

CO<sub>2</sub> fixation by dicopper(II) complexes in  
hypodentate framework of N<sub>8</sub>O<sub>2</sub><sup>†</sup>Cite this: *Dalton Trans.*, 2014, **43**,  
6287Received 13th December 2013,  
Accepted 28th January 2014

DOI: 10.1039/c3dt53497a

www.rsc.org/dalton

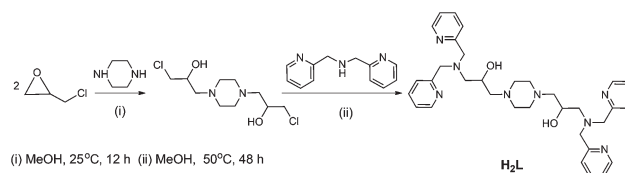
Yi-Hsueh Ho, Mu-Chieh Chang, Kuo-Hsuan Yu, Yi-Hung Liu, Yu Wang,  
Yuan-Chung Cheng\* and Jwu-Ting Chen\*

A new ligand with N<sub>8</sub>O<sub>2</sub> donors containing three potential metal-binding sites (H<sub>2</sub>L) and its tricopper(II) complex **1** are synthesized. The tricopper species is found to be formed from a hypodentate dicopper(II) complex **2** in basic solutions. Complex **2** may be isolated from the reaction of H<sub>2</sub>L with a copper source under acidic conditions. Complex **2** can undergo CO<sub>2</sub>-abstraction to yield an octacopper(II) complex **3**. The single crystal structures of complexes **2** and **3** are characterized by X-ray crystallography.

Polydentate ligands containing multi-metal coordination sites are interesting research targets either in metalloproteins or for designing novel structure–reactivity relationships. Investigation into *p*-MMO metalloenzymes has disclosed a tricopper(II) complex with a rarely known triangular subunit in a cyclic skeleton of (CuO)<sub>3</sub>.<sup>1</sup> The constitution of the ligand in this tricopper(II) complex is composed of three tetradentate components of N<sub>2</sub>O<sub>2</sub> donors with the assistance of two alkoxides and one oxide ion. All three copper centers are in a square planar configuration, although two kinds of coordination sites are involved.<sup>1</sup>

Although trinuclear copper(II) complexes with multidentate ligands in other configurations have been previously reported, the detailed coordination chemistry of such triangular tricopper(II) species remain elusive.<sup>2,3</sup> In order to understand the fundamental properties of coordination in such compounds, we introduced bipyridinyl amine which provides a tridentate coordinating mode and is supposed to offer better coordinating power into the ligand.<sup>4</sup>

In addition, CO<sub>2</sub> fixation has recently been becoming a more important topic in coordination chemistry.<sup>5</sup> Using copper complexes, particularly with a Cu(II)–O(H)–Cu(II)

Scheme 1 Synthesis of the N<sub>8</sub>O<sub>2</sub> polydentate ligand.

component, for such a purpose has been reported.<sup>6</sup> Herein, we report a new polydentate ligand with N<sub>8</sub>O<sub>2</sub> donors that exhibits a hypodentate dinuclear complex without a hydroxide-bridging moiety, and can show reactivity towards CO<sub>2</sub> fixation.

The synthesis of [(2-Py<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>CH(OH)CH<sub>2</sub>]<sub>2</sub>(*c*-C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>) (H<sub>2</sub>L) was succeeded first by the reaction of piperazine with epichlorohydrin in double molar amounts to form the alcohol derivative, and was then followed by the reactions with bis((pyridine-2-yl)methyl)amine to yield the desired product in 33% yields (Scheme 1).<sup>2</sup>

The reaction of H<sub>2</sub>L and three molar amounts of hexaquo-copper(II) perchlorate in acetonitrile with the addition of four molar amounts of triethylamine readily results in the formation of a deep green complex **1**. The electronic spectra show λ<sub>max</sub> appearing at 697 nm ( $\epsilon$ , 196 M<sup>-1</sup> cm<sup>-1</sup>) and a shoulder at *ca.* 860 nm ( $\epsilon$ , ~180 M<sup>-1</sup> cm<sup>-1</sup>). Such spectral data imply that complex **1** may consist of copper(II) centers in both square planar and five-coordinate trigonal bipyramidal configurations.<sup>7</sup>

The measurement of the molar conductivity for **1** in acetonitrile (5 × 10<sup>-4</sup> M) at 25 °C was 353 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, supporting that the complex salt is a trivalent perchlorate.<sup>8</sup> A peak at 998.0325 *m/z* found by HR-ESI-MS matches with a tricopper cation in the form of [LCu<sub>3</sub>(OH)(ClO<sub>4</sub>)<sub>2</sub>]<sup>+</sup>, in which a hydroxide presumably bridges two copper ions. In the infrared spectra, the uncoordinated perchlorate anions were evidenced at 1088 and 624 cm<sup>-1</sup>.

The half-wave potential (*E*<sub>1/2</sub>) of complex **1** was measured by cyclic voltammetry in deoxygenated acetonitrile at 25 °C. Two cathodic waves at -0.58 V and -0.80 V correspond to the

Department of Chemistry, National Taiwan University, Taipei 106, Taiwan.

E-mail: jtchen@ntu.edu.tw; Tel: +886 233661659

<sup>†</sup> Electronic supplementary information (ESI) available: The characterization and synthetic procedure of the new compounds; UV, CV and EPR spectral data; crystallographic data of **2** and **3** in CIF format; magnetic properties of **1** and **3**; ESI titration spectrum of the ligand mixing with copper. CCDC 976265–976266. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53497a

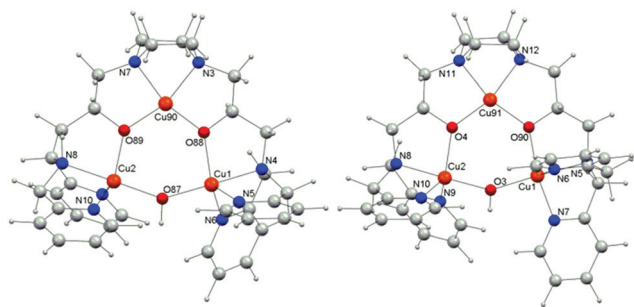


Fig. 1 Optimized DFT structures for complex **1** (*R,S*-, left; *R,R*-, right).

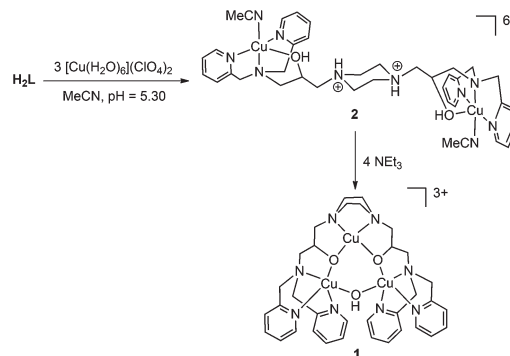
reduction of three Cu(II) atoms.<sup>9</sup> The smaller reversible signal at  $-0.80$  V may be assigned to the central component with  $\text{N}_2\text{O}_2$  coordination and the larger irreversible peak at  $-0.58$  V corresponds to the two terminal coordinations with  $\text{N}_3\text{O}_2$ . One quasi-reversible anodic wave at  $+1.42$  V, that may be assigned to the oxidation of two Cu(II) atoms in an  $\text{N}_3\text{O}_2$  environment, was also observed.

The X-band EPR spectrum for **1** as a powdered sample shows a ground state of  $S = 1/2$  at either 298 or 77 K, although without clear hyperfine splitting.<sup>2</sup> An axial pattern with  $g_{\parallel} = 2.218 > 2.1 > g_{\perp} = 2.04 > 2.00$  may be explained by a tricopper(II) species with the spin localized on the  $d_{x^2-y^2}$  orbital of an unpaired copper(II) ion in square planar or square pyramidal geometry.<sup>10,11</sup> The strong antiferromagnetic coupling in **1** is confirmed by SQUID.

DFT calculations for the structure of **1**, performed with the Gaussian 09 package using B3LYP and the 6-31G\* basis set,<sup>12</sup> provide the expected structure, in which three Cu(II) ions in a triangular arrangement are bridged by three oxygen atoms to constitute a  $(\text{CuO})_3$  ring subunit which is surrounded by **L** as a decadentate. There is one copper center in a distorted square planar configuration with  $\text{N}_2\text{O}_2$  coordination, and the other two copper(II) centers, which hold  $\text{N}_3\text{O}_2$  coordination and share a hydroxide bridge, are in trigonal bipyramidal/distorted trigonal bipyramidal configurations with  $\tau = 0.94$  and  $0.57$ , respectively.<sup>13</sup> Two possible diastereomers are considered (Fig. 1). The *R,S*-form is only 0.6 kcal per mole more stable than the *R,R*-form.<sup>14</sup> The TD-DFT calculated electronic spectrum of **1** with the optimized structure shows similar UV peaks to the experimental data.

An  $\text{N}_8$  ligand which comprises the combination of piperazine and bisimidazolyl amine was reported to also show coordination with di- and tri-copper.<sup>4</sup> On comparing this tri-copper complex with **1**, the latter may form a distorted hexagonal  $(\text{CuO})_3$  ring skeleton with two alkoxides in **L** and one bridging hydroxide, as shown in Fig. 1.

Spectrophotometric titrations for the reaction of  $\text{H}_2\text{L}$  and  $[\text{Cu}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  in the ratio of 1 : 3 in acetonitrile without the addition of  $\text{Et}_3\text{N}$  show that the solution color becomes dark blue at pH 5.30. A maximum absorption grows at 623 nm ( $\epsilon$ ,  $152 \text{ M}^{-1} \text{ cm}^{-1}$ ), which is consistent with a square planar or square pyramidal configuration.<sup>7</sup> The ESI-MS spectrum for the



Scheme 2 Synthesis of the  $\text{N}_8\text{O}_2$  hypodentate dicopper(II) complex and tricopper(II) complex.

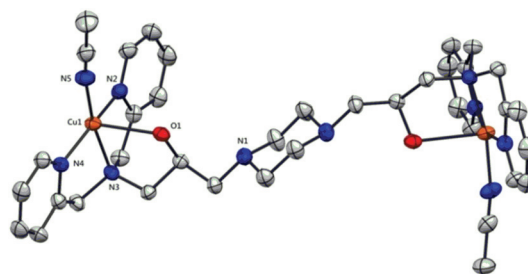
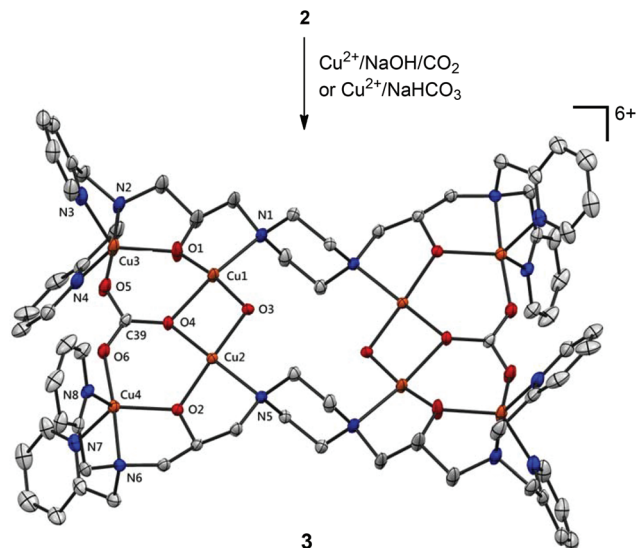


Fig. 2 ORTEP plot and selected atom-labeling scheme of the cationic part of **2** at 150 K, shown with 50% probability displacement ellipsoids. H-atoms and counteranions have been omitted for clarity.

same reaction gives a peak at  $m/z$  1021 amu, corresponding to a hypodentate dinuclear cation that may fit the formula  $[(\text{H}_2\text{L})\text{Cu}_2(\text{ClO}_4)_3]^+$ . The formation of **1** was not observed. For synthetic purposes, indeed, in a reaction of  $\text{H}_2\text{L}$  and  $\text{Cu}(\text{ClO}_4)_2$  in acidic conditions, a dinuclear complex in the form of  $[\text{H}_4\text{LCu}_2](\text{ClO}_4)_6$  (**2**) has been successfully isolated. Treating **2** with sufficient NaOH or triethylamine can result in the formation of **1** (Scheme 2).

Single crystals suitable for X-ray crystallographic analysis were obtained from cosolvents of dichloromethane-acetonitrile. The structure of **2** in  $C2/c$  symmetry has an inversion center (Fig. 2). The distance between the copper ions is extended to  $12.9 \text{ \AA}$ .<sup>11</sup> The Addison-Reedijk parameter,  $\tau$ , is 0.08, which agrees with the UV-Vis data.<sup>15</sup> The Cu–N bonds ( $2.0$ – $2.1 \text{ \AA}$ ) are of normal lengths.<sup>16</sup> However, the long Cu–O bonds ( $2.4 \text{ \AA}$ ) are likely from alcohol coordination.<sup>16</sup> The paramagnetic complex **2** has six perchlorate counteranions, suggesting that the two nitrogen atoms of piperazine should be protonated.

The hypodentate dinuclear complex **2** is expected to be active due to its available coordination capacity. It is found that exposing **1** to air under neutral or acidic conditions results in the formation of a new species. In the reaction of **2** and  $\text{Cu}(\text{ClO}_4)_2$  either under atmospheric conditions or in the presence of  $\text{NaHCO}_3$ , a product labeled as **3** is identified



**Scheme 3** The formation pathway for **3**.

by HR-ESI-MS with a peak at  $m/z$  714.3063, which may be assigned as a complex with the formula  $[(C_{34}H_{42}N_8O_2)_2Cu_8(OH)_2(CO_3)_2(ClO_4)_4]^{3+}$ . In an alternative feasible process, **H<sub>2</sub>L** and  $Cu(ClO_4)_2$  are mixed in acetonitrile in the presence of dry ice. After 10 minutes, the resulting solution may be introduced into  $H_2O$  to form the desired light blue product (**Scheme 3**).

The IR peaks at 1655 and  $1399\text{ cm}^{-1}$  confirm the bridged carbonates in **3**.<sup>17,18</sup> Unequivocal evidence for the unprecedented octacopper structure of **3** was acquired by single crystal crystallography. In the structure of  $[L_2Cu_8(CO_3)_2(OH)_2]^{6+}$ , four Cu(II) centers are in a square planar geometry and the other four are in a trigonal bipyramidal arrangement. Each carbonate ion is in a new  $\mu_4(\eta^1, \eta^1, \eta^2, \text{syn}, \text{anti}, \text{syn})$ -mode to link to four copper ions, with the C–O bond lengths being 1.250(6), 1.258(6), and 1.313(6) Å, which explain the infrared double bands at low frequencies.<sup>18</sup>

The SQUID data show that complex **3** is anti-ferromagnetic. Theoretical fitting suggests that four spin–spin coupling constants,  $J_{12}$ ,  $J_{24}$ ,  $J_{34}$ , and  $J_{14}$ , may be evaluated as  $-88.1$ ,  $-76.3$ ,  $1.1$ , and  $33.0\text{ cm}^{-1}$ , respectively.<sup>19</sup>

A reaction of **1** and  $NaHCO_3$  under the same conditions used for the  $CO_2$ -fixation of **2** does not produce complex **3**. One may thus conclude that the formation of **3** may result *via* the carbonate-coordination, which facilitates intermolecular coupling of **2** with the assistance of additional coordination of  $Cu^{2+}$  ions.

The reactivity for the carbon dioxide capture of **2** indicates that the dinuclear complex in the framework of hypodentate  $N_8O_2$  may also provide the mixed metal species. Indeed, the reaction of **2** with  $Zn(H_2O)_6(ClO_4)_2$  in the presence of  $Et_3N$  in acetone opens a route to the formation of mixed-metal products.<sup>20</sup> Specifically,  $LZnCu_2(OH)(ClO_4)_3$  may be identified by HR-ESI-MS and UV-Vis.<sup>21</sup> Research related to this is currently on going.

## Conclusions

In conclusion, a new polydentate ligand with  $N_8O_2$  donors has been successfully synthesized from the condensation of two bispyridyl amines and a piperazine bisalcohol derivative. Such a ligand can bind Cu(II) ions first through the bispyridyl moieties to yield a new hypodentate dinuclear complex in the form of  $[H_4LCu_2](ClO_4)_6$ . With the assistance of hydroxide,  $[H_4LCu_2]^{6+}$  can react with another Cu(II) ion to generate a tri-copper complex in which the metal and oxygen atoms form a  $(MO)_3$  ring skeleton, which is interesting to metalloenzymes. Exposing  $[H_4LCu_2](ClO_4)_6$  to  $CO_2$  results in a new complex in the form of  $[L_2Cu_8(CO_3)_2(OH)_2]^{6+}$ , which is interesting for  $CO_2$  capture and storage.

## Acknowledgements

This work was supported by the National Science Council, Taiwan, ROC. We thank Y.-C. Su for the SQUID measurement, S.-Y. Sun and P.-Y. Lin for the high resolution ESI-MS spectra, and Y.-C. Wu for the EPR spectra.

## Notes and references

- H.-H. T. Nguyen, A. K. Shiemke, S. J. Jacobs, B. J. Hales, M. E. Lidstrom and S. I. Chan, *J. Biol. Chem.*, 1994, **269**, 14995; J. D. Semrau, D. Zolandz, M. E. Lidstrom and S. I. Chan, *J. Inorg. Biochem.*, 1995, **58**, 235; H.-H. T. Nguyen, S. J. Elliott, J. H.-K. Yip and S. I. Chan, *J. Biol. Chem.*, 1998, **273**, 7957; S. S.-F. Yu, C.-Z. Ji, Y. P. Wu, T.-L. Lee, C.-H. Lai, S.-C. Lin, Z.-L. Yang, V. C.-C. Wang, K. H.-C. Chen and S. I. Chan, *Biochemistry*, 2007, **46**, 13762; A. S. Hakemian, K. C. Kondapalli, J. Telser, B. M. Hoffman, T. L. Stemmler and A. C. Rosenzweig, *Biochemistry*, 2008, **47**, 6793; S. I. Chan, V. C.-C. Wang, J. C.-H. Lai, S. S.-F. Yu, P. P.-Y. Chen, K. H.-C. Chen, C.-L. Chen and M. K. Chan, *Angew. Chem., Int. Ed.*, 2007, **46**, 1992.
- P. P.-Y. Chen, R. B.-G. Yang, J. C.-M. Lee and S. I. Chan, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 14570; S. I. Chan and S. S.-F. Yu, *Acc. Chem. Res.*, 2008, **41**, 969; D. Maiti, J. S. Woertink, R. A. Ghiladi, E. I. Solomon and K. D. Karlin, *Inorg. Chem.*, 2009, **48**, 8342; J. Chen, X. Wang, Y. Shao, J. Zhu, Y. Zhu, Y. Li, Q. Xu and Z. Guo, *Inorg. Chem.*, 2007, **46**, 3306; F. U. Neuba, W. Meyer-Klaucke, M. Salomone-Stagni, E. Bill, E. Bothe, P. Hofer and G. Henkel, *Angew. Chem., Int. Ed.*, 2011, **50**, 4503; S. Maji, J.-C. Lee, Y.-J. Lu, C.-L. Chen, M.-C. Hung, P.-P. Chen, S.-S. F. Yu and S.-I. Chan, *Chem.-Eur. J.*, 2012, **18**, 3955.
- S.-K. Lee, S. D. George, W. E. Antholine, B. Hedman, K. O. Hodgson and E. I. Solomon, *J. Am. Chem. Soc.*, 2002, **124**, 6180; J. Yoon, L. M. Mirica, T. D. P. Stack and E. I. Solomon, *J. Am. Chem. Soc.*, 2004, **126**, 12586; L. M. Mirica and T. D. P. Stack, *Inorg. Chem.*, 2005, **44**,

- 2131; M. P. Suh, M. Y. Han, J. H. Lee, K. S. Min and C. Hyeon, *J. Am. Chem. Soc.*, 1998, **120**, 3819.
- 4 S. Itoh and Y. Tachi, *Dalton Trans.*, 2006, 4531; F. G. Mutti, G. Zoppellaro, M. Gullotti, L. Santagostini, R. Pagliarin, K. K. Andersson and L. Casella, *Eur. J. Inorg. Chem.*, 2009, 554; F. G. Mutti, M. Gullotti, L. Casella, L. Santagostini, R. Pagliarin, K. K. Andersson, M. F. Iozzi and G. Zoppellaro, *Dalton Trans.*, 2011, **40**, 5436; P. Nagababu, S. Maji, M. P. Kumar, P. P.-Y. Chen, S. S.-F. Yu and S. I. Chan, *Adv. Synth. Catal.*, 2012, **354**, 3275; K. H.-C. Chen, H.-H. Wu, S.-F. Ke, Y.-T. Rao, C.-M. Tu, Y.-P. Chen, K.-H. Kuei, Y.-S. Chen, V. C.-C. Wang, W.-C. Kao and S. I. Chan, *J. Inorg. Biochem.*, 2012, **111**, 10.
- 5 E. Bouwman, R. Angamuthu, P. Byers, M. Lutz and A. L. Spek, *Science*, 2010, **327**, 313; T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365.
- 6 N. Kitajima, K. Fujisawa, T. Koda, S. Hikichi and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1990, 1357; G. Kolks, S. J. Lippard and J. V. Waszczak, *J. Am. Chem. Soc.*, 1980, **102**, 4832; F. W. B. Einstein and A. C. Willis, *Inorg. Chem.*, 1981, **20**, 609.
- 7 A. Datta, N. K. Karan, S. Mitra and G. Z. Rosair, *Z. Naturforsch., B: J. Chem. Sci.*, 2002, **57**, 999; B. J. Hathaway, R. J. Dudley and P. Nicholls, *J. Chem. Soc. A*, 1969, 1845; N. Le Poul, B. Douzief, J. Zeitouny, G. Thia-Baud, H. Colas, F. Conan, N. Cosquer, I. Jabin, C. Lagrost, P. Hapiot, O. Reinaud and Y. Le Mest, *J. Am. Chem. Soc.*, 2009, **131**, 17800.
- 8 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
- 9 E. A. Ambundo, M.-V. Deydier, A. J. Grall, N. Agüera-Vega, L. T. Dressel, T. H. Cooper, M. J. Heeg, L. A. Ochrymowycz and D. B. Rorabacher, *Inorg. Chem.*, 1999, **38**, 4233.
- 10 E. I. Solomon, U. M. Sundaram and T. E. Machonkin, *Chem. Rev.*, 1996, **96**, 2563; B. J. Hathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, U.K., 1987, vol. 5, p. 668; M. Duggan, N. Ray, B. Hathaway, G. Tomlinson, P. Brint and K. Pelin, *J. Chem. Soc., Dalton Trans.*, 1980, 1342.
- 11 B. Lucchese, K. J. Humphreys, D.-H. Lee, C. D. Incarvito, R. D. Sommer, A. L. Rheingold and K. D. Karlin, *Inorg. Chem.*, 2004, **43**, 5987; K. D. Karlin, J. C. Hayes, S. Juen, J. P. Hutchinson and J. Zubieta, *Inorg. Chem.*, 1982, **21**, 4106.
- 12 M. J. Frisch *et al.*, *GAUSSIAN09 (Revision A.02)*, Gaussian, Inc., Wallingford, CT, 2009; A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; V. A. Rassolov, J. A. Pople, M. Ratner, P. C. Redfern and L. A. Curtiss, *J. Comput. Chem.*, 2001, **22**, 976; V. A. Rassolov, J. A. Pople, M. Ratner and T. L. Windus, *J. Chem. Phys.*, 1998, **109**, 1223.
- 13 A. W. Addison, T. Nageswara Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
- 14 The calculated energy for the *R,S*-form is  $-6905.51480714$  Hartree and for the *R,R*-form is  $-6905.51308543$  Hartree.
- 15 G. L. Miessler and D. Tarr, *Inorganic Chemistry*, Pearson, USA, 4th edn, 2011; D. F. Shriver and T. L. Atkin, *Inorganic Chemistry*, Oxford, USA, 4th edn, 2006; A. B. P. Lever, *Inorganic Spectroscopy*, Elsevier, Amsterdam, 1968; M. F. El-Shazly and L. S. Refaat, *Transition Met. Chem.*, 1981, **6**, 8.
- 16 W. T. Eckenhoff and T. Pintauer, *Inorg. Chem.*, 2010, **49**, 10617; K. K. Rajak, A. Banerjee, S. Sarkar, D. Chopra and E. Colacio, *Inorg. Chem.*, 2008, **47**, 4023; T. D. P. Stack, L. M. Mirica and X. Otten-waelder, *Chem. Rev.*, 2004, **104**, 1013; P. V. Bernhardt and P. C. Sharpe, *J. Chem. Soc., Dalton Trans.*, 1998, 1087; H. López-Sandoval, R. Contreras, A. Escuer, R. Vicente, S. Bernès, H. Nöth, G. J. Leigh and N. Barba-Behrens, *J. Chem. Soc., Dalton Trans.*, 2002, 2648.
- 17 E. Anders, J. Notni, S. Schenk, H. Görls and H. Breitzke, *Inorg. Chem.*, 2008, **47**, 1382.
- 18 A. Escuer, R. Vicente, S. B. Kumar, X. Solans, M. Font-Bardía and A. Caneschi, *Inorg. Chem.*, 1996, **35**, 3094; B. Verdejo, J. Aguilar and E. García-España, *Inorg. Chem.*, 2006, **45**, 3803; C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, P. Paoletti and B. Valtancoli, *J. Chem. Soc., Chem. Commun.*, 1995, 1555; A. Escuer, R. Vicente, E. Peñalba, X. Solans and M. Font-Bardía, *Inorg. Chem.*, 1996, **35**, 248; C. Bazzicalupi, A. Bencini, A. Bencini, A. Bianchi, F. Corana, V. Fusi, C. Giorgi, P. Paoli, P. Paoletti, B. Valtancoli and C. Zanchini, *Inorg. Chem.*, 1996, **35**, 5540; A. Escuer, F. A. Mautner, E. Peñalba and R. Vicente, *Inorg. Chem.*, 1998, **37**, 4190; K. Bernauer, A. Cabort, N. Guicher, H. Stoeckli-Evans and G. Süss-Fink, *J. Chem. Soc., Dalton Trans.*, 2002, 2069; E. García-España, P. Gaviña, J. Latorre, C. Soriano and B. Verdejo, *J. Am. Chem. Soc.*, 2004, **126**, 5082; P. K. Nanda, M. Bera, G. Aromí and D. Ray, *Polyhedron*, 2006, **25**, 2791.
- 19 The magnetic susceptibility is measured in the temperature range of 4–350 K. At 350 K, the effective magnetic moment of  $4.46\mu_B$  is slightly lower than the  $S = 2$  ideal model system. The experimental data are fitted to the expression derived from the tetranuclear spin center.
- 20 M. Carboni, M. Clemancey, F. Molton, J. Pecaut, C. Lebrun, L. Dubois, G. Blondin and J. M. Latour, *Inorg. Chem.*, 2012, **51**, 10447; B. Habermeyer, A. Takai, C. P. Gros, M. El Ojaimi, J. M. Barbe and S. Fukuzumi, *Chem.-Eur. J.*, 2011, **17**, 10670; A. Neves, C. Piovezan, R. Jovito, A. J. Bortoluzzi, H. N. Terenzi, F. L. Fischer, P. C. Severino, C. T. Pich, G. G. Azzolini, R. A. Peralta and L. M. H. Rossi, *Inorg. Chem.*, 2010, **49**, 2580; B. Colasson, N. Le Poul, Y. Le Mest and O. Reinaud, *J. Am. Chem. Soc.*, 2010, **132**, 4393.
- 21 The HR-ESI-MS peak of  $\text{LZnCu}_2(\text{OH})(\text{ClO}_4)_3$  appears at  $m/z = 999.0324$  amu, and the UV-Vis spectrum shows two absorption bands at 892 nm (228) and 324 nm (2423).