Supramolecular self-assembly and anion-dependence of copper(II) complexes with cationic dihydro-imidazo phenanthridinium (DIP)-containing ligands†

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We present two new ligands, 2,3-dihydro-1-(2-pyridyl-methyl)-imidazo[1,2-f]phenanthridinium bromide (L1·Br) and 2,3-dihydro-1-(4-pyridyl-methyl)-imidazo[1,2-f]phenanthridinium bromide (L2·Br), which have been synthesized and fully characterized as coordinating cations. The reactions of Cu(BF4)2 (compound 1), Cu(NO3)2 (compound 2), CuBr2 (compound 3), Cu(NO3)2 and NaN3 (compound 4), Cu(NO3)2 and NaSCN (compound 5) with L1·Br and CuBr2 with L2·Br (compound 6) have been carried out. The crystal structures of the resulting metal–organic assemblies have been determined and the intermolecular interactions of the compounds in the crystalline phase have been analysed. A mononuclear copper(II) compound has been obtained with CuBr2, in which the copper(II) ion adopts a tetrahedral geometry with a CuNBr3 coordination motif. With Cu(BF4)2, two L1+ cations and two bromide anions chelate the copper ion giving a CuN2Br2 motif, while the BF4− is present as a non-coordinating counterion. With Cu(NO3)2, a five coordinated copper complex is obtained whereas bridging ligands such as NaN3 and NaSCN are added into the reaction mixture of L1·Br and Cu(NO3)2; two novel dinuclear copper coordination cores of [Cu2(μ1,1-N3)2(N3)4]2− and Cu(CH3)2(SCN)4]2− form. The presence of the large heteroaromatic cationic DIP moiety within the ligand system leads to the formation of 1-, 2- and 3-D supramolecular arrays based on the interactions of the π systems between adjacent molecules.

Introduction

An extraordinary and often bewildering structural diversity exists in the coordination geometries of copper(II) complexes, which is dictated by the flexible and labile coordination sphere of the copper ion along with steric effects and intermolecular forces between coordinated ligands, such as hydrogen bonding and π–π stacking interactions.1,2 The coordination geometry can be influenced by factors such as the variation of counterion nature and different ligand systems with coordinating, non-coordinating and bridging types. Therefore the nature of the ligand is of great interest due to the fact that the ligand donor geometry can impose a preferred geometry on the copper(II) ion and this is relevant to understanding the active sites of copper-containing metalloproteins,3,4 and metallointercalators.5 The supramolecular arrangements of coordination complexes in the crystalline phase are determined by a range of different intermolecular interactions that vary widely in their strength and directionality,6 and the structural importance of these interactions is an area of considerable interest and importance for the fields of crystal engineering, molecular recognition, and crystal structure determination/prediction.7 π–π Stacking and CH–π interactions, in particular, play a significant role in defining structures which lack strong H-bond donors or acceptors. Therefore the use of structural elements which take advantage of these interactions can be important in the manipulation of the supramolecular architectures. In this respect we are interested in the design of coordinating ligands that are also capable of π–π and CH–π interactions.8

We have recently developed a simple, one-pot, three-step reaction for the synthesis of a new class of phenanthridinium derivatives (Scheme 1).9 The reaction of a primary amine with 2-bromoethyl phenanthridinium bromide leads to the formation of dihydro-imidazo phenanthridinium (DIP) moiety, which contains a cationic polycyclic aromatic system (see Scheme 1).

Nitrogen heteroaromatic cations containing a phenanthridinium moiety have received a lot of attention because of their application in the scaffold of a number of DNA intercalating agents with anti-cancer activities.10,12 DNA drug targeting applications13,14 and DNA probes.15 DIP derivatives are of interest as they exhibit tunable DNA binding, via an intercalative mode, and cytotoxicity in human ovarian cancer cell lines, dependent on the structure and functionality of the primary amines.16 We are therefore keen to exploit the coordination potential of DIP-containing molecules in the search for novel metallointercalators.

In this paper, two new ligand systems (2,3-dihydro-1-(2-pyridylmethyl)-imidazo[1,2-f]phenanthridinium bromide (L1·Br) and 2,3-dihydro-1-(4-pyridyl-methyl)-imidazo[1,2-f]phenanthridinium bromide (L2·Br) have been designed by attaching pyridine groups to the DIP moiety. Anion-dependent self-assembly of a series of mono- and dinuclear copper(II) complexes is

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reported and the influence of both the anionic counterions and the intermolecular interactions on the final structure of the assemblies is discussed.

results and discussion

L1·Br and L2·Br have been obtained by using a one-pot reaction between primary amines and 2-bromoethyl phenanthridinium bromide, in which DIP (dihydro-imidazo-phenanthridinium), as a large planar polyaromatic core, is attached with a pyridyl group. By grafting a pyridyl ring on the DIP framework (see Scheme 2) and complexation with copper(II) ions, we are able to obtain a series of copper(II) complexes as metallointercalators, which contain a higher positive charge than DIP, as well as introduce further REDOX active components into the system.

By carrying out anion exchange from bromide to tetraphenylborate, we were able to obtain the crystals of L1·BPh₄, which crystallizes from methanol in a monoclinic P2₁/n system. The asymmetric unit of the crystal structure includes one DIP cation and one BPh₄⁻ anion. The pyridine ring locates in such a way as to be almost perpendicular to the phenanthridinium plane with a dihedral angle of around 88.34°. The almost perpendicular arrangement of the ligands represents the possibility of two orthogonal sets of π interactions in the complexes of these ligands, see Fig. 1.

Green, needle-shape crystals of compound 1 are obtained by slow evaporation of the methanolic solution of one equivalent of L1·Br with two equivalents of Cu(BF₄)₂·6H₂O. The asymmetric unit of compound 1 contains a [Cu₂Br₂(L1·Br₀.05)]⁺ with the chelating ligand partially brominated at C4 position, an...
uncoordinated $\text{L1-Br}_{0.45}$ molecule which has been partially brominated on C25 position and two $\text{BF}_4^-$ anions as non-coordinating counterions. The crystal structure shows that the copper(II) ion is coordinated by two $\text{L1-Br}_{0.05}$ and two bromides, resulting in a CuN$_2$Br$_2$ donor set with a square-planar geometry (Cu–N distance = 1.959(4) Å and Cu–Br distance = 2.453(4) Å), see Fig. 2. The Cu–N bond lengths and all bond angles are in the normal range when compared with other copper(II) complexes from the CSD database with such CuN$_2$Br$_2$ donor set. The pyridine ring forms about 82.56° dihedral angle with the DIP plane, while the two DIP planes from two coordinated (4) moieties of the coordinated and uncoordinated ligand molecules ($d_{\pi-\pi} = 3.665$ Å) in the crystal structure. Fig. 2 shows the structure of these chains with the uncoordinated ligand molecules linked by further $\pi-\pi$ stacking interactions of the pyridyl section of the ligand ($d_{\pi-\pi} = 3.444$ Å).

Recent work by Houser et al. has introduced the concept of a new four coordinate geometry index, $\tau_4$, which is similar in principle to the standard $\tau_5$ used to describe trigonal distortion of a five coordinate species from square pyramidal geometry. $^{19}$ Like $\tau_5$, $\tau_4$ is defined using the two largest $\theta$ angles in the four coordinate species ($\tau_4 = |360 - (\alpha + \beta)/141|$) and ranges from 0 for a square planar geometry to 1 for tetrahedral geometry. In the case of compound 1, it gives a $\tau_4$ value of 0, indicating a high degree of square planar character. The copper(II) ion, nevertheless, is not in a perfectly square planar geometry due to the lack of $D_{4h}$ symmetry in the coordination environment of the copper ion, as evidenced by the 89.20(14)° of N–Cu–Br (see Table 1).

It should be mentioned here that there is partial bromination in the C25 position of the coordinated $\text{L1-Br}_{0.05}$ with a C–Br distance of 1.739(7) Å (the occupancy of the bromine atom is about 5%) and the uncoordinated $\text{L1-Br}_{0.45}$ is also partially brominated with a 50% occupancy at the C4 position. Some examples of oxybromination of aromatic compounds have been reported, in which different types of catalysts, $^{20-22}$ or biphasic media,$^{23,24}$ have been utilized in order to achieve the brominated products. In contrast, the copper(II)-mediated bromination reaction seen here is a very unusual result (the reaction mixture contains only the ligand and copper salt). More detailed investigation to understand the mechanism of this bromination is underway.

By changing copper(II) salt from $\text{BF}_4^-$ to $\text{NO}_3^-$, compound 2 has been obtained with a copper(I) centre surrounded by a CuBr$_2$NO$_3$ donor set, of which two bromide anions come from $\text{L1-Br}$ (see Fig. 3), so that compound 2 can be formulated as [Cu(NO$_3$)$_2$Br$_2$L1]. The compound crystallises in a triclinic $P1$ system and the copper(II) center is five coordinate with an almost ideal square pyramidal geometry (the parameter $\tau_5$ is 0.28 for the copper ion ($\tau_5$ is 0 for an ideal square pyramid and 1 for an ideal trigonal bipyramid). The basal

### Table 1 Typical bond length (Å) and bond angles (°) of L1 and compound 1–6

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plane is constituted by a nitrogen from the pyridine ring, two bromides and one of the oxygens from NO$_3^–$. The other oxygen from NO$_3^–$ occupies the apical position. The Cu–N and Cu–O bond lengths and the corresponding bond angles in the crystal structure are in the normal range for such CuBr$_2$NO$_2$ donor set checked from the CSD database.

Crystal packing of compound 2 is highly influenced by the π–π stacking interactions of the DIP moieties with the phenanthridinium sections of the compound exhibiting a ‘bowed’ conformation and stacking to form supramolecular columns in the crystal structure ($d_{\pi-\pi} = 3.515$ Å). In contrast to the previous structure, however, there are no π–π stacking interactions involving the pyridyl sections of the ligands.

Fig. 4 shows the crystal structures of compound 3 and compound 6, which are obtained from $\text{L}_1\cdot\text{Br}$ and $\text{L}_2\cdot\text{Br}$ with CuBr$_2$, respectively. Compound 3 can be formulated as [Cu(Br)$_3$(L1)] and crystallises in triclinic P-1, while the copper complex in compound 6 can be formulated as [Cu(Br)$_3$(L2)$_2$]Br$_2$H$_2$O and crystallises from a monoclinic C2/c system. Importantly, the copper(II) ions in compound 3 show quite unusual tetrahedral geometry; the dihedral angle between two planes of Br–Cu–Br and Br–Cu–N is 89.47°. π values for Cu1 and Cu2 are 0.662 and 0.663 respectively. In this case, the copper centre is coordinated by one nitrogen from the pyridine ring and three bromide anions with average Cu–Br and Cu–N distances of 2.384(3) Å and 2.022(16) Å. In contrast, in compound 6 two $\text{L}_2^+$ cations and three bromide anions are bound to the copper(II) center, resulting in a trigonal bipyramidal geometry ($\tau_5$ value is 0.78). The equatorial plane of the copper centre is occupied by three bromides with an average distance of 2.5298(18) Å, and two nitrogens from pyridine rings of two $\text{L}_2^+$ cations occupy the apical positions. The pyridine rings and the phenanthridinium planes form a dihedral angle of 80.46° while the pyridine rings themselves form a dihedral angle of 37.17°. Unlike compound 3 the crystal structure of compound 6 also contains uncoordinated water molecules, which exhibit hydrogen bonding between the coordinated and uncoordinated bromide anions, thus linking the structure along the crystallographic $a$ axis. For both compounds 3 and 6, a CSD check shows that the Cu–N and Cu–Br bond lengths and all the bond angles are in the normal range of copper complexes.

The main difference between these two structures results from the positions of the nitrogen donors in the ligand systems. The phenanthridinium plane in $\text{L}_2\cdot\text{Br}$ is connected to the para-position nitrogen donor of the pyridine ring. After complexation, there is enough space for two $\text{L}_2^+$ cations to chelate. In the case of $\text{L}_1\cdot\text{Br}$, the phenanthridinium plane is linked in the ortho-position and the steric effect is more pronounced when $\text{L}_1^+$ chelates to the copper(II) ion. As a result, the copper ions in compound 3 and compound 6 show unusual tetrahedral and trigonal bipyramidal geometries, respectively.

This differences in ligand structures and, hence, the coordination of the species also have large repercussions for the intermolecular interactions that these compounds experience in the crystalline phase. While compound 3 displays π–π stacking interactions on both the pyridyl ($d_{\pi-\pi} = 3.342$ Å) and DIP ($d_{\pi-\pi} = 3.145$ Å) portions of the complex, compound 6 experiences only DIP based π–π interactions ($d_{\pi-\pi} = 3.367$ Å). As can be seen in Fig. 4, the crystal structure of compound 3 shows that the π–π stacking of the pyridyl moieties produces dimers of the complex which are then connected to its neighbours in two dimensions via the π–π stacking of the DIP moieties. Compound 6 also forms sheets, however the interactions which hold them...
together are solely between the DIP moieties of the two coordinated ligand molecules in a ladder-like arrangement, and the pyridyl $\pi$ systems do not interact with each other.

The dinuclear copper(II) complex of compound 4 is obtained from a reaction mixture of L : Cu(NO$_3$)$_2$ : NaN$_3$ = 1 : 2 : 8 in MeOH/DMF and 4 can be formulated as [Cu(N$_3$)$_3$(L1)$_2$] where the crystal structure has a $C_2$ axis symmetry, resulting in the $cis$ conformation of two coordinated L1$^-$ DIP moieties. Each of the copper(II) ions is coordinated by four end-on azido-ligands in the equatorial plane (the average Cu–N distance is 2.012(2) Å) and the nitrogen from the pyridine ring occupies the axial position with a longer Cu–N distance of 2.294(3) Å, giving a CuN$_2$ donor set with a distorted square pyramidal geometry ($\tau_2 = 0.12$). The dinuclear copper ions with a Cu–Cu distance of 3.143(2) Å are bridged by a $\mu_1$-azido ligand with the Cu–N distance of 2.027(2) Å and 2.055(2) Å and Cu–N–Cu angles of 100.70(10)$^\circ$ (see Table 1). The two pyridine rings are almost parallel to each other with a dihedral angle of around 4.01$^\circ$. All the bond lengths and bond angles are in the normal range of copper complexes. The molecular packing of the crystal structure shows that the two phenanthridinium planes in the unit cell are almost parallel to each other, forming strong intermolecular interaction with a distance of 3.36 Å. The DIP planes of the two ligands show a dihedral angle of 69.71$^\circ$ and the DIP regions of the molecules exhibit $\pi$–$\pi$ interactions in an antiparallel arrangement forming supramolecular chains running through the crystal structure (see Fig. 5).

It should be noted that, to the best of our knowledge, the dinuclear core shown in Fig. 5 is the second example of this kind of azido-bridged dinuclear copper complex reported so far (if the apical positions occupied by ligand nitrogens are neglected, there are another three examples, reported).25,26

Compound 5 crystallises in a triclinic $P$-1 system with $Z = 1$. The crystal structure of compound 5 shows a bis($\mu$-methoxy)-bridged dinuclear copper(II) complex where two NCS$^-$ anions coordinate through the nitrogen atoms to the copper(II) ion. The copper(II) ion is five coordinate with an almost ideal square pyramidal geometry ($\tau_5 = 0.016$) and the Cu–Cu distance is 3.021(3) Å. The bond lengths and bond angles are also in the normal range for copper complexes.

![Fig. 5](image1.png) The asymmetric unit of the crystal structure of compound 4 (top left). The dinuclear core of the structure (top right) and a view of the molecular packing showing the alternating arrangement of adjacent molecules and the $\pi$–$\pi$ stacking of the DIP moieties.

Fig. 6 Crystal structure of compound 6 shows that S–S interactions between adjacent thiocyanate ligands (top) and S–$\pi$ interactions between thiocyanate ligands and the coordinated pyridyl regions of the DIP ligand (bottom).

The unusual coordination core around the copper(II) ion here represents the first example of a methoxy bridged dinuclear copper(II) complex with four monodentate coordinating thiocyanate anions. Compared with compound 4, the crystal structure of compound 5 shows two different features: (1) two methoxy ligands, instead of thiocyanate anions, are bridging the copper(II) ions in the dinuclear complex; (2) two DIP-containing ligands are located in a trans-mode. Intermolecular S–S interactions with a distance of 3.411(5) Å can be observed in the unit cell (see Fig. 6). Also observed in the molecular packing of this compound are interactions between the sulfur atoms and the $\pi$ system of the pyridyl region of the ligand on an adjacent molecule with a distance of around 3.320 Å. Such sulfur–$\pi$ interactions are important in biological systems.27

Along with these sulfur-based interactions the molecular packing is further stabilised by extensive interactions between the $\pi$–$\pi$ systems of the coordinated ligand (see Fig. 7). CH–$\pi$ interactions between the pyridyl hydrogens and the DIP regions of the neighbouring molecules can be observed with distances in the range of 2.511–2.716 Å. The DIP regions also stack with neighbouring DIP regions with a distance of about 3.40 Å. Each DIP moiety takes part in $\pi$–$\pi$ stacking with another DIP region...
on one face and CH–π interactions from the pyridyl hydrogens on the opposite face.

Infrared spectra of these copper(II) complexes show the most important bands for characterisation of the compound with different anions. In compound 1, the vibration of the tetrafluoroborate anion is observed at 1056 cm\(^{-1}\) as a single strong band and the most sensitive characteristic vibrations of the coordinating nitrate vibrations can be found at 1282 cm\(^{-1}\) for compound 2. In compound 5, the vibrations of the thiocyanate anion are observed as a strong band at 2077.2 cm\(^{-1}\), while in compound 4, the vibration of the azide anion is found as a split strong band at 2250 and 2125 cm\(^{-1}\), in agreement with the two different types of bonding of the azide anions.

Conclusions

By linking pyridine groups to the DIP moiety, we have designed and synthesized two new, cationic ligands with potential coordinating sites. A number of copper(II) complexes of DIP-containing ligand systems have been obtained and crystallographically characterized, of which a great variety of geometries have been observed with a copper(II) ion depending on the selected copper(II) salts. From all six crystal structures, it is clear that the geometry and size of the anion along with its ability to interact with the metal center is essential in determining the structure of the metal assembly.

The intermolecular forces which determine the packing of the synthesized complexes in the crystalline state are largely dependent on the ability of the DIP region of the ligands to interact with other structural features via the phenanthridinium π-system. It has been observed that the DIP regions of the ligands experience π–π stacking interactions with other DIP moieties in every crystal structure obtained, leading to the formation of one- and two-dimensional arrays of molecules, with further S···S interactions linking molecules in the third dimension in one instance (see Fig. 8). The role played by the pyridyl region of the ligand structures exerts a more subtle influence on the overall structure, with no direct interaction between the π-systems of pyridyl and DIP moieties observed in any of the structures. π–π stacking is observed only between adjacent pyridyl moieties, whether inter- or intramolecularly, however the pyridyl region of the ligands experiences a variety of other interactions, such as S···π interactions with thiocyanate groups or CH–π interactions with DIP aromatic systems. As the pyridyl group is the coordinating moiety in the ligand structures, the two ligands differ significantly in their coordination behaviour as discussed below and it should be noted that compound 6, the only complex utilising L2\(^+\) cation as a chelating ligand, experiences no intermolecular interactions on the pyridyl ring.

In all cases, the DIP moiety is quite rigid and only the pyridine nitrogen is involved in the coordination. With Cu(BF\(_4\))\(_2\), the copper ion is coordinated by two L1\(^+\) DIP moieties through pyridine nitrogen and two Br\(^-\) anions coming from the ligand source, while the BF\(_4\)\(^-\) remains a noncoordinating counterion. With CuBr\(_2\), bromide anions appear to coordinate with Cu(II) centre and an interesting tetrahedral geometry is observed around Cu(II) ion. With Cu(NO\(_3\))\(_2\), the nitrate anion chelates with Cu(II) ion and two bromide anions from L1\(^+\) are coordinating with the copper centre. As a result, a distorted square-pyramidal geometry is formed. When an additional bridging ligand such as N\(_3\)\(^-\) and SCN\(^-\) is added to the mixture of L1–Br and Cu(NO\(_3\))\(_2\), besides L1\(^+\), only the bridging ligands or solvents, instead of nitrate anions, are present in the coordination surrounding the Cu(II) ion.

Four-coordinate copper(II) complexes, varying from square planar to novel tetrahedral geometries are observed with BF\(_4\)\(^-\) and Br\(^-\), respectively. With nitrate, azide and thiocyanate as anions, five-coordinate copper(II) structures have been observed. Comparing the copper(II) bromide complexes, two different geometries of copper complexes have been obtained. The difference of the coordination environment around Cu\(^{2+}\) ion results apparently from the two to four position of the pyridine nitrogen in L1\(^+\) and L2\(^+\), respectively. Compounds 4 and 5 also represent very unusual copper(II) complexes with unique dinuclear cores.

Experimental

Synthesis of 2,3-dihydro-1-(2-pyridyl-methyl)-imidazo[1,2-f]phenanthridinium bromide (L1–Br)

2-(Aminomethyl)-pyridine (237 mg, 2.2 mmol) was dissolved in ethyl acetate (40 mL), to which a 5% aqueous Na\(_2\)CO\(_3\) solution (40 mL) was added. The biphasic mixture was cooled to 0 ºC and 2-bromoethyl phenanthridinium bromide (700 mg, 1.91 mmol) was added. The above reaction mixture was allowed to warm to room temperature and under stirring for 2 h. The organic layer was separated, washed with water and transferred to a separate round bottomed flask covered with aluminium foil, to which N-bromosuccinimide (NBS, 373 mg, 2.1 mmol) was added. The reaction was then stirred for another 1 h, during which time a white precipitate formed. The precipitate was isolated by filtration and recrystallised from MeOH to give

Fig. 8 Schematic representations of the reported compounds 1–6, grouped by their intermolecular interactions in the crystalline phase.
L1 (681 mg, 91%) as a white powder. 1H NMR (δ, DMSO-400 MHz): δ 4.434 (t, 2 H, J = 10.4 Hz), 4.855 (t, 2 H, J = 10.6 Hz), 5.579 (s, 2 H), 7.453 (t, 1 H, J = 6.0 Hz), 7.639 (t, 1 H, J = 7.6 Hz), 7.710 (m, 2 H), 7.789 (d, 1 H, J = 8.0 Hz), 7.861 (t, 1 H, J = 7.8 Hz), 7.983 (t, 1 H, J = 7.7 Hz), 8.073 (t, 1 H, J = 7.7 Hz), 8.384 (d, 1 H, J = 8.4 Hz), 8.600 (d, 1 H, J = 4.3 Hz), 8.720 (d, 1 H, J = 8.8 Hz), 8.860 (d, 1 H, J = 8.3 Hz), 9.190 (s, 1 H). 13C NMR (DMSO, 100 MHz): δ 46.25 (CH2), 52.13 (CH2), 54.25 (CH2), 115.39 (Cq), 116.05 (CH), 119.95 (Cq), 122.45 (CH), 123.53 (CH), 123.93 (CH), 124.13 (CH), 125.42 (CH), 125.77 (CH), 129.14 (CH), 131.46 (CH), 132.67 (Cq), 134.71 (Cq), 135.30 (CH), 138.26 (CH), 149.13 (CH), 153.64 (Cq), 154.07 (Cq). ESI-MS (positive mode): 312.3 (M+).

Synthesis of 2,3-dihydro-1-(4-pyridyl-methyl)-imidazo[1,2-f]phenanthridinium bromide (L2Br)

The synthetic procedure is similar to that of L1. Yield 86%. 1H NMR (δ, DMSO-400 MHz): δ 4.404 (t, 2 H, J = 10.8 Hz), 4.851 (t, 2 H, J = 9.6 Hz), 5.508 (s, 2 H), 7.636 (d, 2 H, J = 6.7 Hz), 7.700 (m, 3 H), 7.905 (t, 1 H, J = 7.2 Hz), 8.102 (d, 2 H, J = 8.0 Hz), 8.474 (d, 1 H, J = 6.8 Hz), 8.649 (d, 1 H, J = 6.4 Hz), 8.799 (t, 1 H, J = 4.8 Hz); 13C NMR (DMSO, 100 MHz): δ 46.38 (CH2), 52.06 (CH2), 52.58 (CH2), 115.34 (Cq), 116.03 (CH), 120.07 (Cq), 121.52 (CH), 124.00 (CH), 124.29 (CH), 125.48 (CH), 127.23 (CH), 129.28 (CH), 131.55 (CH), 132.79 (Cq), 134.91 (Cq). ESI-MS (positive mode): 312.3 (M+).

Synthesis of compound 1

L1-Br (100 mg, 0.25 mmol) dissolved in 5 mL of MeOH was added dropwise to a solution of CuBF42-6H2O (175 mg, 0.5 mmol) in 5 mL of MeOH. A colour change of the solution was observed from originally transparent blue to dark green. A few drops of dilute Et3N (triethylamine) in 10 mL of MeOH was added. The solution was filtered and dark green crystals were formed after slow evaporation. Yield: 35 mg (0.018 mmol, 37%). The ligand (30 mg) was dissolved in MeOH (30 mL), to which a methanolic solution of NaBPh4 (10 mL) was added. A small amount of precipitates was filtered and slow evaporation of the filtrate resulted in the formation of white crystals of L1-BPH4.

Synthesis of compound 2

L1-Br (100 mg, 0.25 mmol) in 5 mL of MeOH was added to Cu(NO3)2-3H2O (123 mg, 0.5 mmol) in 10 mL of MeOH. A colour change of the solution was observed from an opaque, straw yellow colour to a transparent bright green solution. The solution was filtered and the filtrate was allowed to evaporate slowly, yielding well formed green grass crystals suitable for X-ray single crystal diffraction measurement. Yield: 55 mg (0.092 mmol, 37%).

for Cu(L1)Br2(NO3)3 (CuC21H18Br2N2O3; 597.7 g mol−1): C 42.20, H 3.04, N 9.37; Found C 41.72, H 2.94, N 9.04. IR (KBr, cm−1): 1609.1 (s), 1573.1 (s), 1551.0 (s), 1309.2 (w), 780.5 (w), 761.5 (s), 743.4 (m), 720.3 (w), 682.2 (m).

Synthesis of compound 3

L1-Br (100 mg, 0.25 mmol) in 5 mL of MeOH was added dropwise to a solution of CuBr2 (113.8 mg, 0.5 mmol) in 10 mL of MeOH. Colour change was observed from a transparent blue to a dark brown solution, from which a dark brown precipitate was formed. The solution was filtered and the filtrate was allowed to evaporate slowly yielding more of the dark crystalline powder, which was isolated by filtration and combined with the previous sample. The precipitate was dried under vacuum and recrystallization of the product from a MeOH/MeCN (2:1) led to the brown crystals. Yield: 54 mg (0.088 mmol, 35%).

Synthesis of compound 4

L1-Br (100 mg, 0.25 mmol) in 5 mL of MeOH was added to Cu(NO3)2-3H2O (123 mg, 0.5 mmol) in 5 mL of MeOH, to which NaN3 (132.5 mg, 2.0 mmol) was added dropwise. The solution was cooled down to room temperature and filtered. Slow evaporation of the filtrate led to the formation of brown crystals. Yield: 33 mg (0.033 mmol, 26%).

Synthesis of compound 5

L1-Br (50 mg, 0.13 mmol) in 5 mL of MeOH was added to Cu(NO3)2-3H2O (61 mg, 0.25 mmol) in 5 mL of MeOH, to which NaSCN (82.7 mg, 1.02 mmol) was added dropwise. The colour of the solution changed from green to brown and some brown precipitates were formed after stirring for 30 min. The solution was heated to 50 °C and 15 mL of DMF was added to aid solvation. The solution was cooled down to room temperature and filtered. Slow evaporation of the filtrate resulted in the formation of brown crystals. Yield: 17 mg (0.016 mmol, 25%).

Synthesis of compound 6

L2-Br (200 mg, 0.51 mmol) was dissolved in MeOH. This solution was added dropwise to a solution of CuBr2 (110 mg, 0.39 mmol) in 5 mL of MeOH. A colour change of the solution was observed from a straw yellow colour to a transparent deep brown solution, from which a dark brown precipitate was formed. The solution was filtered and the filtrate was allowed to evaporate slowly, yielding well formed dark brown crystals suitable for X-ray single crystal diffraction measurement. Yield: 54 mg (0.092 mmol, 37%).
0.51 mmol) in MeOH and dark green precipitates were produced immediately. The precipitate was collected, dried and suspended in MeOH, to which water was added until the suspension was dissolved forming a pale green solution. This solution was filtered and yellow crystals suitable for X-ray diffraction measurement were formed after slow evaporation of the filtrate for two weeks. Yield: 136 mg (0.13 mmol, 26%).

X-Ray crystal structure determination

Suitable single-crystals of $\text{L1-BPh}_4$ and complexes 1–6 were mounted onto the end of a thin glass fiber using Formblin oil. X-Ray diffraction intensity data were measured at 273 K for compound 3 and 100 K for other compounds on a Nonius Kappa-CCD diffractometer ($\lambda$(Mo Kα) = 0.7107 Å). Structure solution and refinement were carried out with SHELXS-97 and SHELXL-97 via WinGX.30 Corrections for incident and diffracted beam absorption effects were applied using empirical31 or numerical methods.32 All structures were solved by a combination of direct methods and difference Fourier synthesis and refined against $F^2$ by the full-matrix least-squares technique. See Table 2 for a summary of the crystallographic parameters.

Acknowledgement

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Table 2 X-ray crystallographic data of compounds 1–6 and L1

| Compound | Formula | $M_{r}$/g mol$^{-1}$ | Crystal system | Space group | $a$/Å | $b$/Å | $c$/Å | $\beta$/° | $\gamma$/° | $\rho$/g cm$^{-3}$ | $\mu$/Mo | $Z$ | $T$/K | No. rflns (measd) | No. rflns (indep) | No. rflns (obsd) | $R_1$ ($I > 2\sigma(I)$) | $wR2$ (all data) |
|----------|---------|------------------|---------------|------------|------|------|------|-----------|--------|------------------|-------|-----|------|-----------------|----------------|----------------|------------------|----------------|------------------|
| Compound 1 | Ca$_4$H$_7$Br$_5$CuF$_{10}$N$_{12}$ | 1899.04 | Monoclinic | $P2_1/c$ | 28.53(2) | 8.854(5) | 11.867(4) | 97.265(8) | 100.00(2) | 1.636 | 1.934 | 2 | 100 | 23213 | 4747 | 3725 | 0.0590 | 0.1137 |
| Compound 2 | Ca$_4$H$_7$Br$_5$Cu$_2$N$_4$O$_3$ | 597.75 | Triclinic | $P-1$ | 8.2201(6) | 11.6779(7) | 13.477(5) | 90.00(2) | 90.00(2) | 1.843 | 4.756 | 2 | 100 | 16793 | 3787 | 3088 | 0.0425 | 0.1056 |
| Compound 3 | Ca$_3$H$_8$Br$_5$Cu$_3$N$_3$ | 615.65 | Triclinic | $P-1$ | 100.746(3) | 76.612(3) | 104.342(8) | 90.00(2) | 90.00(2) | 1.912 | 6.637 | 4 | 273 | 5690 | 4038 | 2906 | 0.0810 | 0.2489 |
| Compound 4 | Ca$_3$H$_8$Cu$_2$N$_2$ | 1004.03 | Monoclinic | $C2/c$ | 78.007(2) | 100.370(7) | 90.00(2) | 116.81(3) | 118.61(5) | 1.601 | 1.508 | 4 | 100 | 18504 | 3981 | 2959 | 0.0381 | 0.0885 |
| Compound 5 | Ca$_3$H$_8$Cu$_2$N$_1$O$_6$S$_4$ | 1078.28 | Monoclinic | $P-1$ | 107.690(11) | 2139.1(12) | 4164.3(4) | 1187.40(16) | 3936.1(4) | 1.731 | 1.126 | 4 | 100 | 18035 | 3771 | 2813 | 0.0455 | 0.1210 |
| Compound 6 | Ca$_3$H$_8$Br$_5$Cu$_2$N$_1$O$_2$ | 1025.96 | Monoclinic | $C2/c$ | 107.690(11) | 2139.1(12) | 4164.3(4) | 1187.40(16) | 3936.1(4) | 1.731 | 1.126 | 4 | 100 | 13804 | 3771 | 2813 | 0.0553 | 0.1513 |
| L1 | Ca$_3$H$_8$BN$_3$ | 631.59 | Monoclinic | $P2_1/n$ | 107.690(11) | 2139.1(12) | 4164.3(4) | 1187.40(16) | 3936.1(4) | 1.731 | 1.126 | 4 | 100 | 13804 | 3771 | 2813 | 0.0466 | 0.1334 |

References