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 $Cu(BF_4)_2$ (compound **1**), $Cu(NO_3)_2$ (compound **2**), $CuBr_2$ (compound **3**), $Cu(NO_3)_2$ and NaN_3 (compound **4**), $Cu(NO_3)_2$ and NaSCN (compound **5**) with **L1**·**Br** and $CuBr_2$ 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 $CuBr_2$, in which the copper(II) ion adopts a tetrahedral geometry with a $CuNBr_3$ coordination motif. With $Cu(BF_4)_2$, two $\mathbf{L1}^+$ cations and two bromide anions chelate the copper ion giving a CuN_2Br_2 motif, while the BF_4^- is present as a non-coordinating counterion. With $Cu(NO_3)_2$, a five coordinated copper complex is obtained whereas when bridging ligands such as NaN_3 and NaSCN are added into the reaction mixture of **L1**·**Br** and $Cu(NO_3)_2$, two novel dinuclear copper coordination cores of $[Cu_2(\mu_{1,1}\text{-}N_3)_2(N_3)_4]^{2-}$ and $Cu(CH_3O)_2(SCN)_4]^{2-}$ 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 set 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] for instance. Also, this type of potential tunability is interesting given the various applications of copper complexes in fields such as catalysis,[5] nucleic acid research[6] and magnetochemistry.[7]

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,[8] 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.[9] 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.[10]

We have recently developed a simple, one-pot, three-step reaction for the synthesis of a new class of phenanthridinium derivatives (Scheme 1).[11] 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,[12,13] DNA drug targeting applications[14,15] and DNA probes.[16] 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.[17] 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-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**) 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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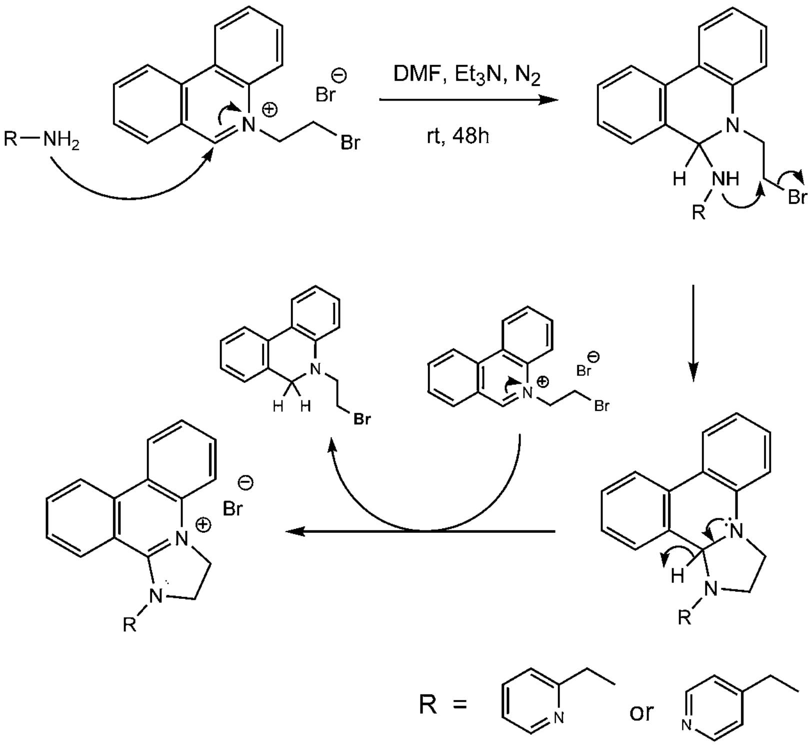


Scheme 1 One-pot synthetic pathway leads to the new heteroaromatic frameworks of L1·Br and L2·Br.

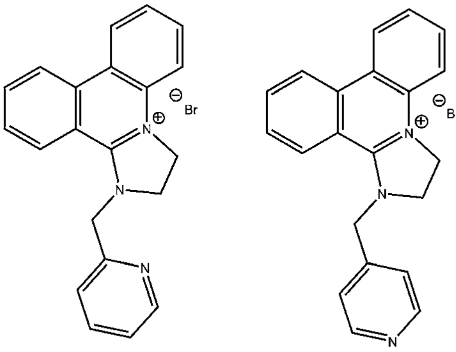
reported and the influence of both the anionic counterions and the intermolecular interactions on the final structure of the assemblies is discussed.

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,[11] 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·BPh_4, which crystallizes from methanol in a monoclinic $P2_1/n$ system. The asymmetric unit of the crystal structure includes one DIP cation and one BPh_4^- 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 $Cu(BF_4)_2 \cdot 6\,H_2O$. The asymmetric unit of compound **1** contains a $[Cu_{0.5}Br(\mathbf{L1\text{-}Br_{0.05}})]^+$ with the chelating ligand partially brominated at C4 position, an



Scheme 2 Molecular structures of 2,3-dihydro-1-(2-pyridyl-methyl)-imidazo[1,2-*f*]phenanthridinium bromide (**L1·Br**, left) and 2,3-dihydro-1-(4-pyridyl-methyl)-imidazo[1,2-*f*]phenanthridinium bromide (**L2-Br**, right).

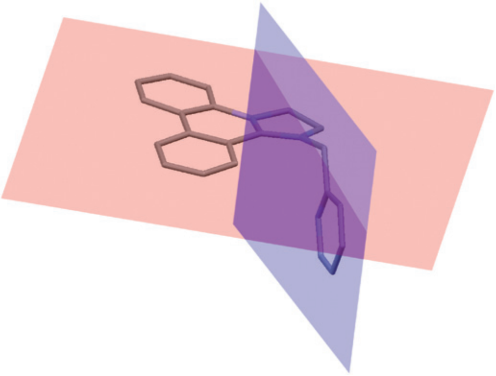


Fig. 1 Crystal structure of **L1·BPh4** shows the almost perpendicular arrangement of the planes of the pyridyl and DIP moieties. The BPh_4^- counterion has been omitted for clarity.

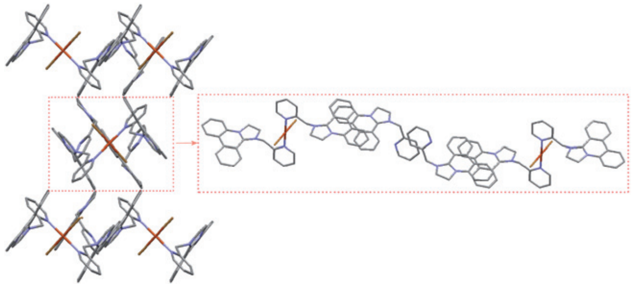


Fig. 2 Crystal structure of compound **1** shows π–π interactions between the phenanthridinium moieties of adjacent molecules forming 1D supramolecular chains through the crystal structure. The structure is viewed along the crystallographic *a* (left) and *b* (right) axes, and the counter ions are omitted for clarity.

uncoordinated **L1-Br$_{0.45}$** molecule which has been partially brominated on C25 position and two BF_4^- anions as non-coordinating counterions. The crystal structure shows that the copper(II) ion is coordinated by two **L1-Br$_{0.05}$** and two bromides, resulting in a CuN_2Br_2 donor set with a square-planar geometry (Cu–N distance = 1.959(4) Å and Cu–Br distance = 2.4534(1) 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_2Br_2 donor set. The pyridine ring forms about 82.56° dihedral angle with the DIP plane, while the two DIP planes from two coordinated **L1-Br$_{0.05}$** are almost parallel to each other with a dihedral angle of around 5.62°. Compound **1** forms supramolecular chains in the crystalline phase *via* π–π stacking interactions between the DIP 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 π–π stacking interactions of the pyridyl section of the ligand ($d_{\pi-\pi}$ = 3.444 Å).

Recent work by Houser[18] *et al* has introduced the concept of a new four coordinate geometry index, τ_4, which is similar in principle to the standard τ_5 used to describe trigonal distortion of a five coordinate species from square pyramidal geometry.[19] Like τ_5, τ_4 is defined using the two largest θ 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 τ_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 **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 uncordinated **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 BF_4^- to NO_3^-, compound **2** has been obtained with a copper(II) centre surrounded by a $CuBr_2NO_2$ donor set, of which two bromide anions come from **L1·Br** (see Fig. 3), so that compound **2** can be formulated as [Cu(NO$_3$)Br$_2$**L1**]. The compound crystallises in a triclinic *P*-1 system and the copper(II) center is five coordinate with an almost ideal square pyramidal geometry (the parameter τ_5,[19] which is used to describe the percentage of trigonal distortion from square pyramidal geometry, is 0.28 for the copper ion (τ_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**

L1	C13 1.338(3)	N1 C1 1.392(3)	C13 N1 C1 125.0(2)	C13 N1 C14 111.2(2)	C1 N1 C14 123.2(2)
	C14 1.480(3)	N2 C13 1.337(3)	C13 N2 C16 130.1(2)	C13 N2 C15 110.5(2)	C16 N2 C15 119.4(2)
	C16 1.451(3)	N2 C15 1.458(3)	C17 N3 C21 116.3(3)		
	C17 1.321(3)	N3 C21 1.340(4)			
Compound 1	Cu1 N3 1.959(4)	Cu1Br1 2.4534(14)	N3Cu1 N3 180.0(1)	N3 Cu1 Br1 90.80(14)	N3 Cu1 Br1 89.20(14)
			N3 Cu1 Br1 89.20(14)	N3 Cu1 Br1 90.80(14)	Br1 Cu1 Br1 180.00(9)
Compound 2	Cu1 N3 1.986(4)	Cu1 O2 1.989(4)	N3 Cu1 O2 160.8(18)	N3 Cu1 Br2 90.64(12)	O2 Cu1 Br2 94.22(12)
	Cu1 O3 2.492(4)	Cu1 Br2 2.4035(9)	N3 Cu1 Br1 92.79(12)	O2 Cu1 Br1 90.14(12)	Br2 Cu1 Br1 156.40(4)
	Cu1 Br1 2.4097(8)		N4 O2 Cu1 103.4(3)		
			N4 O2 Cu1 103.4(3)		
Compound 3	Cu1 N3 2.024(15)	Cu1 Br3 2.363(3)	N3 Cu1 Br3 133.6(5)	N3 Cu1 Br1 97.6(4)	Br3 Cu1 Br1 101.6(12)
	Cu1 Br1 2.394(3)	Cu1 Br2 2.402(3)	N3 Cu1 Br3 133.6(5)	Br3 Cu1 Br2 99.33(10)	Br1 Cu1 Br2 133.01(15)
	Cu2 N6 2.019(16)	Cu2 Br5 2.334(3)	N3 Cu1 Br2 97.5(5)	N6 Cu2 Br6 97.1(5)	Br5 Cu2 Br6 100.18(12)
	Cu2 Br6 2.400(4)	Cu2 Br4 2.409(3)	N6 Cu2 Br4 97.5(5)	Br5 Cu2 Br4 101.28(12)	Br6 Cu2 Br4 133.79(14)
Compound 4	Cu N10 1.981(3)	Cu N7 1.987(2)	N10 Cu N7 94.82(10)	N10 Cu N4 91.23(10)	N7 Cu N4 166.98(10)
	Cu N4 2.027(2)	Cu N4 2.055(2)	N10 Cu N4 159.90(10)	N7 Cu N4 91.30(10)	N4 Cu N4 79.30(10)
	Cu N3 2.294(2)		N10 Cu N3 107.40(10)	N7 Cu N3 92.83(9)	N4 Cu N3 96.35(9)
			N4 Cu N3 91.36(9)		
Compound 5	Cu N3 2.010(6)	Cu N3 2.010(6)	N3CuN3 176.3(4)	N3 Cu Br1 88.13(19)	Br1 Cu Br2 129.00(3)
	Cu Br1 2.4888(18).	Cu Br2 2.5709(12)	N3 Cu Br2 94.3(2)	N3 Cu Br2 88.1(2)	Br1 Cu Br2 129.00(3)
	Cu Br2 2.5709(12)	N1 C13 1.350(10	N3 Cu Br2 88.1(2)	N3 Cu Br2 94.3(2)	Br1 Cu Br2 129.00(3)
			Br2 Cu Br2 101.99(6)		
Compound 6	Cu N3 2.010(6)	Cu Br1 2.4888(18)	N3 Cu N3 176.3(4)	N3 Cu Br1 88.13(19)	N3 Cu Br1 88.13(19)
	Cu Br2 2.5709(12)		N3 Cu Br2 94.3(2)	N3 Cu Br2 88.1(2)	Br1 Cu Br2 129.00(3).
			N3 Cu Br2 88.1(2	N3 Cu Br2 94.3(2)	Br2 Cu Br2 101.99(6)

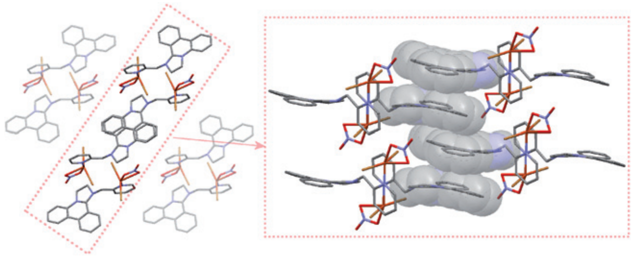


Fig. 3 The crystal structure of compound **2** shows the view along the crystallographic *a* axis (left) and the π–π stacking interactions of the DIP moieties (right).

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 $CuBr_2NO_2$ 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 **L1**·**Br** and **L2**·**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$(Br)_3$($\mathbf{L2}_2$)]Br·H_2O and crystallises from a monoclinic *C*2/*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°; τ_4 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 **L2**$^+$ cations and three bromide anions are bound to the copper(II) center, resulting in a trigonal bipyramidal geometry (τ_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 **L2**$^+$ 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 **L2**·**Br** is connected to the *para*-position nitrogen donor of the pyridine ring. After complexation, there is enough space for two **L2**$^+$ cations to chelate. In the case of **L1**·**Br**, the phenanthridium plane is linked in the *ortho*-position and the steric effect is more pronounced when **L1**$^+$ 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

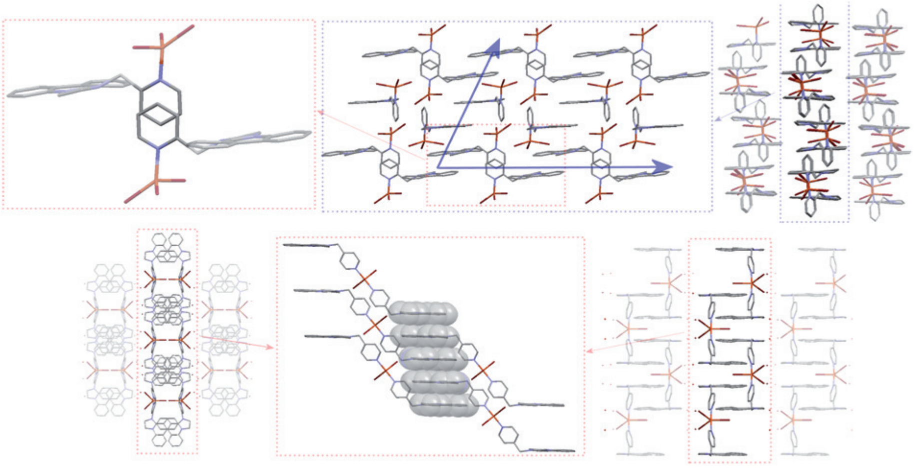


Fig. 4 (Top) Crystal structure of compound **3** shows the 'Dimers' formed by π-stacking of the pyridyl moieties (left), the stacking of the DIP moieties through the structure viewed along the crystallographic *a* axis with 2-D nature (middle) and a view of the 'sheets' that these interactions produce (right). (Bottom) Crystal structure packing of compound **6** along the crystallographic *c* (left), *b* (middle) and *a* (right) axes with the stacking of the DIP moieties

together are solely between the DIP moieties of the two coordinated ligand molecules in a ladder-like arrangement, and the pyridyl π 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 $[Cu(N_3)_3(\mathbf{L1})]_2$ where the crystal structure has a C_2 axis symmetry, resulting in the *cis* conformation of two coordinated $\mathbf{L1}^+$ 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_5 donor set with a distorted square pyramidal geometry (τ_5 = 0.12). The dinuclear copper ions with a Cu–Cu distance of 3.143(2) Å are bridged by a $\mu_{1,1}$-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)° (see Table 1). The two pyridine rings are almost parallel to each other with a dihedral angle of around 4.01°. 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° and the DIP regions of the molecules exhibit π–π interactions with neighbouring complexes 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(μ-methoxo)-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 (τ_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.

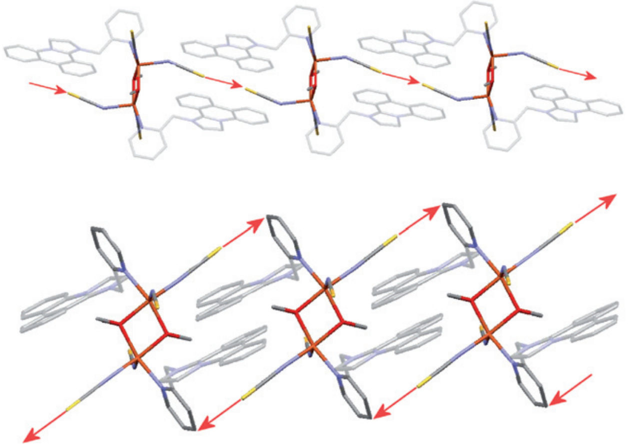


Fig. 6 Crystal structure of compound **6** shows that S–S interactions between adjacent thiocyanate ligands (top) and S–π interactions between thiocyanate ligands and the coordinated pyridyl regions of the DIP ligand (bottom).

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 π system of the pyridyl region of the ligand on an adjacent molecule with a distance of around 3.320 Å. Such sulfur–π interactions are important in biological systems.[27]

Along with these sulfur-based interactions the molecular packing is further stabilised by extensive interactions between the π–π systems of the coordinated ligand (see Fig. 7). CH–π 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 π–π stacking with another DIP region

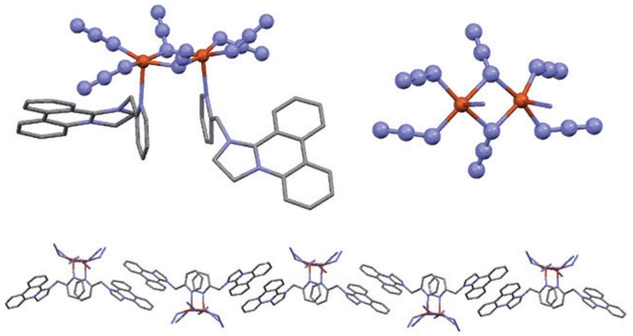


Fig. 5 The asymmetric unit of the crystal structure of compound **4** (top left). The dinuclear core of the structure (top right) and a view of the molecular packing showing the alternating arrangement of adjacent molecules and the π–π stacking of the DIP moieties.

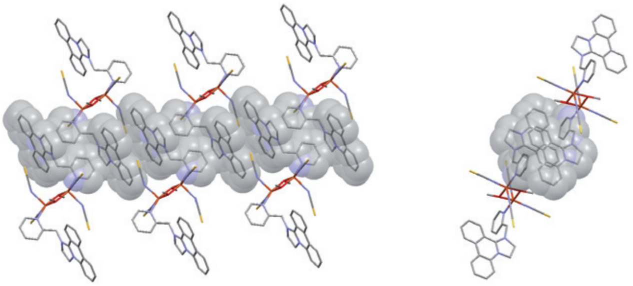


Fig. 7 The crystal structure of compound **5** shows π–π interactions between DIP regions and the complimentary CH–π interactions between pyridyl and DIP regions. Viewed along the crystallographic *a* (left) and *c* (right) axes.

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 synthesised 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.

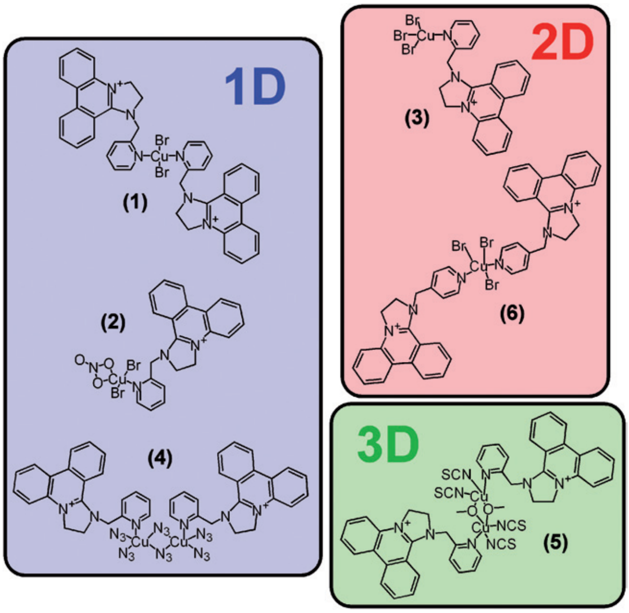


Fig. 8 Schematic representations of the reported compounds **1**–**6**, grouped by their intermolecular interactions in the crystalline phase.

In all cases, the DIP moiety is quite rigid and only the pyridine nitrogen is involved in the coordination. With $\text{Cu(BF}_4)_2$, the copper ion is coordinated by two **L1**$^+$ DIP moieties through pyridine nitrogen and two Br^- anions coming from the ligand source, while the $\text{BF}_4{}^-$ remains a noncoordinating counterion. With CuBr_2, bromide anions appear to coordinate with Cu(II) centre and an interesting tetrhedral geometry is observed around Cu(II) ion. With $\text{Cu(NO}_3)_2$, 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 $\text{N}_3{}^-$ and SCN^- was added to the mixture of **L1·Br** and $\text{Cu(NO}_3)_2$, 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 $\text{BF}_4{}^-$ 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_2CO_3 solution (40 mL) was added. The biphasic mixture was cooled to 0 °C 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

L1 (681 mg, 91%) as a white powder. ^{1}H NMR (d_6-DMSO, 400 MHz): δ 4.443 (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 = 8.3 Hz), 8.860 (d, 1 H, J = 8.3 Hz); ^{13}C NMR (DMSO, 100 MHz): δ 46.25 (CH_2), 52.13 (CH_2), 54.25 (CH_2), 115.39 (Cq), 116.05 (CH), 119.95 (Cq), 122.45 (CH), 123.53 (CH), 123.93 (CH), 124.13 (CH), 125.42 (CH), 127.57 (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^+). Calcd for L1·Br ($C_{21}H_{18}BrN_3$): C 64.30, H 4.62, N 10.71; Found C 64.26, H 4.44, N 10.21. The ligand (30 mg) was dissolved in MeOH (30 mL), to which a methanolic solution of $NaBPh_4$ (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-BPh_4.

Synthesis of 2,3-dihydro-1-(4-pyridyl-methyl)-imidazo[1,2-*f*] phenanthridinium bromide (L2·Br)

The synthetic procedure is similar to that of L1. Yield 86%. ^{1}H NMR (d_6-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 Hz), 7.700 (m, 3 H), 7.905 (t, 1 H, J = 7.2 Hz), 8.102 (t, 2 H, J = 8 Hz), 8.474 (d, 1 H, J = 8 Hz), 8.649 (d, 1 H, J = 6 Hz), 8.799 (t, 1 H, J = 8 Hz); ^{13}C NMR (DMSO, 100 MHz): δ 46.38 (CH_2), 52.06 (CH_2), 52.58 (CH_2), 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), 135.37 (CH), 144.16 (Cq), 150.09 (CH), 154.10 (Cq). ESI-MS (positive mode): 312.2 (M^+). Calcd for L2·Br ($C_{21}H_{18}BrN_3$): C 64.30, H 4.62, N 10.71; Found C 64.54, H 4.40, N 10.47.

Synthesis of compound 1

L1·Br (100 mg, 0.25 mmol) dissolved in 5 mL of MeOH was added dropwise to a solution of $Cu(BF_4)_2·6\ H_2O$ (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 Et_3N (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, 30%). Calcd for $[Cu(L1\text{-}Br_{0.05})_2Br_2](L1\text{-}Br_{0.45})_2(BF_4)_4$ ($CuC_{84}H_{71}B_4Br_3F_{16}N_{12}$; 1899.0 g mol^{-1}): C 53.13, H 3.77, N 8.85; Found C 52.87, H 3.33, N 8.97. IR (KBr, cm^{-1}): 1578.4 (s), 1555.3 (s), 1434.8 (s), 1359.6 (m), 1307.5 (s), 1056.8 (vs), 749.2 (m), 716.4 (w), 670.1 (w), 521.6 (w).

Synthesis of compound 2

L1·Br (100 mg, 0.25 mmol) in 5 mL of MeOH was added to $Cu(NO_3)_2·3\ H_2O$ (123 mg, 0.5 mmol) in 10 mL of MeOH. A colour change 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 grass green crystals suitable for X-ray single crystal diffraction measurement. Yield: 55 mg (0.092 mmol, 37%). Calcd for $Cu(L1)Br_2(NO_3)$ ($CuC_{21}H_{18}Br_2N_4O_3$; 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}): 1608.3 (s), 1577.5 (s), 1428.0 (s), 1282.4 (s), 1014.4 (w), 760.8 (s), 717.4 (m), 670.1 (w).

Synthesis of compound 3

L1·Br (100 mg, 0.25 mmol) in 5 mL of MeOH was added dropwise to a solution of $CuBr_2$ (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%). Calcd for $Cu(L1)Br_3$ ($CuC_{21}H_{18}N_3Br_3$; 615.6 g mol^{-1}): C 40.97, H 2.95, N 6.83; Found C 40.75, H 2.78, N 6.64. IR (KBr, cm^{-1}): 3433.6 (m), 1609.1 (s), 1573.1 (s), 1551.0 (s), 1309.2 (w), 780.5 (w), 761.5 (m), 743.6 (m), 720.3 (w), 668.2 (m).

Synthesis of compound 4

L1·Br (100 mg, 0.25 mmol) in 5 mL of MeOH was added to $Cu(NO_3)_2·3\ H_2O$ (123 mg, 0.5 mmol) in 5 mL of MeOH, to which NaN_3 (132. 5 mg, 2.0 mmol) was added dropwise. The colour of the solution changed from green to brown and 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 led to the formation of brown crystals. Yield: 33 mg (0.033 mmol, 26%). Calcd for $Cu_2(L1)_2(N_3)_6$ ($Cu_2C_{42}H_{36}N_{24}$; 1003.9 g mol^{-1}): C 50.24, H 3.61, N 33.48; Found C 49.95, H 3.27, N 33. 70. IR (KBr, cm^{-1}): 3427.4 (w), 2125.2 (s), 2101 (s), 1625.3 (s), 1436.0 (w), 1625.6 (s), 1296.2 (w), 1273.7 (w), 694.9 (m).

Synthesis of compound 5

L1·Br (50 mg, 0.13 mmol) in 5 mL of MeOH was added to $Cu(NO_3)_2·3\ H_2O$ (61 mg, 0.25 mmol) in 5 mL of MeOH, to which NaSCN (82.7 mg, 1.02 mmol) was added. The colour of the solution was changed from green to brown and some brown precipitates were formed. Several drops of Et_3N were added till the solution colour became blue green and the solution was filtered. Slow evaporation of the solution resulted in the formation of green crystals suitable for X-ray diffraction measurement. Yield: 17 mg (0.016 mmol, 25%). Calcd for $Cu_2(L1)_2(NCS)_4(OCH_3)_2$ ($Cu_2C_{48}H_{42}N_{10}O_2S_4$; 1046.3 g mol^{-1}) (the crystallized MeOH is lost during the elemental analysis measurement): C 55.10, H 4.00, N 13.39; Found C 55.03, H 3.51, N 13.20. IR (KBr, cm^{-1}): 3429.5 (m), 2077.2 (vs), 1598.7 (m), 1576.7 (s), 1554.6 (m), 1433.6 (w), 1305.6 9 m), 749.7 (m), 713.3 (w), 662.7 (w).

Synthesis of compound 6

L2-Br (200 mg, 0.51 mmol) was dissolved in MeOH. This solution was added dropwise to a solution of $CuBr_2$ (110 mg,

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

	Compound **1**	Compound **2**	Compound **3**	Compound **4**	Compound **5**	Compound **6**	**L1**
Formula	$C_{84}H_{71}B_4Br_3CuF_{16}N_{12}$	$C_{21}H_{18}Br_2CuN_4O_3$	$C_{21}H_{18}Br_3CuN_3$	$C_{42}H_{36}Cu_2N_{24}$	$C_{49}H_{46}Cu_2N_{10}O_3S_4$	$C_{42}H_{38}Br_4CuN_6O$	$C_{45}H_{38}BN_3$
M_r/g mol^{-1}	1899.04	597.75	615.65	1004.03	1078.28	1025.96	631.59
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	P-1	P-1	$C2/c$	P-1	$C2/c$	$P2_1/n$
a/Å	28.553(2)	8.8546(5)	11.867(4)	31.917(2)	9.2344(7)	13.1236(6)	10.3685(7)
b/Å	8.2201(6)	11.6779(7)	13.477(5)	8.5868(5)	11.5240(9)	22.2503(11)	18.5863(11)
c/Å	16.7163(13)	12.0660(7)	14.980(5)	15.9626(10)	12.4542(9)	13.7765(1)	18.5508(11)
α/°	90	63.335(3)	106.773(8)	90	65.526(3)	90	90
β/°	100.746(3)	76.612(3)	104.342(8)	107.844(2)	88.615(3)	101.917(2)	104.445(3)
γ/°	90	78.007(3)	100.370(8)	90	80.281(3)	90	90
V/Å^3	3854.7(5)	1076.90(11)	2139.1(12)	4164.3(4)	1187.40(16)	3936.1(4)	3461.9(4)
Z	2	2	4	4	1	4	4
ρ/g cm^{-3}	1.636	1.843	1.912	1.601	1.508	1.731	1.212
μ(Mo Kα)/mm^{-1}	1.934	4.756	6.637	1.089	1.126	4.658	0.07
T/K	100	100	273	100	100	100	100
No. rflns (measd)	23213	16793	5690	18504	18035	13804	45379
No. rflns (indep)	4747	3787	4038	3981	3771	2829	4248
No. rflns(obsd)	3725	3088	2906	2959	2813	2157	2842
$R1$ ($I > 2\sigma(I)$)	0.0590	0.0425	0.0810	0.0381	0.0455	0.0553	0.0466
$wR2$ (all data)	0.1137	0.1056	0.2489	0.0885	0.1210	0.1513	0.1334

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%). Calcd for [Cu(Br)$_3$(**L2**)$_2$]Br·H$_2$O ($C_{42}H_{38}Br_4CuN_6O$; 1025.9 g mol^{-1}): C 49.17, H 3.73, N 8.19; Found C 49.25, H 3.88, N 8.61. IR (KBr, cm^{-1}) 3432.2 (m), 1612.4(m), 1597.9 (m), 1578.5 (s), 1549.7 (w), 1459.3 (w), 1424.6(m), 1306.8 (m), 755.7 (w), 718.1(w).

X-Ray crystal structure determination

Suitable single-crystals of **L1**·**BPh$_4$** and complexes **1**–**6** were mounted onto the end of a thin glass fiber using Fomblin 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 [λ(Mo Kα) = 0.7107 Å]. Structure solution and refinement were carried out with SHELXS-97[28] and SHELXL-97[29] *via* WinGX.[30] Corrections for incident and diffracted beam absorption effects were applied using empirical[31] 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.

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