Dalton Transactions

COMMUNICATION

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Cite this: Dalton Trans., 2018, 47, 17206

Received 26th September 2018, Accepted 13th November 2018 DOI: 10.1039/c8dt03884h

rsc.li/dalton

Fluxional motion in a dinuclear copper(I) complex with a propeller-type ligand: metal hopping on both sides[†]

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The first study of fluxional motion in $[Cu_2(2-HPB)(MeCN)_2Cl_2]$ (1,2-HPB = hexa(2-pyridyl)benzene) is presented. For detailed examination of the fluxional motion mechanism, a monofluorinated derivative of the ligand (MFHPB) and its copper(I) complexes were synthesized and characterized. The solution NMR studies of monofluoro copper(I) complex 1a suggest the existence of five species in equilibrium. NMR spectra and DFT calculations suggest the fluxional motion of 1 resulting in the "metal hopping process" of two copper(I) ions.

The study of fluxional processes in coordination chemistry provides a comprehensive explanation of the bonding between the metals and ligands involved¹⁻⁸ and subsequently assists in rationalizing chemical reactivity patterns.9-16 Several fluxional coordination systems were previously reported. (See Table S3[†]) Among them, metal complexes with highly symmetrical multidentate ligands often exhibit rich fluxional behaviour, while metal atoms interchange between symmetry-equivalent positions.¹⁷⁻²³ In this context, hexapyridylbenzene (HPB) derivatives with six identical pyridyl units are highly attractive symmetric ligands that can coordinate to metal centers forming complexes exhibiting fluxional behaviour.24-29 The Shionoya group reported a trinuclear Ag(I) sandwich complex that exhibits 'ball bearing' molecular behaviour.30-34 In our group, coordination properties of the 2-HPB ligand in copper (I) complexes of variable stoichiometry have been studied as well as the dynamic behaviour of the dinuclear 2-HPB copper (1) complexes.²² In the previous article, we briefly described the fluxional behaviour of complex 1, [Cu₂(2-HPB)(MeCN)₂Cl₂]. In complex 1, the 2-HPB ligand acts as a bis-bidentate ligand for two Cu(I) centers which are located on the opposite sides of the central benzene ring, while two remaining pyridines are uncoordinated (Fig. 1).

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In this paper, we present a more detailed mechanistic study of the fluxional behaviour of [Cu₂(2-HPB)(MeCN)₂Cl₂] complex, 1, which was cursorily presented in the previously published article.²² We successfully synthesized monofluorohexa(2pyridyl)benzene (MFHPB) for detailed mechanism elucidation of the fluxional behaviour. Among six pyridine rings in this ligand, one contains a fluorine atom in the meta-position to nitrogen, while the other five pyridine rings remain unsubstituted. The presence of the fluorine atom was expected to give rise to isomers of the corresponding dicopper(I) complex by breaking the symmetry of the ligand (from D_{3d} for 2-HPB to C_s for MFHPB), thus providing additional information about the fluxional processes of 1 (Scheme 1). We also propose the structures of the intermediate species formed in the course of the fluxional motion of 1 based on 19F NMR data and other experimental evidence. Finally, the mechanism of the fluxional motion is also supported by density functional theory (DFT) calculations.

The ¹H NMR spectra of complex **1** in d_3 -acetonitrile solution at 323 K showed only four signals for 24 protons instead of twelve signals for coordinated and non-coordinated pyridine



Fig. 1 Top view (a) and side view (b) of $[Cu_2(2-HPB)(MeCN)_2Cl_2]$, 1. Ellipsoids are shown at the 50% probability level and hydrogen atoms are omitted for clarity.

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[†]Electronic supplementary information (ESI) available. CCDC 1552119 and 1874373. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt03884h



Scheme 1 Synthesis of hexa(2-pyridyl)benzene (2-HPB), penta(2-pyridyl)benzene (2-PPB), and monofluorohexa(2-pyridyl)benzene (MFHPB).

rings, which indicates dynamic motion in the complex (Fig. 2(b)). At 223 K, the signals were separated in accordance with the proton ratio in the solid state structure (Fig. 2(c)). The two-dimensional exchange spectroscopy (2D-EXSY) spectrum of 1 shows the exchange process between coordinated and uncoordinated pyridines with the following activation parameters: $\Delta H^{\ddagger} = 16.47 \pm 0.02 \text{ kcal mol}^{-1}$, $\Delta S^{\ddagger} = 13.40 \pm 0.16 \text{ e.u.}$, ΔG^{\ddagger} = 13.36 ± 0.11 kcal mol⁻¹, and $E_{\rm a}$ = 16.9 kcal mol⁻¹ (Fig. S8 and S18[†]). The positive ΔS^{\ddagger} indicates that the transition state is more disordered than the starting material. Therefore, it is proposed that in the course of the fluxional motion, one of the copper(I) atoms dissociates to facilitate the exchange, *i.e.*, the mechanism is dissociative. In addition to the signals of 1, cross peaks from the unassigned broad signals in the range of 8.3 to 8.4 ppm were observed indicating the presence of an intermediate in the course of fluxional behaviour. The other ¹H signals of this species probably overlap with signals of 1 (Fig. S9[†]).²²



Fig. 2 ¹H NMR spectra of 2-HPB (a), complex 1 at 323 K (b), complex 1 at 223 K (c), MFHPB (d), 1a at 323 K (e), and 1b at 223 K (f) in d_3 -acetonitrile.

The ¹H NMR spectrum of the MFHPB ligand is similar to that of the unsubstituted 2-HPB ligand with the integration ratio of 5:1 for the ortho-proton region, due to one 5-fluoropyridine unit. The MFHPB ligand with 2 equivalents of copper(1) chloride gives the corresponding complex [Cu₂(MFHPB) (MeCN)₂Cl₂], **1a** which has an identical coordination mode to 1 in d_3 -acetonitrile solution (Fig. 2). At 323 K, the ¹H NMR spectrum of **1a** is similar to that of the free ligand **MFHPB**, suggesting rapid dynamic motion in the complex. As the temperature decreases, the signals become broad and the coalescence temperature was determined to be 273 K. At 223 K, all proton signals split, showing a pattern analogous to that of 1 at the same temperature (Fig. 2(c) and (f)). In the complex, signals arising from six protons in the ortho-position to nitrogen were considered. At 323 K, the six protons integrate as 5:1 in the ¹H NMR spectrum (Fig. 2(e)). At 223 K, the signals from the *ortho*-protons split into five signals in the (3:3):(1:1:1)ratio (i.e., 2:1 ratio for coordinated pyridine and non-coordinated pyridine) (Fig. S10[†]). At 323 K, the ¹⁹F NMR spectrum of 1a shows only one signal at -131.03 ppm which is downfield shifted compared to the signal from the free ligand (Fig. S7[†]). The coalescence of the signal was observed at 273 K. At 223 K, the signal split into five peaks at -127.7, -129.6, -129.8, -130.4, and -130.7 ppm with the integration ratio of 1.00:0.21:0.12:0.24:1.82 (Fig. 3(a)). Due to high resolution of the fluorine nuclei, the signals from the intermediate species were now distinguishable. In an NMR titration experiment, the ¹⁹F NMR signals in the solution of MFHPB with one equivalent of copper(1) chloride differ from the signals of 1a, while signals in solution containing three equivalents of copper(1) chloride remain the same as those in 1a. This implies that all five different isomeric species contain two copper(1) atoms per one ligand molecule (Fig. S11[†]). In ¹⁹F 2D EXSY, cross signals between the five fluorine signals were observed (Fig. 3(b)).

The proposed structures of the five different isomeric species of **1a** are shown in Fig. 4. The structures of **1a_1** and **1a_2** are analogous to the structure of **1** obtained by single crystal X-ray diffraction (SCXRD) and the fluorine atom is attached to the non-coordinated ring and coordinated ring, respectively. The structure of **1a** obtained by SCXRD clearly indicates that the fluorine atom is disordered in six pyridine



Fig. 3 VT ¹⁹F NMR spectra of **1a** (a) and ¹⁹F NMR 2D-EXSY of **1a** at 223 K (τ = 200 ms) (b).



Fig. 4 The calculated rate constants for fluxional motion (s^{-1}) in **1a**.

rings (Fig. S15[†]). Our earlier study of the coordination modes of 2-HPB allows us to suggest the structures 1b_1, 1b_2, and 1b_3 for the three intermediate species observed in the low temperature ¹⁹F NMR spectrum.²³ In those complexes, two copper(1) atoms located on the opposite sides of the benzene ring coordinate with four pyridines in a row leaving two pyridines in the ortho-position to each other non-coordinated (Fig. 5(b)). This coordination mode can explain the presence of three non-equivalent fluorine nuclei in the same ligand conformation (Fig. S12[†]). By correlating the integration values of ¹⁹F NMR and ¹H NMR data, we could surely perceive that two major signals at -127.7 ppm and -130.7 ppm correspond to 1a_1 and 1a_2, respectively. Based on the chemical shifts in 19 F NMR spectra, we propose that the three signals at -129.6, -129.8, and -130.4 ppm correspond to 1b_1, 1b_2 and 1b_3, respectively. The rate constants for the exchange between the two major isomers $1a_1$ and $1a_2$ are 0.153 ± 0.044 s⁻¹ and $0.338 \pm 0.048 \text{ s}^{-1}$, while the exchange rate of 1a (1a_1 and 1a_2) to 1b (1b_1, 1b_2 and 1b_3) ranged from 1.02 ± 0.19 to $5.03 \pm 0.10 \text{ s}^{-1}$ (Fig. 4 and Fig. S17[†]).

Complex **1** is a dinuclear copper(i) complex with six pyridine binding sites. Equal population of all pyridine binding sites can be achieved *via* a rapid 180 degree rotation of the non-coordinated pyridine rings, followed by a dissociation-recombination process. In such a "hopping" process, one of the copper(i) centers (red in Fig. 6) disconnects itself from the pyridine ring 1 and then coordinates to the ring 3. The two copper(i) centers in **1** can move between the pyridine nitrogen atoms following three pathways: (i) concerted hopping of the two copper(i) atoms by simultaneous dissociation of the two copper-nitrogen bonds, followed by bond formation with previously non-coordinated pyridine rings, or (ii) dissociation of the relatively unstable intermediate **1B_1**, followed by recombination with new pyridine rings, or (iii) subsequent hopping



Fig. 5 The optimized structures of the proposed intermediates **1B_1** (a) and **1B_2** (b). Energy diagram for the proposed metal hopping process (c) (pathway (ii) – dotted line, pathway (iii) – solid line). Atom colors in (a) and (b): C, gray; N, blue; Cl, green; Cu, brown. Hydrogen atoms are omitted for clarity. In (c), red labeled atoms are pointing up from the plane. Blue labeled atoms are pointing downside from the plane. The ΔG° values are given in kcal mol⁻¹.



Fig. 6 The proposed mechanism for the fluxional motion of 1. Red labeled atoms are pointing up from the plane. Blue labeled atoms are pointing down from the plane.

of both copper centers, this pathway proceeds *via* the relatively stable intermediate **1B_2** (Fig. 5(a) and (b)).

¹⁹F 2D EXSY of **1a** at 223 K shows that five different dicopper(i) species are involved in the fluxional motion of the complex. By considering the presence of the intermediate species, we can rule out the concerted pathway (i). The pathways (ii) and (iii) can be considered since the conformations of both the proposed intermediates **1B_1** and **1B_2** would give three different signals in ¹⁹F NMR spectra when **MFHPB** is used as a ligand (Fig. S13†). To explain the experimental observations and to provide information about the thermodynamic stability of possible intermediate species, DFT calculations at

the B3LYP/6-31G(d,p) level of theory were performed (see the ESI†). In the calculation of ΔG° , solvation free energies (acetonitrile) using SMD were included. The calculated structures and energy profiles for the exchange between **1** and two proposed intermediate species **1B_1** and **1B_2** are shown in Fig. 5.

Fig. 5(c) shows the calculated energy diagram for two possible pathways for the fluxional motion in complex **1**. In pathway (ii) (dotted line), one copper(1)–nitrogen bond dissociates (**1** to **1A**), and then dissociation of another copper(1)– nitrogen bond occurs (**1A** to **1B_1**). After that, one copper atom forms a copper(1)–nitrogen bond with a new pyridine (**1B_1** to **1C**). This is followed by second copper(1)–nitrogen bond formation, thus restoring the original conformation (**1C** to **1**). On the other hand, in pathway (iii) (solid line), one copper(1)– nitrogen bond dissociates (**1** to **1A**) and the copper atom associates with a new pyridine (**1A** to **1B_2**), and then **1B_2** converts to **1** *via* the intermediate **1C**.

The calculated energy difference between 1 and 1B_2 is 0.34 kcal mol⁻¹ indicating comparable stability of both complexes and implies that the two isomers should exist in noticeable amounts in equilibrium. This is supported by the fact that the signal from isomer $1B_2$ was observed in the ¹H 2D EXSY. Likewise, the isomeric species 1b_1, 1b_2 and 1b_3 were observed as three different signals in ¹⁹F NMR spectra when using MFHPB as a ligand. The calculated energy differences between 1 and 1A, and 1 and 1C are around 4 kcal mol⁻¹ and the difference between 1 and $1B_1$ is around 5 kcal mol⁻¹ (for calculation of 1a, see Table S2[†]). Therefore, the equilibrium between the two isomers should be shifted toward 1. Thus, 1A, 1B_1 and 1C would not be observed in the NMR spectra (the ratio of 1:1A in equilibrium is calculated to be 12000:1 at T = 223 K, following the equation $\Delta G^{\circ} = -RT \ln K$, which is in accordance with the observations and allows pathway (ii) to be ruled out. Therefore, from the DFT calculation results and the experimental observations, pathway (iii) is the most plausible mechanism among the three proposed ones to explain the fluxional motion of 1.

The rotational barriers of the non-coordinated pyridine ring in **1** and **1B_2** were calculated (Fig. S19 and S20†). The calculated rotational barriers around central arene–pyridine bonds are around 13 kcal mol⁻¹ (13.0 and 13.8 kcal mol⁻¹ for **1** and **1B_2**, respectively), which are comparable with the ΔG^{\ddagger} value of fluxional motion calculated by 2D-EXSY (13.36 ± 0.11 kcal mol⁻¹).²² Based on this good agreement between experimental and theoretical results, we propose that the barrier for the metal-hopping process may come from the rotation of the non-coordinated pyridine.

To conclude, the mechanism of a new type of metal hopping process in a hexa(2-pyridyl)benzene (2-HPB) system was investigated. In complex 1, two copper atoms on both sides of the ligand hop through the six pyridine nitrogen atoms. The five different isomeric species in equilibrium were observed in ¹⁹F NMR spectra when a monofluorinated unit (MFHPB) was used as a ligand. DFT calculations reveal the possible pathway for the fluxional motion of 1, showing the comparable stability of the proposed intermediate 1B_2 and 1.

In addition, the rotational barriers for the non-coordinated pyridine ring in 1 and $1B_2$ were calculated. We conclude that the hopping process of two copper atoms between six pyridines occurs along with a rotation of the pyridine ring in the complex 1.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Institute for Basic Science (IBS) [IBSR007-D1], MSIP and PAL, Korea. The X-ray crystallography analysis with synchrotron radiation was performed at the Pohang Accelerator Laboratory (PLS-II BL2D SMC). We thank MSc ETH Ewa Pietrasiak, Dr Young Ho Ko, and Prof. Donghwan Lee for helpful discussions.

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