ChemComm

Accepted Manuscript

ChemComm

Chemical Communications

www.rsc.org/chemcomm

Volume 46 | Number 32 | 28 August 2010 | Pages 5813–5976

ISSN 1359-7345

RSCPublishing

COMMUNICATION
J. Fraser Stoddart et al.
Directed self-assembly of a
ring-in-ring complex

FEATURE ARTICLE
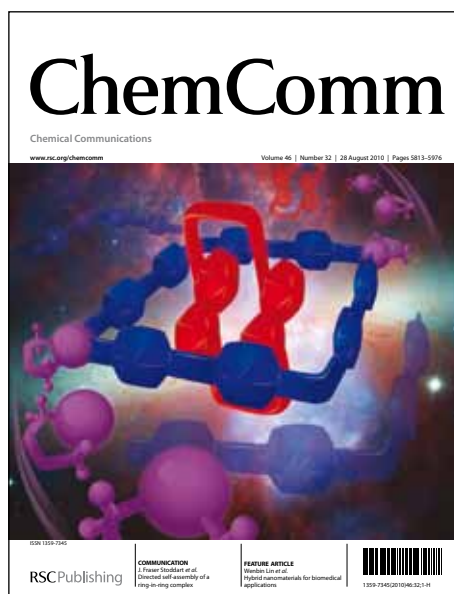Wenbin Lin et al.
Hybrid nanomaterials for biomedical
applications

1359-7345(2010)46:32;1-H

This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

RSCPublishing

www.rsc.org/chemcomm
Registered Charity Number 207890

Journal Name

Dynamic Article Links ▶

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Suppression of the Jahn-Teller Distortion in a Six-Coordinate Copper(II) Complex by Doping it into a Host Lattice†

Rebecca Docherty[a], Floriana Tuna[a], Colin A. Kilner[b], Eric J. L. McInnes[a],*** and Malcolm A. Halcrow[b],*

The electronic structures of $[Cu(terpy)_2]^{2+}$ and $[Cu(bpp)_2]^{2+}$ (bpp = 2,6-di[pyrazol-1-yl]pyridine) are different, when doped into $[M(bpp)_2][BF_4]_2$ ($M^{2+} = Fe^{2+}$ or Zn^{2+}). The $[Cu(terpy)_2]^{2+}$ dopant is a typical pseudo-Jahn-Teller
10 elongated copper(II) center. However, the $[Cu(bpp)_2]^{2+}$ sites show EPR spectra consistent with a tetragonally compressed $\{d_{z^2}\}^1$ configuration.

Like the vast majority of six-coordinate copper(II) complexes,[1,2] compounds of the $[CuL_2]^{2+}$ type (L = 2,2':6',2''-terpyridine
15 [terpy] or a related tridentate ligand)[3,4] adopt (pseudo)-Jahn-Teller elongated structures, with $\{d_{y^2-z^2}\}^1$ electron configurations‡. This corresponds to a structural elongation along one of the two equivalent distal N–Cu–N axes in the coordination sphere (structure A, Scheme 1). However, some years ago we
20 reported that this Jahn-Teller distortion in $[Cu(bpp)_2]^{2+}$ (bpp = 2,6-di[pyrazol-1-yl]pyridine]; Scheme 1, R = H) can be quenched by sterically bulky 'R' ligand substituents, leading to a change in electronic ground state from $\{d_{y^2-z^2}\}^1$ to $\{d_{z^2}\}^1$ that is easily detected by EPR (structure B, Scheme 1) ‡,¶.[5,6] This change in
25 ground state can also be effected in other, stereochemically comparable copper(II) complexes by steric protection;[7] by ligand conformational strain;[7] or by tuning the basicities of the ligand donor atoms.[8] These are still the only molecular copper(II) centers known to exhibit such a quenched Jahn-Teller effect¶,
30 although it is also observed in a small number of inorganic lattices under ambient conditions, or under pressure.[2,9]

More recently, we have shown that $[M(terpy)_2]^{2+}$ ($M^{2+} = Ru^{2+}$ [10] or Co^{2+} [11]) can be co-crystallised with the spin-crossover material $[Fe(bpp)_2][BF_4]_2$, yielding solid solutions that combine
35 the functionalities of the two precursor complexes. Thus, for example, the metal centres in $[Co(terpy)_2]_x[Fe(bpp)_2]_{1-x}[BF_4]_2$ (x = 0.03-0.23) show allosteric behavior, with the cobalt sites undergoing spin-crossover in concert with the iron host lattice.[11,12] We were therefore interested to examine whether
40 copper(II) dopants in $[Fe(bpp)_2][BF_4]_2$ and related host lattices would be similarly sensitive to their environment. The use of EPR-active probes to monitor spin-crossover is well-established. This is usually done by following changes in the zero-field splitting of Mn^{2+} dopant ions during the spin-transition,[13,14]
45 although Cu^{2+} [14,15] and Co^{2+} [16] probe ions have also been used on occasion. As a result of this investigation, we have found that the electronic structure of $[Cu(bpp)_2]^{2+}$ centers diluted into host lattices is unexpectedly complicated.

A
$\{d_{y^2-z^2}\}^1$

B
$\{d_{z^2}\}^1$
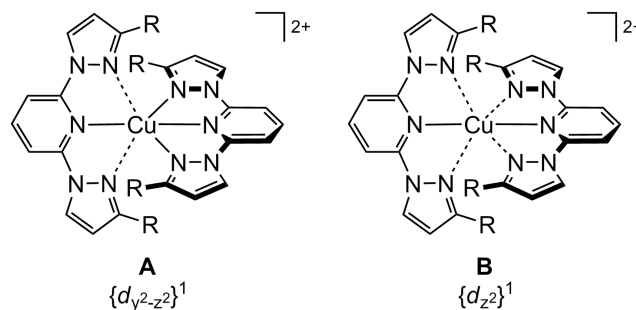
50 **Scheme 1** The structures and ground-state configurations adopted by $[Cu(bpp)_2]^{2+}$ (R = H; structure A) and its derivatives $[Cu(L^R)_2]^{2+}$ (R = Ph, Mes; structure B)‡,¶.[5-7] Short and long Cu–N bonds are indicated by solid and dashed lines, respectively.

55 The following solid solutions were prepared, by crystallising the appropriate mole ratios of the preformed precursors[5,17,18] from nitromethane/diethyl ether: $[Cu(terpy)_2]_y[M(bpp)_2]_{1-y}[BF_4]_2$ (M^{2+} = Fe^{2+} [**1a**] and Zn^{2+} [**1b**]) and $[Cu_yM_{1-y}(bpp)_2][BF_4]_2$ ($M^{2+} = Fe^{2+}$
60 [**2a**] and Zn^{2+} [**2b**]) §,‖. The stoichiometry y in each sample was determined by elemental microanalysis as 0.03-0.04, while X-ray powder diffraction confirmed that the solid solutions are isostructural with the pure $[M(bpp)_2][BF_4]_2$ host lattices (ESI†). As in our earlier work,[10,11] ES mass spectrometry and ^{1}H NMR
65 showed no evidence for ligand exchange between the metal centers in the mixed-ligand materials **1a** and **1b**. The homogeneity of the composition and structure of these materials is difficult to confirm when y is small. Importantly, however, there is no evidence of heterogeneous copper(II) sites in the EPR
70 data from **1a** and **1b** described below, which are consistent with the sole presence of $[Cu(terpy)_2]^{2+}$ centers in those samples. The iron centers in **1a** and **2a** undergo the expected, abrupt high/low spin-transition at 260 K. The transition for **2a** retains the 3-4 K thermal hysteresis loop exhibited by pure $[Fe(bpp)_2][BF_4]_2$,[17] but
75 the hysteresis for **1a** is narrower at <2 K (ESI†).

The X-band (9.5 GHz) EPR spectra of **1a** and **1b** were as expected for a typical pseudo-Jahn-Teller elongated copper(II) center (structure A, Scheme 1), showing g_1 = 2.28-2.29, g_2 = 2.10, g_3 = 2.06-2.07 and $A_1\{^{63,65}Cu\}$ = 158-160 G (Fig. 1;
80 superhyperfine coupling to ^{14}N was also resolved at low temperatures). These values are similar to the EPR parameters of $[Cu(terpy)_2]^{2+}$ in frozen solutions.[20] In contrast to earlier reports,[14,15] cooling **1a** below its spin-transition temperature does not change the EPR linewidth, but does lead to small apparent

[journal], [year], **[vol]**, 00–00 | **1**

decreases in g_1 and g_3 (ESI†). These minor changes are not observed for **1b** under the same conditions, and so might be attributed to the effects of the change in crystal pressure in **1a** associated with the host lattice spin-transition. Be that as it may,
5 spin-crossover in $[Fe(bpp)_2][BF_4]_2$ clearly has a minimal effect on the electronic structure of the $[Cu(terpy)_2]^{2+}$ dopant in **1a**.

Unexpectedly, the X-band EPR spectra of **2a** and **2b** were very different from **1a** and **1b**, showing a stronger rhombicity and observable $A\{^{63,65}Cu\}$ hyperfine couplings in both the low-field
10 and high-field regions of the spectra (Fig. 1 and ESI†). This is inconsistent with the expected $\{d_{y2-z2}\}^1$ copper(II) centers previously observed in $[Cu(bpp)_2][BF_4]_2$ ‡, as a neat solid or in frozen solution.[5,18,21] Moreover, unlike **1a** and **1b**, these spectra showed a marked temperature dependence between 290-120 K.
15 Further clarity was obtained by measuring the spectra at Q-band (34 GHz), which clearly resolved the three components of the g tensor. Simulation of the X- and Q-band spectra yielded the parameters listed in Table 1. The two compounds behave similarly, in that g_1 and $A_1\{^{63,65}Cu\}$ increase, and g_2 and
20 $A_2\{^{63,65}Cu\}$ decrease, as the temperature is lowered to 150 K. The g and A values in Table 1 are comparable to other compounds of the $[Cu(L^R)_2]^{2+}$ type that adopt structure B (Scheme 1).[2,5,6] Moreover, a similar temperature-dependence has been observed in other structure B complexes. In at least one case, this was
25 caused by small structural perturbations about the copper ion

associated with an anion order:disorder transition.[8] Notably the temperature dependence of **2a** and **2b** is very similar, so the spin-transition in **2a** again does not have a detectable effect on the EPR parameters of its $[Cu(bpp)_2]^{2+}$ dopant.
35 Hence, the electronic structure of $[Cu(bpp)_2]^{2+}$ is strongly perturbed by doping into an isostructural $[M(bpp)_2][BF_4]_2$ ($M^{2+} =$ Fe^{2+} or Zn^{2+}) host lattice. In contrast, the structure of $[Cu(terpy)_2]^{2+}$ is essentially unaffected upon doping into $[M(bpp)_2][BF_4]_2$, or another $[M(terpy)_2]X_2$ salt ($M^{2+} \neq Cu^{2+}$, X^-
40 = anion).[4] The sensitivity of the electronic structure of a molecule of $[Cu(bpp)_2]^{2+}$ to its local environment is unprecedented in molecular chemistry. The most comparable literature system involves Cu^{2+} ions doped into binary metal oxides. Solid $(Cu,Mg)O$ contains typical $\{d_{x2-y2}\}^1$ copper centres, but $(Cu,Ca)O$
45 has a mixture of $\{d_{x2-y2}\}^1$ and $\{d_{z2}\}^1$ sites.[22] This was attributed to lattice strain associated with the larger metal sites in CaO, which would favour the longer average Cu–O bond length in a $\{d_{z2}\}^1$ configuration (structure B, Scheme 1). Such a steric argument

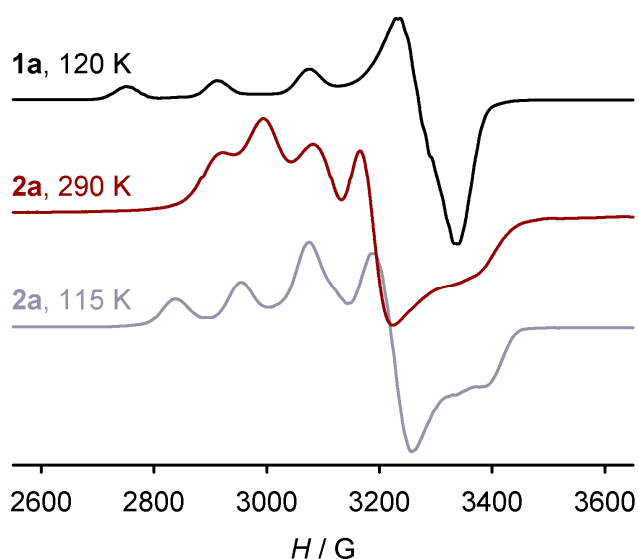**Fig. 1** X-band powder EPR spectra of $[Cu(terpy)_2]_y[Fe(bpp)_2]_{1-y}[BF_4]_2$ [**1a**] at 120 K (black, top); $[Cu_yFe_{1-y}(bpp)_2][BF_4]_2$ [**2a**] at 290 K (red,
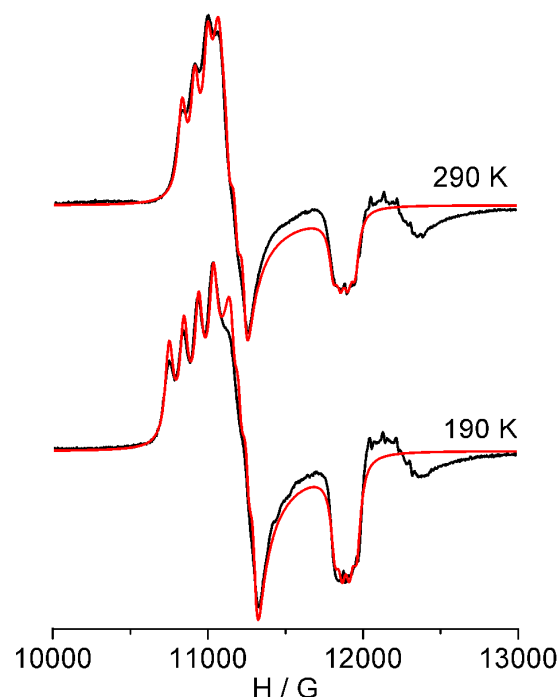30 centre); and **2a** at 115 K (grey, bottom).

50 **Fig. 2** Experimental (black) and simulated (red) Q-band EPR spectra of $[Cu_yZn_{1-y}(bpp)_2][BF_4]_2$ [**2b**]. The weak signal at g = 2.00 is not incorporated in the simulation, and arises from a Mn^{2+} impurity in the metal salt used to prepare the $[Zn(bpp)_2][BF_4]_2$ host lattice.

55 **Table 1** EPR parameters for the $[Cu_yM_{1-y}(bpp)_2][BF_4]_2$ solid solutions in this work, and for representative $[Cu(L^R)_2]^{2+}$ complexes (R = H $\{L^H = bpp\}$ or mesityl). Hyperfine couplings are to the $^{63,65}Cu$ nucleus. Data for $[Cu(bpp)_2][BF_4]_2$ are given in frozen solution, because its EPR spectra as a neat powder are complicated by Jahn-Teller disorder phenomena that are not quenched above 5 K.[18,21]

	Ground state‡	Phase	T / K	g_1	g_2	g_3	A_1 / G	A_2 / G	A_3 / G	Ref.
$[Cu(bpp)_2][BF_4]_2$	$\{d_{y2-z2}\}^1$	MeCN	120	2.281	2.099	2.051	137	–	–	17
$[Cu(L^{Mes})_2][ClO_4]_2$	$\{d_{z2}\}^1$	powder	115	2.248	2.145	2.015	105	–	100	5
2a	$\{d_{z2}\}^1$	powder	290	2.204	2.163	2.030	84	56	46	This work
	$\{d_{z2}\}^1$	powder	150	2.220	2.143	2.032	98	43	46	This work
2b	$\{d_{z2}\}^1$	powder	290	2.207	2.168	2.035	81	53	46	This work
	$\{d_{z2}\}^1$	powder	150	2.222	2.155	2.035	93	46	46	This work

cannot be applied to **2a** and **2b**, however, because the low-spin iron centres in **2a** below 260 K (ionic radius 75 pm) are smaller than the dopant copper ions (87 pm).

Rather, we attribute the properties of **2a** and **2b** to a combination of two factors. First, is the lower basicity of the distal pyrazole donor groups in $[Cu(bpp)_2]^{2+}$ compared to the distal pyridyl groups in $[Cu(terpy)_2]^{2+}$. The weaker N{pyrazole}→Cu dative bonding in $[Cu(bpp)_2]^{2+}$ will make structure B more accessible for that complex.[8] Second, is the near-axial symmetry of the metal sites in the $[M(bpp)_2][BF_4]_2$ (M^{2+} = Fe^{2+} or Zn^{2+}) host lattices. These are monoclinic with $a \approx b$ and $\beta \approx 90°$, and have near-regular D_{2d} site symmetry with no structural distortion at the molecular level.[17,18] The axial local environment about a dopant molecule would be strongly perturbed by the pseudo-Jahn-Teller elongation in structure A, but would be relatively unaffected by structure B. We conclude that the effectively axial lattice pressure in $[M(bpp)_2][BF_4]_2$ is insufficient to perturb the structure of a $[Cu(terpy)_2]^{2+}$ dopant, but does switch the electronic structure in $[Cu(bpp)_2]^{2+}$.

The authors thank Lesley Neve (University of Leeds) for the powder diffraction data, and Algy Kazlauciunas (University of Leeds) for the DSC measurements (ESI†). This work was funded by the EPSRC, the University of Manchester and the University of Leeds.

Notes and references

ªEPSRC National UK EPR Facility, School of Chemistry and Photon Science Institute, University of Manchester, Oxford Road, Manchester, UK M13 9PL. E-mail: eric.mcinnes@manchester.ac.uk; Fax: +44 161 275 4616; Tel: +44 161 275 4469.

ᵇSchool of Chemistry, University of Leeds, Woodhouse Lane, Leeds, UK LS2 9JT. E-mail: m.a.halcrow@leeds.ac.uk; Fax: +44 113 343 6565; Tel: +44 113 343 6506.

† Electronic Supplementary Information (ESI) available: Experimental details; X-ray powder diffraction and elemental microanalysis data; single crystal and EPR data for $[Cu(terpy)_2][BF_4]_2$; and descriptions of the spin-state transitions in **1a** and **2a**. CCDC 866481 and 866482. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/####.

‡ $[Cu(bpp)_2]^{2+}$ and $[Cu(terpy)_2]^{2+}$ are described as exhibiting a pseudo-Jahn-Teller effect, because the structural distortion does not occur along the unique symmetry axis of the molecule (in its undistorted form)¶.[2] Similarly, the electronic configuration of structure A (Scheme 1) is given as $\{d_{y^2-z^2}\}^1$ rather than $\{d_{x^2-y^2}\}^1$, because the structural elongation occurs along the molecular x-axis, rather than the unique symmetry axis z.

¶ Structure B in Scheme 1 is not a Jahn–Teller compression, because the e_g d-orbitals are not degenerate in the idealised D_{2d} symmetry of these complexes. Rather, it corresponds to a suppression of the pseudo-Jahn-Teller elongation in structure A.[2]

§ The salts $[Cu(terpy)_2][BF_4]_2$ and $[Zn(terpy)_2][BF_4]_2$ have not been published before. The copper salt crystallises in the monoclinic space group Cc, and is isostructural with other published $[M(terpy)_2][BF_4]_2$ salts (M = Co and Ru).[10,11] Its copper ions have a typical pseudo-Jahn-Teller elongated configuration, with the elongation axis crystallographically disordered in a similar manner to several other $[Cu(terpy)_2]^{2+}$ salts.[3,4] $[Zn(terpy)_2][BF_4]_2$ is isostructural with the copper complex by X-ray powder diffraction, but $[Fe(terpy)_2][BF_4]_2$[19] is not (ESI†).

‖ Solid solutions of composition $[Cu(bpp)_2]_y[M(terpy)_2]_{1−y}[BF_4]_2$ (M^{2+} = Fe^{2+} [**3a**] and Zn^{2+} [**3b**] §; y = 0.02-0.03) were also prepared, which were analytically pure but contained heterogeneous copper(II) sites by EPR that could not be unambiguously interpreted (ESI†).

1   M. A. Hitchman, *Comments Inorg. Chem.*, 1994, **15**, 197; L. R. Falvello, *J. Chem. Soc., Dalton Trans.*, 1997, 4463; B. Murphy and B. Hathaway, *Coord. Chem. Rev.*, 2003, **243**, 237.

2   M. A. Halcrow, *Dalton Trans.*, 2003, 4375 and refs. therein.

3   W. Henke and D. Reinen, *Z. Anorg. Allg. Chem.*, 1977, **436**, 187; R. Allmann, W. Henke and D. Reinen, *Inorg. Chem.*, 1978, **18**, 378.

4   J. V. Folgado, W. Henke, R. Allmann, H. Stratemeier, D. Beltrán-Porter, T. Rojo and D. Reinen, *Inorg. Chem.*, 1990, **29**, 2035.

5   N. K. Solanki, E. J. L. McInnes, F. E. Mabbs, S. Radojevic, M. McPartlin, N. Feeder, J. E. Davies and M. A. Halcrow, *Angew. Chem., Int. Ed.*, 1998, **37**, 2221.

6   A. J. Bridgeman, M. A. Halcrow, M. Jones, E. Krausz and N. K. Solanki, *Chem. Phys. Lett.*, 1999, **314**, 176; N. K. Solanki, M. A. Leech, E. J. L. McInnes, J. P. Zhao, F. E. Mabbs, N. Feeder, J. A. K. Howard, J. E. Davies, J. M. Rawson and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 2001, 2083.

7   J. M. Holland, X. Liu, J. P. Zhao, F. E. Mabbs, C. A. Kilner, M. Thornton-Pett and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 2000, 3316.

8   M. A. Halcrow, C. A. Kilner, J. Wolowska, E. J. L. McInnes and A. J. Bridgeman, *New J. Chem.*, 2004, **28**, 228 and 887 (correction); C. A. Kilner and M. A. Halcrow, *Acta Crystallogr., Sect. B*, 2010, **66**, 206.

9   F. Aguado, F. Rodríguez, R. Valiente, J. P. Itié and P. Munsch, *Phys. Rev. B*, 2004, **70**, 214104; F. Aguado, F. Rodríguez, R. Valiente, M. Hanfland and J. P. Itié, *J. Phys. Condens. Matter*, 2007, **19**, 346229.

10 C. A. Tovee, C. A. Kilner, J. A. Thomas and M. A. Halcrow, *CrystEngComm*, 2009, **11**, 2069.

11 M. A. Halcrow, *Chem. Commun.*, 2010, **46**, 4761.

12 G. Chastanet, C. A. Tovee, G. Hyett, M. A. Halcrow and J.-F. Létard, *Dalton Trans.*, in the press.

13 P. S. Rao, A. Reuveni, B. R. McGarvey, P. Ganguli and P. Gütlich, *Inorg. Chem.*, 1981, **20**, 204; A. Ozarowski, B. R. McGarvey, A. B. Sarkar and J. E. Drake, *Inorg. Chem.*, 1988, **27**, 628 and 2650 (correction); P. E. Doan and B. R. McGarvey, *Inorg. Chem.*, 1990, **29**, 874; R. C. W. Sung and B. R. McGarvey, *Inorg. Chem.*, 1999, **38**, 3644; H. Daubric, C. Cantin, C. Thomas, J. Kliava, J.-F. Létard and O. Kahn, *Chem. Phys.*, 1999, **244**, 75; H. Daubric, R. Berger, J. Kliava, G. Chastanet, D. Chasseau, O. Nguyen and J.-F. Létard, *Phys. Rev. B*, 2002, **66**, 054423.

14 A. Ozarowski and B. R. McGarvey, *Inorg. Chem.*, 1989, **28**, 2262; P. J. Kunkeler, P. J. van Koningsbruggen, J. P. Cornelissen, A. N. van der Horst, A. M. van der Kraan, A. L. Spek, J. G. Haasnoot and J. Reedijk, *J. Am. Chem. Soc.*, 1996, **118**, 2190.

15 W. Vreugdenhil, J. G. Haasnoot, O. Kahn, P. Thuéry and J. Reedijk, *J. Am. Chem. Soc.*, 1987, **109**, 5272.

16 M. Shirai, N. Yonemura, T. Tayagaki, K. Kan'no and T. Tanaka, *J. Luminesc.*, 2001, **94–95**, 529.

17 J. M. Holland, J. A. McAllister, Z. Lu, C. A. Kilner, M. Thornton-Pett and M. A. Halcrow, *Chem. Commun.*, 2001, 577.

18 N. K. Solanki, M. A. Leech, E. J. L. McInnes, F. E. Mabbs, J. A. K. Howard, C. A. Kilner, J. M. Rawson and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 2002, 1295.

19 E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1992, 2947.

20 R. P. Bonomo and F. Riggi, *Transition Met. Chem.*, 1984, **9**, 308; E. Narr, H. Zimmermann, A. Godt, D. Goldfarb and G. Jeschke, *Phys. Chem. Chem. Phys.*, 2003, **5**, 3959.

21 M. A. Leech, N. K. Solanki, M. A. Halcrow, J. A. K. Howard and S. Dahaoui, *Chem. Commun.*, 1999, 2245; G. S. Beddard, M. A. Halcrow, M. A. Hitchman, M. P. de Miranda, C. J. Simmons and H. Stratemeier, *Dalton Trans.*, 2003, 1028.

22 R. W. Reynolds, L. A. Boatner, M. M. Abraham and Y. Chen, *Phys. Rev. B*, 1974, **10**, 3802; A. Raizman, J. Barak, R. Englman and J. T. Suss, *Phys. Rev. B*, 1981, **24**, 6262; R. S. de Biasi and M. L. N. Grillo, *Solid State Commun.*, 2002, **121**, 697.

Chemical Communications Accepted Manuscript

TOC Entry
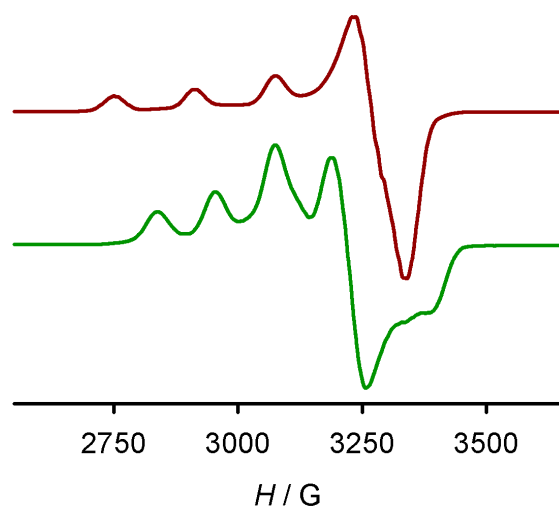
5

The electronic structures of $[Cu(terpy)_2]^{2+}$ (red) and $[Cu(bpp)_2]^{2+}$ (bpp = 2,6-di[pyrazol-1-yl]pyridine; green) are different, when doped into $[M(bpp)_2][BF_4]_2$ (M^{2+} = Fe^{2+} or Zn^{2+}). The $[Cu(terpy)_2]^{2+}$ dopant is a typical pseudo-Jahn-Teller elongated copper(II) center. However, the $[Cu(bpp)_2]^{2+}$ sites show EPR spectra consistent with a tetragonally compressed $\{d_{z^2}\}^1$ configuration.

15