal treatment of $Cu(NO_3)_2 \cdot 2.5H_2O$, Me_3SnBr and 3,4′-bpy and its crystal structure shows a novel infinite double chain composed of two 3,4′-bpy and Br as well as copper(I) ions with an approximately rectangular molecular box of 4.0 × 10.68 Å.

4,4′-Bipyridine (4,4′-bpy) metal coordination chemistry has received extensive attention mainly due to the ligand being used to bridge metal centers to form one-, two-, and three-dimensionally connected polymer networks.[1–4] Furthermore, supramolecular chemistry and self-assembly with 4,4′-bpy and its derivatives are at the frontiers of the molecular sciences, as demonstrated by the intense interest and the near exponential growth of publications in this area in just the last decade.[5] However, novel structural types of metal coordination compounds using 4,4′-bpy as a linear spacer are limited owing to its symmetry and linearity.

More recently, a variety of attempts to synthesize 4,4′-bpy derivatives, such as 3,3′-bipyridine and 2,4′-bipyridine, the former of which is not commercially available, were made and their metal coordination chemistry also appears in the current literature, showing that unprecedented structural types were observed, in comparison with the 4,4′-bpy.[6,7] The use of 2,2′-bipyridine as a bidentate chelating ligand has also been extensively investigated in coordination chemistry.[7c] A search of the CCDC database gave no hits for any metal complex containing 3,4′-bipyridine or 2,3′-bipyridine ligands. Consequently, it is of interest to study the bipyridine system's coordination chemistry. Herein, we report the synthesis, structure and fluorescence of $[(3,4'\text{-bpy})(Br)Cu^{I}]_n$ **1** which represents the first example of a metal coordination polymer containing the 3,4′-bpy ligand. Complex **1**† was prepared by hydrothermal treatment of $Cu(NO_3)_2 \cdot 2.5H_2O$, Me_3SnBr and 3,4′-bpy for one day at 110 °C. Perfect one-phase yellow-orange rectangular crystals were harvested. There is no broad absorption peak at *ca.* 1100 cm^{-1} in the IR spectrum of **1**, suggesting that the nitrate group does not persist in **1**

Single crystal X-ray diffraction analysis‡ indicates that the crystal structure of **1** (Fig. 1) contains an unprecedented double chain involving a twenty-membered ring with an approximately rectangular molecular box of 4.0 × 10.68 Å (a space-filling diagram is depicted in Fig. 2) which consists of two 3,4′-bpy, Br atoms as well as copper(I) ions, unlike Cu–quinoxaline–Cu chains in which Cl atoms act as one of the two bridging ligands.[8] To the best of our knowledge, **1** is the first example of a double chain structure with a bipyridine system in MX_2 (X = halide) complexes. The structure is formed mainly due to the bent angle (about 120°) between the two nitrogen atoms of the 3 and 4′ positions (the dihedral angle between the two pyridine rings is about 34° after the formation of **1**). Furthermore, the polymer is composed of $Cu_2(\mu\text{-}Br)_2(3,4'\text{-bpy})_2$ units in which two 3,4′-bpy ligands bridge between four copper pairs to form a polymeric chain of tetramers.

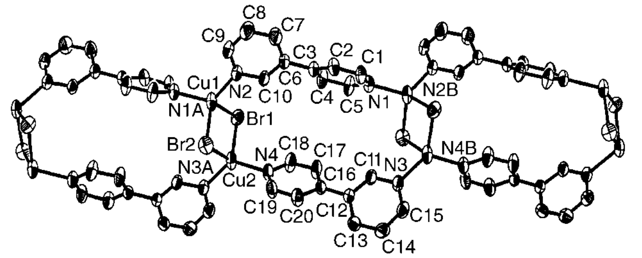

Fig. 1 An ORTEP[15] view of $[(3,4'\text{-bpy})(Br)Cu^{I}]_n$ showing a double chain and a rectangular molecular box along the *b*-axis.

The local environment around the Cu(I) ion is a slightly distorted tetrahedron with a Cu–Cu distance of 2.798(1) Å, slightly smaller than the sum of the van der Waals radii of copper(I) (2.8 Å), suggesting that there is a degree of metal–metal bonding character. The Cu–Cu distance is significantly shorter than those in the polymers $[(Ph_3P)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-pyz})]_n$ [3.095(1)] (pyz = pyrazine), $[Cu_2(\mu\text{-}Cl)_2(\mu\text{-phz})]_n$ [3.258(1)] (phz = phenazine) and $[Cu_2(\mu\text{-}Br)_2(\mu\text{-phz})]_n$ [3.391(2)] but longer than that in $[Cu_2(\mu\text{-}I)_2(\mu\text{-phz})]_n$ [2.525(1)], metallic copper (2.56) and $[Cu(\mu\text{-}I)(NCR)]_n$ (2.54–2.66 Å), respectively.[9] The metal–ligand distances are typical for copper(I) complexes. In comparison with distances in similar polymers, the range of the Cu–N distances of 1.991(2)–2.105(2) Å is basically in agreement with 2.044(3), 1.993(8) and 1.97(2) Å in $[(Ph_3P)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-pyz})]_n$, $[Cu(\mu\text{-}Cl)(py)]$ and $[Cu(TTA)(4,4'\text{-bpy})]_n$ [TTA = 4-(3-thienyl)-1,1,1-trifluorobutane-2,4-dionate], respectively.[10] The range of the Cu–Br distances of 2.522–2.570 Å is also comparable to that of $[Cu_2(\mu\text{-}Br)(\mu\text{-phz})]_n$ [2.515(1)–2.614(1) Å].[9] The molecules run along the *c*-axis as a one-dimensional layer in which the same laminar one-dimensional polymers are stacked together in a zigzag mode by van der Waals interactions.

The diffuse reflectance UV-vis spectrum of **1** shows a high energy band at *ca.* 275 nm and a low-energy band at *ca.* 345 nm, respectively (Fig. 3). The former may be assigned to the intra-ligand transition of the free ligand due to the 3,4′-bpy as it shows a band at a similar wavelength. With reference to previous spectroscopic work on related systems,[11] the low-energy band is assigned to a metal-to-ligand charge transfer (MLCT). However, the metal center d to s orbital transition is not ruled out.[12] The strong emission spectrum of **1** in the solid state at room temperature, shown in Fig. 3, has a maximum at *ca.* 580 nm, very similar to that of $Cu_4I_4(py)_4$ (py = pyridine) with λ_{max} 580 nm at 294 K.[13]

In $[Re(CO)_3(SR)]_4(\mu\text{-}4,4'\text{-bpy})_2$,[14] although the rectangular framework is of dimensions 3.81 × 11.57 Å as defined by the rhenium center, the dihedral angle between the two pyridyl ring

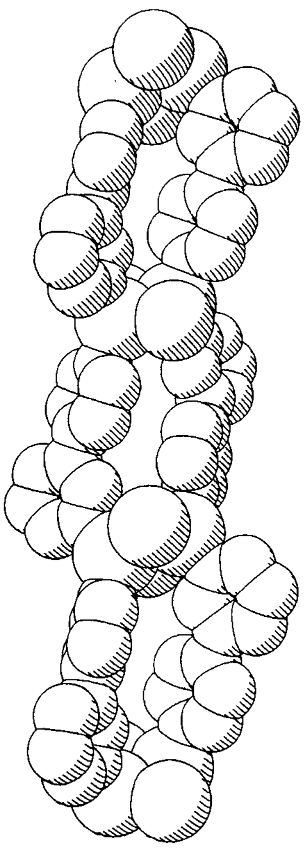

Fig. 2 A space-filling diagram of [(3,4′-bpy)(Br)Cu^I]$_n$.

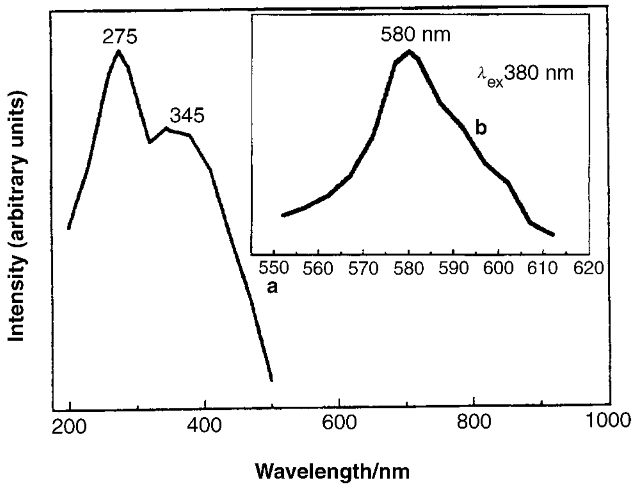

Fig. 3 (*a*) The diffuse reflectance UV-vis and (*b*) fluorescence spectra of [(3,4′-bpy)(Br)Cu^I]$_n$.

planes is about 1°. As a result, once van der Waals radii are taken into account, the box fails to be an acceptor site, even for planar molecules, such as benzene. However, in **1**, even if one of the dimensions in the rectangular box is 4 Å, guest molecules, such as phenol, may be sited in the bow surrounded by the pyridyl rings because the dihedral angle between the two pyridyl planes is large (*ca.* 34°). As a result, the luminescence characteristics of the rectangular box makes **1** a candidate for sensing applications on the basis of recognition and inclusion of appropriate guest molecules.[14]

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Notes and references

† Preparation of [(3,4′-bpy)(Br)Cu^I]$_n$ **1**: hydrothermal treatment of Cu(NO$_3$)$_2$·2.5H$_2$O (1.2 mmol), trimethyltin bromide (1 mmol), 3,4′-bpy (1 mmol) and water (10 ml) for one day at 110 °C yielded an orange-yellow rectangular crystalline product (only one pure phase). The yield of **1** was 45% based on 3,4′-bpy (Calc.: C, 40.07; H, 2.67; N, 9.35. Found for $C_{20}H_{16}Br_2Cu_2N_4$: C, 39.82; H, 2.43; N, 10.10%). IR (KBr/cm^{-1}): 1602vs, 1540vw, 1470vs, 1428m, 1401vs, 1324w, 1220w, 1123vw, 1067vw, 1023m, 1015m, 844m, 796vs, 692vs, 636w, 539m.

‡ Crystal data for **1**: $C_{20}H_{16}Br_2Cu_2N_4$, monoclinic, $P2_1/n$, a 9.4944(1), b 12.9445(2), c 16.9514(1) Å, β 90.924(1)°, V 2083.06(4) Å^3, Z 4, M 599.27, D_c 1.911 Mg m^{-3}, $R1$ 0.032, wR 0.070 (4759 reflections). T 293 K, μ 5.891 mm^{-1}. CCDC reference no. 186/1428. See http://www.rsc.org/suppdata/dt/1999/1711/ for crystallographic files in .cif format.

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