What is the coordination number of copper(II) in metallosupramolecular chemistry?

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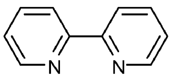
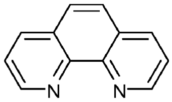
Analysis of structural and solution data shows a specific stabilisation of copper(II) in ternary complexes containing one 2,2′:6′,2″-terpyridine and one 2,2′-bipyridine ligand. This is not a general phenomenon relating to five-coordinate copper(II), but rather a specific consequence of the two ligand donor sets. The consequences of this observation for metallosupramolecular chemistry are discussed.

Introduction

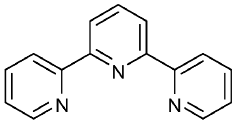
Metallosupramolecular chemistry utilises the interaction of specific metal-binding domains with appropriate metal centres for the construction of complex functional structures.[1] The methodology is frequently quantified in terms of algorithms based upon the preferred coordination numbers and geometries of metal ions and the denticity and organised or preorganised arrangement of donor sets in ligands.[1,2] In many cases, the coordination requirements of metal ions are relatively precisely defined and the ligand donor sets are strictly predefined. Oligopyridine metal-binding domains are very popular in metallosupramolecular chemistry as the molecules are readily prepared in reasonable quantities using well-established methodology.[3,4] When metal ions such as ruthenium(II) interact with oligopyridine metal-binding domains, there is a reasonable expectation that a six-coordinate pseudooctahedral structure will result. Similarly, the interaction of oligopyridines with copper(I) centres is expected to result in local pseudotetrahedral coordination environments. These strong preferences for particular geometries and coordination numbers have been widely-utilised in metallosupramolecular chemistry. A disadvantage of using metal ions with such strong preferences for particular coordination environments is that ligand design must become rather more precise. In contrast, the use of metal centres with variable coordination geometries and coordination numbers, or indeed with no strong preference for any particular geometry, allows for less precisely optimised ligands to be used. This is effectively utilising fuzzy logic for processing the metal–ligand interaction data by allowing partial set membership (different coordination numbers) rather than crisp set membership or non-membership.[5]



bpy



phen



tpy

In recent years, there has been a trend to introduce new metal centres to metallosupramolecular systems and to investigate the consequences of redox transformations at specific metal ions. In particular, dynamic behaviour initiated by copper(II)–copper(I) redox changes has been elegantly used by Sauvage and co-workers for the design of molecular machines.[6] The Sauvage systems incorporate bidentate phen and terdentate tpy metal-binding domains and show a swing from four-coordinate {M(phen)$_2$} to five-coordinate {M(phen)(tpy)} coordination environments upon oxidation of copper(I) to copper(II). Observations of this type have led to a more general and uncritical assumption that the favoured coordination number of copper(II) is five. In the course of our use of metal ions to assemble unnatural modified oligonucleotides[7] we have reassessed the data relating to copper(I) and copper(II) centres in supramolecular chemistry. The aim of this short article is to critically assess whether copper(II) has, in general, a favoured coordination number of five for use in metallosupramolecular chemistry and, in particular, if there is a preference for the specific {M(phen)(tpy)} or {M(bpy)(tpy)} environment.

Results and discussion

The abbreviations bpy, tpy and phen have their conventional meanings; the use of the italicised terms *bpy*, *tpy* or *phen* refers to bpy, tpy or phen metal-binding domains—*i.e.* substituted derivatives or sub-domains within polytopic ligands.

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Analysis of solid state structural data

What is the commonest coordination number of copper(II)?

The question of coordination number in copper(II) complexes is far from simple and the consequences of Jahn–Teller and related distortions have been discussed in detail elsewhere.[8] However, in terms of statistical simplicity it is reasonable to ask how many copper(II) complexes of a particular coordination number are to be found in the CSD (Cambridge Structural Database)—with the *caveat* that species with a purely inorganic constitution will be omitted and that the definition of coordination number is often somewhat in the eye of the beholder. Nevertheless, with these cautionary notes, using the default radii (r_{cov}: Cu, 1.52 Å; N, 0.68 Å; O, 0.68 Å; F, 0.64 Å; r_{vdW}: Cu, 1.40 Å; N, 1.55 Å; O, 1.52 Å; F, 1.47 Å) and definitions of coordination number, the CSD contains 4649 copper(II) complexes with coordination number four, 6501 with coordination number five and 4513 with coordination number six. It appears, on the basis of the structural data within the CSD, that copper(II) exhibits a slight preference for a coordination number of five, but that this is by no means overwhelming. It is relevant to note that a slight expansion (0.1 Å) in the coordination sphere of the copper(II) reveals additional interactions tending towards a six-coordinate geometry and that a significant number of these "five-coordinate" complexes show a longer sixth interaction in a position that approximately describes an octahedral arrangement of donors.

Having made this observation, it is relevant to restrict the discussion to a particular class of ligands of importance in metallosupramolecular chemistry, the oligopyridines.

Is six-coordinate copper(II) with six pyridine donors expected?

Implicit in the formation of five-coordinate complexes with $[\text{Cu}(bpy)(tpy)]^{2+}$ or $[\text{Cu}(phen)(tpy)]^{2+}$ motifs when copper(II) is presented with *tpy* and *bpy* or *phen* ligands, is an inherent preference over the alternative $[\text{Cu}(bpy)_n]^{2+}$, $[\text{Cu}(phen)_n]^{2+}$ or $[\text{Cu}(tpy)_2]^{2+}$ (n = 2 or 3) motifs. A search of the CSD for all compounds containing a copper coordinated to six pyridine ligands yielded a total of 52 hits. Unfortunately, no salts of the "parent" complex cation $[\text{Cu(py)}_6]^{2+}$ have been structurally characterised. Refinement of the 52 hits into those of mononuclear compounds containing oligopyridines yielded 16 examples of $[\text{Cu}(phen)_3]^{2+}$, 8 examples of $[\text{Cu}(bpy)_3]^{2+}$ and 10 examples of $[\text{Cu}(tpy)_2]^{2+}$ complexes. The $[\text{Cu}(tpy)_2]^{2+}$ cations possess an idealised $D_{2\text{d}}$ symmetry in which, in contrast to O_h symmetry, the $\text{d}_{x^2-y^2}$ and d_{z^2} orbitals are not degenerate—although the bond lengths to the central and terminal rings of the *tpy* ligands are unequal, this is a ligand-imposed constraint although further modulation of the bond through second-order or pseudo-Jahn–Teller effects is possible.[9] As expected, the Cu–N$_{\text{central}}$ distances are shorter (range 1.915–2.025 Å, mean 1.9793 Å) than the Cu–N$_{\text{terminal}}$ bond lengths (range 2.059–2.335 Å, mean 2.180 Å) and the local symmetry is often considerably lower than $D_{2\text{d}}$. The commonest distortion involves a twisting of the least squares planes of the individual *tpy* ligands about the N$_{\text{central}}$–Cu–N$_{\text{central}}$ axis and observed (smallest) angles ϕ between the least squares planes range from 74.93° to the ideal 90° (Fig. 1). The definition of a least squares plane of the *tpy* is not entirely innocent, as in some cases the ligands are considerably riffled.

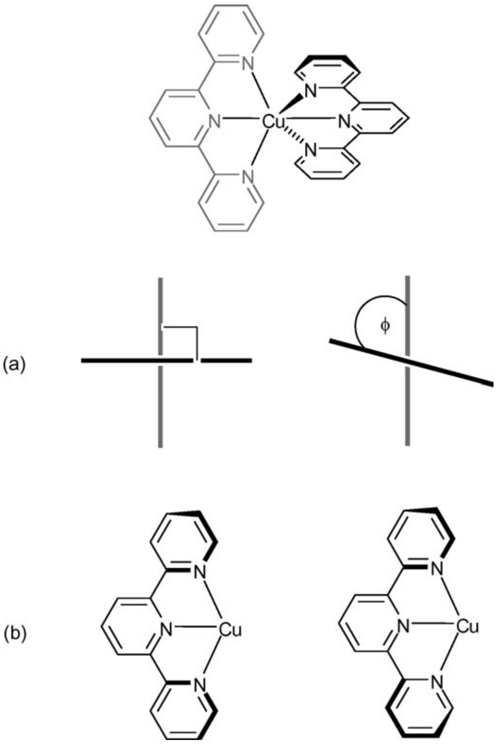
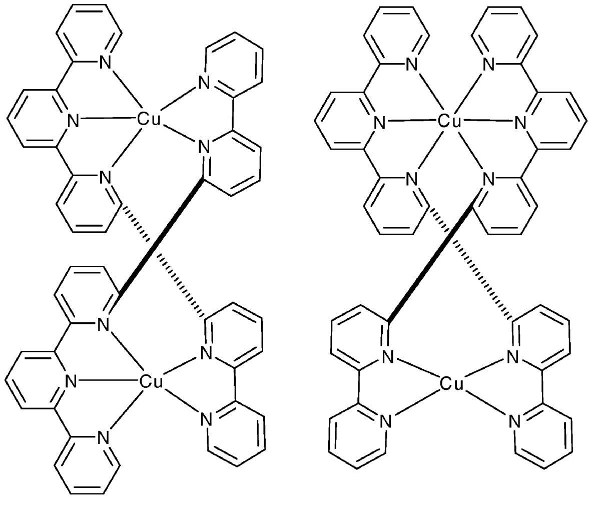


Fig. 1 Distortions within {Cu(*tpy*)$_2$} motifs commonly include (a) flattening arising by rotation about the N$_{\text{central}}$–Cu–N$_{\text{central}}$ axis and (b) non-planarity of individual *tpy* rings.

The case of $[\text{Cu}(phen)_3]^{2+}$ and $[\text{Cu}(bpy)_3]^{2+}$ cations is marginally more complex, as in this case the idealised symmetry of the cation is D_3. On changing from O_h symmetry to D_3, the $\text{d}_{x^2-y^2}$ and d_{z^2} orbitals remain as a degenerate e set, although the $\text{t}_{2\text{g}}$ is split into e and a levels. Accordingly, one expects Jahn–Teller effects to be observed in $[\text{Cu}(phen)_3]^{2+}$ and $[\text{Cu}(bpy)_3]^{2+}$ cations. The majority of the structurally characterised $[\text{Cu}(bpy)_3]^{2+}$ complexes exhibit a typical tetragonal elongation with Cu–N$_{\text{axial}}$ distances in the range 2.221–2.519 Å and Cu–N$_{\text{equatorial}}$ distances in the range 2.020–2.086 Å. In two cases, a moderate[10] or pronounced[11] tetragonal compression is observed; the latter effect is of particular interest as it involves the sterically more demanding 5,5′-dimethyl-2,2′-bipyridine ligand and illustrates the critical influence of detailed ligand structure upon the microscopic detail of coordination geometry. The $[\text{Cu}(phen)_3]^{2+}$ structural data closely parallel those for $[\text{Cu}(bpy)_3]^{2+}$ with the majority of the cations exhibiting a tetragonal elongation but again with two examples of a tetragonal compression.[12,13]

The data for $[\text{Cu}(bpy)_3]^{2+}$, $[\text{Cu}(phen)_3]^{2+}$ and $[\text{Cu}(tpy)_2]^{2+}$ complexes show clearly that there is no inherent destabilisation of the CuN_6 environment with such ligands. Although the complexes do not exhibit regular octahedral symmetry, the Cu–N bond distances are all within the usually accepted limits.

Rather more interesting are the cases of dinuclear helicates which have been reported for higher oligopyridines[3a,14–16] in which the donor sets are partitioned into bpy or tpy metal-binding domains (Fig. 2). $2,2':6',2'':6'',2''':6''',2''''$-



[5+5] [6+4]

Fig. 2 The two possible double helicates from the interaction of two 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridines with two copper(II) centres. The ligands are each partitioned into a bpy and tpy domain and in the [5 + 5] helicate each metal centre is in a {Cu(*bpy*)(*tpy*)} environment whereas in the (observed) [4 + 6] helicate there is one $\{Cu(bpy)_2\}$ and one $\{Cu(tpy)_2\}$ centre.

Quinquepyridines can partition the five donor atoms into a *tpy* and a *bpy* set and dinuclear double helicates $[Cu_2(qpy)_2]^{n+}$ (n = 3 or 4) contain ten nitrogen donors which could be distributed in two {Cu(*tpy*)(*bpy*)} motifs to give a [5 + 5] helicate or one $\{Cu(bpy)_2\}$ and one $\{Cu(tpy)_2\}$ domain in a [4 + 6] helicate. As expected on the basis of charge distribution at the metal centres, mixed oxidation state copper(II,I) helicates always partition the donor sets to generate [4 + 6] helicates with $\{Cu^{II}(tpy)_2\}$ and $\{Cu^{I}(bpy)_2\}$ domains, and with no ancillary ligands involved.[17–21] Uncritical acceptance of the view that copper(II) prefers a five-coordinate environment might lead one to expect a [5 + 5] helicate structure for dicopper(II) complexes with *qpy* ligands. In practice, dicopper(II) helicates adopt the [4 + 6] structure with $\{Cu(bpy)_2\}$ and $\{Cu(tpy)_2\}$ domains,[17,18,22] although the coordination number at the $\{Cu(bpy)_2\}$ domain is increased to five or six by interaction with acetate counterions.

Further evidence for the stability of CuN_6 environments in metallosupramolecular systems comes from the structures of dinuclear complexes with 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2⁗′-sexipyridines or spaced bis(2,2′:6′,2″-terpyridine) ligands which contain two $\{Cu(tpy)_2\}$ domains.[23,24]

Is there evidence for five-coordinate copper(II) with five pyridine donors?

Having established above that there is ample structural evidence for the formation of stable complexes with six-coordinate CuN_6 centres with pyridine donors, the related question about evidence for five-coordinate copper(II) complexes with CuN_5 centres with pyridine donors becomes relevant. Surprisingly, the CSD only contains a total of 11 compounds defined with five-coordinate copper(II) centres and five pyridine donors. Seven of these compounds contain oligopyridines: three with $\{Cu(phen)_2(py)\}$ domains,[24–27] one with a $\{Cu(bpy)_2(py)\}$ domain,[28] and, most relevantly, three with {Cu(*tpy*)(*bpy*)} domains.[29] A five-coordinate {Cu(*tpy*)(*bpy*)} centre is expected to adopt a local C_{2v} symmetry with the *tpy* and *bpy* domains orthogonal to one another. The detailed analysis of the solid state data reveals a number of interesting features. The copper(II) centre in $[Cu(phen)_2(3,5\text{-}Me_2py)][ClO_4]_2$ is accurately described as five-coordinate on the basis of there only being five donor atoms within 3.5 Å of the metal.[25] However, the distribution of the five donors maps well onto the two axial and three of the four equatorial sites of an octahedron, with the 3,5-Me_2py and one of the phen nitrogen atoms occupying the axial sites. The octahedral frame arises from the bond angles within the coordination sphere, with $\angle N_{ax}$–Cu–N_{ax}' 159.46°, $\angle N_{ax}$–Cu–N_{eq} 89.5, 92.75 and 100.19°, $\angle N_{phen\ eq}$–Cu–$N_{phen\ eq}$ 170.27° and phen bite angles 77.09 and 81.26°, and the coordination geometry is accurately described as square-based pyramidal. The remaining equatorial site is protected partially by H2 of the 3,5-Me_2py ligand but the oxygen of a perchlorate counterion is found at a distance of 3.653 Å with $\angle O\cdots$Cu–$N_{phen\ eq}$ 162.53°. Although there is rather severe disorder of the anions, a very similar arrangement occurs in $[Cu(phen)_2(py)][ClO_4]_2$[26] with $\angle N_{ax}$–Cu–N_{ax} 160.84°, $\angle N_{ax}$–Cu–N_{eq} 89.97, 93.76 and 108.37°, $\angle N_{phen\ eq}$–Cu–$N_{phen\ eq}$ 176.06° and phen bite angles 79.21 and 81.88°. In this case, the coordination sphere of the copper is completed by an oxygen atom at 3.079 Å with $\angle O\cdots$Cu–$N_{phen\ eq}$ 166.02°. The analogous bpy complex $[Cu(bpy)_2(py)][PF_6]_2\cdot 0.5py$[28] is also best described as octahedral with Cu–N bonds of 2.001–2.251 Å and a Cu···F interaction of 2.855 Å. The Cu···F interaction is *trans* to the longer Cu–N bond with $\angle F\cdots$Cu–N′ 167.85°. The only compound in this series which can genuinely be described as five-coordinate is $[Cu(phen)_2(4\text{-}NH_2py)][PF_6]_2\cdot Me_2CO$[26] which has a CuN_5 coordination environment very similar to the compounds discussed above (Cu–N_{ax} 1.998 and 2.003 Å, $\angle N_{ax}$–Cu–N_{ax} 172.44° and $\angle N_{eq}$–Cu–N_{eq} 93.20, 117.36 and 149.42°) but with the closest atoms in the coordination void being fluorines at 3.659 and 3.702 Å.

Three compounds possessing {Cu(*tpy*)(*bpy*)} centres have been described, with varying patterns of peripheral methyl group substitution.[29] The compounds are remarkably similar and the structural features are conveniently discussed together. In each case, the apparent CuN_5 coordination geometry is described as a square-based pyramid with the *tpy* and one of the *bpy* donors making the basal plane (Cu–N_{bpy} 1.984–1.998 Å, Cu–$N_{tpy\ terminal}$ 2.022–2.049 Å and Cu–$N_{tpy\ central}$ 1.924–1.926 Å) and the remaining *bpy* nitrogen axial (Cu–N_{bpy} 2.180–2.189 Å). However, as in the cases discussed above, the description is not so simple and the coordination geometry can just as well be described as octahedral with a CuN_5F donor set in which the remaining axial site is occupied by the fluorine of a hexafluorophosphate counterion (Cu···F 2.823, 2.890 and 2.990 Å; $\angle F\cdots$Cu–N_{ax} 165.82, 166.19 and 168.77°) (Fig. 3).

In conclusion, an analysis of apparently five-coordinate complexes containing CuN_5 coordination geometries with pyridine donors reveals a tendency to adopt square-based pyramidal structures which exhibit additional strong interactions to form quasi-octahedral systems. In the light of these

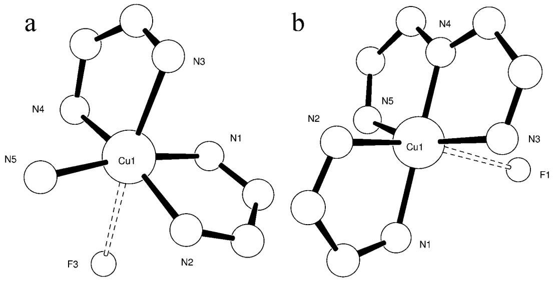


Fig. 3 The detailed coordination geometry around the "five-coordinate" complexes (a) $[Cu(bpy)_2(py)][PF_6]_2 \cdot 0.5py$[28] in which the equatorial plane is defined by N1, N2, N4 and N5 and with Cu···F 2.855 Å and (b) $[Cu(4,4'\text{-}Me_2bpy)(tpy)][PF_6]_2 \cdot MeCN$[29] in which the axial direction is defined by N2 and F1 with Cu···F 2.823 Å. Chelating ligands are represented by minimal skeletal atoms and pyridine by just the nitrogen atom.

data, in which weakly coordinating anions such as hexafluorophosphate occupy axial sites, it is very dangerous to assume that, in solution, complexes of apparent {Cu(*tpy*)(*bpy*)} stoichiometry are actually five-coordinate. It is also noteworthy that the C_{2v} symmetry expected for simple $\{Cu(tpy)X_2\}$ species is not observed.

What are the geometrical preferences of $\{Cu(tpy)X_n\}$ complexes?

Is there something special about a copper(II) centre with a *tpy* ligand coordinated to it that particularly favours the formation of five-coordinate complexes? In contrast to the strong tendency to show a weak sixth interaction in the {Cu(*tpy*)(*bpy*)} complexes discussed above, the case of $\{Cu(tpy)X_n\}$ species is rather different. All of the 17 examples of copper(II) complexes with a tpy ligand and two halogen ligands are five-coordinate with a geometry close to square-based pyramidal. Only in one case, that of $[Cu(tpy)(3\text{-}Mepy)(BF_4)][BF_4]$, is there an additional sixth contact (Cu–F 2.394 Å, Cu···F 2.847 Å).[30]

Behaviour in solution

Schubert *et al.* have shown that the only isolated solid state products from the reaction of one equivalent of *tpy* and one equivalent of *bpy* with copper(II) salts are five- or six-coordinate {Cu(*tpy*)(*bpy*)} species.[29] It is relevant to ask whether the solution speciation also favours the formation of the heteroleptic complexes.

The most relevant study is that by Rizzarelli and co-workers who made ESR spectroscopic and potentiometric studies of the copper(II)–bpy–tpy–H_2O system.[31] The ESR spectrum of the 1 : 1 : 1 ternary complex is compatible with a square-pyramidal geometry (although this does not necessarily preclude a weakly bound water ligand in the sixth coordination site). The ternary complex is found to be significantly more stable than the 1 : 1 and 1 : 2 complexes with bpy or tpy. The stabilisation of the ternary complex is both entropic and enthalpic.

From where does the stability of the copper(II) ternary complex arise? Analysis of the literature data reveals a somewhat surprising origin. Using consistent values (aqueous, 298 K, ~0.1 M electrolyte) of log β_2 for bpy (13.60[32,33]) and tpy (19.1[34]) complexes of copper(II) and taking the log *K* value of 17.51[31] for the formation of the ternary $[Cu(tpy)(bpy)]^{2+}$ species the eqn (1)–(3) may be combined to give eqn (4).

$$Cu^{2+} + 2bpy = [Cu(bpy)_2]^{2+} \; \log K = 13.6, \quad \Delta G = -77.9 \text{ kJ mol}^{-1} \tag{1}$$

$$Cu^{2+} + 2tpy = [Cu(tpy)_2]^{2+} \; \log K = 19.1, \quad \Delta G = -109.0 \text{ kJ mol}^{-1} \tag{2}$$

$$Cu^{2+} + tpy + bpy = [Cu(bpy)(tpy)]^{2+} \; \log K = 17.51, \quad \Delta G = -99.9 \text{ kJ mol}^{-1} \tag{3}$$

$$2[Cu(bpy)_2]^{2+} + 2[Cu(tpy)_2]^{2+} = [Cu(bpy)(tpy)]^{2+} \quad \Delta G = -12.9 \text{ kJ mol}^{-1} \tag{4}$$

The thermodynamic stability of the ternary $[Cu(bpy)(tpy)]^{2+}$ arises from the relative instability of the 2 : 1 bpy complex.

Finally, we may make a comment on the consequences of changing oxidation state. This is of particular relevance to our studies of oligonucleotides which are modified to bind copper(I) in aqueous conditions. The most important observation stems from the classical work of Williams and James[33] who demonstrated that (i) copper(I) complexes of 6,6-disubstituted *bpy* or 2,9-disubstituted *phen* ligands did not disproportionate in aqueous conditions and (ii) the introduction of these substituents dramatically stabilised the copper(I) complexes with respect to the copper(II) (log β_2 for 6,6′-Me_2bpy with copper(II) and copper(I) as 7.48 and 15.8, respectively). The order of stability constants is inverted for the parent bpy ligand, with log β_2 for bpy with copper(II) and copper(I) as 13.1 and 13.6, respectively.[33] These observations have far reaching consequences for metallosupramolecular chemistry: firstly, in Sauvage's[6] heteroditopic *bpy–tpy* ligands the change in coordination to $\{Cu^{I}(bpy)_2\}$ motifs from $\{Cu^{II}(tpy)(bpy)\}$ upon reduction is a natural and inevitable consequence and, secondly, treatment of oligonucleotides modified with 6,6′-disubstituted *bpy* or 2,9-disubstituted *phen* ligands with either copper(II) or copper(I) in aqueous conditions leads to copper(I) complexes.[7] It does not necessarily follow that other donor sets will stabilise copper(I) or five-coordinate copper(II).

Conclusions

In this paper, we have made a detailed analysis of the coordination behaviour of copper(II) in supramolecular systems. An analysis of the solid state data in the Cambridge Structural Database reveals that four-, five- and six-coordinate complexes are all common. The favoured coordination number is six, although the consequences of ligand asymmetry and Jahn–Teller related effects mean that this usually comprises one or two less strongly bound ligands. Limiting the discussion to the specific case of oligopyridine ligands, solid state and solution studies reveal a special stability of ternary $[Cu(tpy)(bpy)]^{2+}$ complexes, although it is unclear whether, in solution, these species are five- or six-coordinate. This is a specific stabilisation resulting from the (*tpy*)(*bpy*) donor set and cannot be extended to a general statement about the favoured coordination number of copper in metallosupramolecular systems.

Experimental

All crystallographic data were obtained by searching the Cambridge Structural Database (CSD)[35] of the Cambridge Crystallographic Data Centre (CCDC) using CONQUEST version 1.8[36] and version 5.27 of the CSD update through May 2005. Metrical data were extracted using the program VISTA[37] and transferred to Excel for data analysis. This latter procedure allowed the manual addition of metrical data for compounds for which data had not been lodged with the CCDC—in such cases, the original literature was consulted and wherever possible the data incorporated.

Acknowledgements

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