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New Cu(II) coordination polymer by chiral tridentate Schiff base ligand

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ABSTRACT

The present research reports the synthesis, X-ray, magnetic and electronic properties for novel coordination polymer based upon copper (II) with chiral tridentate Schiff base ligand synthesized at condensation of acetylacetone and L-leucine amino acid. The investigation was also conducted by quantum mechanical calculations. The large energy gap indicates a high kinetic stability. Magnetic measurement gives predominant antiferromagnetic interactions within the chain. Results reveals further insight into copper(II) chiral tridentate Schiff base complexes.

1. Introduction

Studies of coordination polymers (CPs) began about 30 years ago. In 1989, Robson and Hoskins [1] found that a new and potentially extensive class of solid polymeric materials with unprecedented and possibly useful properties may be afforded by linking centers with rod like connecting units [2–7]. The number of studies on this type material increased greatly in the early 1990s [8–11]. Design and fabrication of CPs have attracted extensive interests and they have led to new possibilities in molecular magnetic materials [12].

New class materials having some physical properties together with magnetic properties include a great variety of different types compounds. They are classified into two main groups. In one of them, magnetic properties can be tuned by the application of external stimuli (light, temperature or pressure) [13–15] while properties for other coexist in ligands, for example, chiral magnets [16–20] that tentatively show magneto-chiral dichroism [20,21]. Major aim is to synthesize and research original properties of this new class materials which show multi-functional properties [22].

Though many such interesting CPs have been reported, the control of structural dimensionality remains a challenge. Therefore, further studies on the structure directing roles of the spacer ligands are thus of fundamental importance [23,24]. Different ligand system such as oximate [25–27], pyrazolide [28,29], triazolide [30,31] and ketonate [32,33] peripheral ligands has been adopted for new CPs [34].

In the literature there are several examples of CPs obtained from chiral amino acids. Boris Le Guennic et al. [34] obtained a quasi-orthogonal MOs from an amino acid Schiff base, but no example of CPs with a chiral Schiff base containing this type donor ligand has been reported so far. Since carboxylic group may generate several coordination modes with metal, the initiative idea for the current research was the utilization of chiral amino acid as primary amine. A novel Cu (II) CP using such ligand was synthesized and its structural, magnetic and electronic properties were researched by a detailed investigation. Spectroscopic or theoretical results are herein reported.

2. Experimental

2.1. Synthesis

At first step 10 mL of KOH (0.88 g, 20 mmol) solution was added to 10 mL of L-leucine (2.62 g, 20 mmol) solution under stirring. After half an hour under stirring, 2.0 g/20 mmol acetylacetone dissolved

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in methanol (10 mL) was added to mixture prepared drop wise. The final mixture was left for stirring all-night. The obtained product was washed with petroleum ether, dissolved in methanol and then filtered. After the removing of solvent, as seen Fig. 1a, the ligand molecule (L-LHK) was obtained in its salt form (yield %75). IR spectrum of L-LHK shows the bands at 1629 and 1398 cm^{-1} which are assigned as the asymmetric and symmetric OCO stretching frequencies, respectively (Fig. SI1; SI: Supplementary Information). Further, the band at 1594 cm^{-1} is assigned to C=N stretching. ^1H NMR shifts of the molecule (Fig. SI2) are listed as follows: ^1HNMR ($CDCl_3$, d ppm, 400 MHz): 0.9 (dd, 6 H), 1.74 (m, 2 H), 1.90 (s, 3 He), 2.00 (s, 3 Hd), 2.2 (m, 1 Hc), 3.3 (dd, 1 Ha), 4.9 (s, 1 H, C-Hb), 11 (d, 1 H, NH).

For the synthesis of complex, at first step ligand was dissolved in methanol (10 mL), then to this solution $CuCl_2 \cdot 2H_2O$ (170 mg, 1 mmol) was added drop by drop, while stirring. 0.3 mL of triethylamine was added to the mixture prepared to allow the deprotonation of the ligands. After, the solution was observed to have a deep green colour. Blue-green single crystals were obtained after several days of slow evaporation of the solvent according to reaction scheme described in Fig. 1b.

2.2. Measurements

FTIR spectrum was reported in frequency region from 400 to 4000 cm^{-1} with a FTIR Nexus Nicolet Spectrometer by KBr pellets and 120 scans at a resolution of 4 cm^{-1}. ^1H NMR spectrum was reported by a Bruker 400 MHz instrument at 23 °C. Diffraction data were collected at room temperature by a Nonius Kappa CCD. Structure was solved by direct methods using SIR2004 [35] and was refined by full-matrix least squares technique on F^2 including all reflections by SHELXL-1997 [36]. Both softwares were included within the WingX package [37]. A quantum design SQUID magnetometer MPMS-XL was utilized for magnetic measurements on a polycrystalline sample of the complex. Magnetometer operates between 2 and 300 K for dc applied fields ranging from −5 to 5 T.

3. Computational method

Gaussian, GaussView and GaussSum programs were used for the calculations, visualizations of figures and to obtain optimized structures [38–40]. Based on the X-ray refinement data, the starting geometry of the complex was constructed and optimized until no imaginary frequencies were seen at the end of the calculations. Natural bond orbital (NBO) analyses, frontier molecular orbitals, density of state (DOS) spectrum and electrostatic potential surface (EPS) were also performed together with some electronic properties such as band gap or chemical hardness. All computations were performed by B3LYP/6-31G(d) level of theory. Multiwfn program was also included to find out Mayer bond order (MBO), Wiberg bond index (WBI) and Fuzzy bond order (FBO) and to gain more understandings in the nature of bonding [41].

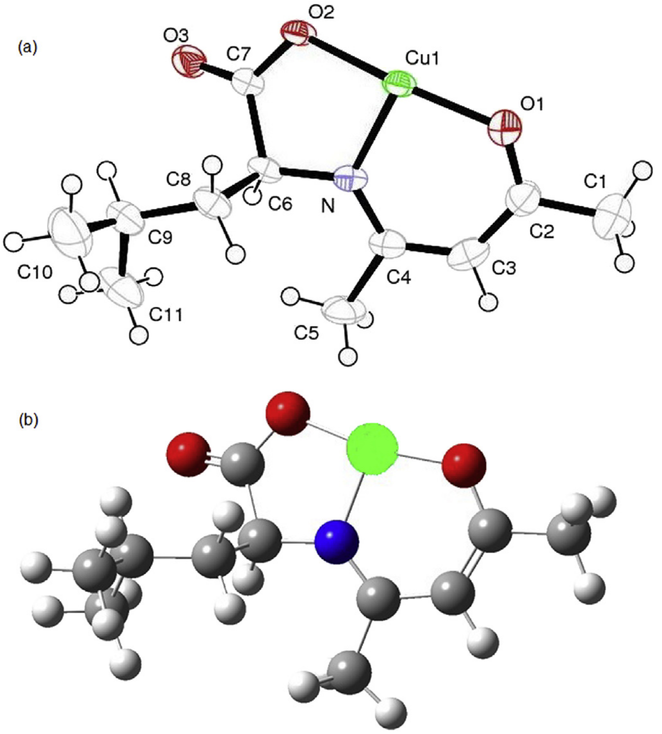

Fig. 2. (a) Ortep diagram of the complex. Showing 50% probability thermal ellipsoids. (b) Optimized structure of the complex.

4. Results and discussion

4.1. Structural analysis

Single crystal X-ray diffraction analysis suggests that the new CP crystallizes in the non-centrosymmetric orthorhombic $P2_12_12_1$ space group. Lattice parameters are a = 4.9668 Å, b = 8.9975 Å, c = 27.7349 Å and V = 3397.8 $Å^3$ and adopts a 2D coordination network structure. CCDC 1511780 deposition number contains supplementary crystallographic data for the complex. Molecular structure and atom-labeling scheme are shown in Fig. 2. Data collection and parameters for structure refinement are given in Table 1. Atomic coordinates and equivalent thermal parameters are also given in Table SI1.

The asymmetric unit is built up from one metal cation Cu(II) and a deprotonated ligand. All Cu (II) atoms are surrounded with five donor atoms as one N and four O atoms. Due to the Jahn-Teller effect of the Cu(II) ion, the apical position of Cu is occupied by one oxygen Cu–O3 bond length (2.567 Å) from the carboxylate group of the neighbour ligand. Cu (II) ions lie in the center of the square (O, O, O, N). The trigonal index-plane τ [42] of 0.069 also confirms the slightly distorted square pyramid (Fig. 3a). Some theoretical and experimental structural parameters are listed in Table SI2.

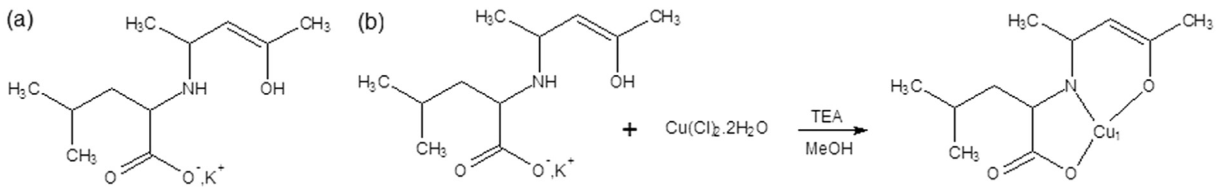

Fig. 1. (a) Structure of L-LHK ligand molecule (b) Reaction of the complex.

Table 1
Data collection and structure refinement for the investigated structure.

Crystal data	$CuC_{11}H_{17}NO_3$
Formula weight (g mol^{-1})	274.80
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Hall symbol	*P* 2ac 2 ab
Unit cell dimensions (Å)	
a	4.9668
b	8.9975
c	27.7349
Volume ($Å^3$)	1239.44
Z	4
F(000)	572
Density (g/cm^3)	1.473
Wavelength (Mo Kα),Å	0.71073
Shape, Color	Plate, Green-Blue
Crystal size (mm^3)	0.04 × 0.08 × 0.05
$\theta_{max}-\theta_{min}$ (°)	2.94–29.07
Absorption coefficient (mm^{-1})	1.754
Temperature (K)	293
Refinement Method	F^2
Least-squares matrix	Full
$R[F^2 > 2\sigma(F^2)]$	0.0470
$wR(F^2)$	0.1091
Measured reflections	7175
Independent reflections	2861
Reflections with $I > 2\sigma(I)$	2317
R_{int}	0.043
h	−6 → 6
k	−12 → 149
l	−37 → 35
$R_1 = P\|F_o-F_c\|/F_o$. wR_2	$\{P[w(F_o^2-F_c^2)2]/P[w(F_o^2)2]\}1/2$
S	$\{P[w(F_o^2 - F_c^2)2]/(N_{obs}-N_{var})\}1/2$
$\Delta_{\rho max}$ (e A^{-3})	0.897
$\Delta_{\rho min}$ (e A^{-3})	−0.968
Flack Parameter	0.0131

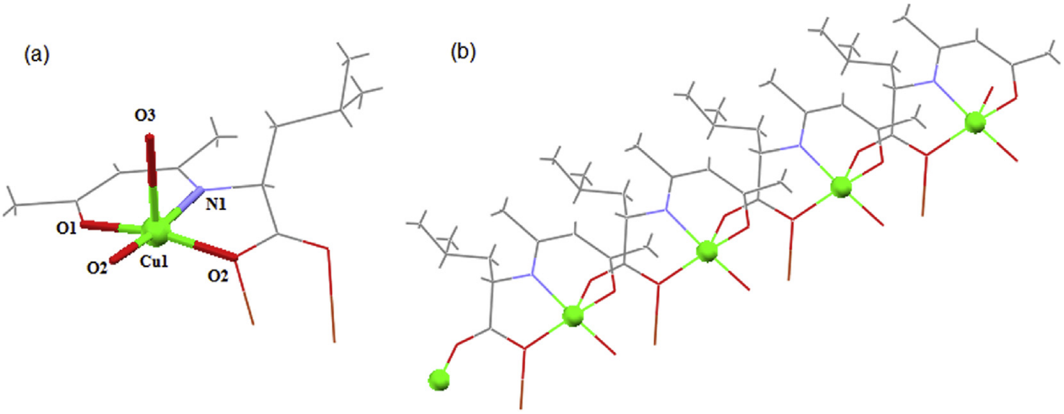

Fig. 3. (a) Environment of the metal center. (b) View of the chain in the OZ way.

Each copper coordinates three ligands at the same time; in such away copper is penta-coordinated with a nitrogen atom (Cu–N: 1.915 Å), two oxygen atoms of the first ligand (Cu–O1: 1.887 Å and Cu–O2: 1.989 Å), an oxygen atom (Cu1–$O2^{iv}$: 1.978 Å) from a second neighbour ligand and a third oxygen atom that belongs to a third neighbouring ligand (Cu1–$O3^{ii}$: 2.567 Å) by (ii): 1 + x, y, z and (iv): 1/2 + x, 1/2-y, -z symmetry codes. Each asymmetric unit is connected to an adjacent parallel asymmetric unit through of Cu1–$O3^{ii}$ of 2.567 Å to connect two adjacent coppers with a long bridge (Cu···Cu: 7.069 Å) in such a way to give infinite 1D Cu chain along ox axis (Fig. 3b). Furthermore, another carboxylate from a third asymmetric unit link the Cu ions in these 1D Cu chains by Cu1–$O2^{iv}$ of 1.978 Å to form a 2D sheet (Fig. SI3), where the Cu–O–Cu angle is 128.16° and the Cu···Cu distance is 3.967 Å.

4.2. Electronic properties

DOS spectra, molecular frontier orbitals and EPS of the complex are given in Fig. 4. EPS enables to visualize the charge distributions for compounds. Colour ranges (in a.u.) are more positive than 0.01 for blue and more negative than −0.01 for red. Areas of low and high potentials, red and blue, are characterized by an abundance of electrons and a relative absence of electrons, respectively. According to results, electrophiles interact red areas which seem as the most probable candidates as active sites for the compound while nucleophiles attack blue regions. The complex has large dipole moment as 6.426 D. HOMO (−6.161 eV) and LUMO (−1.515 eV) are delocalized on almost all atoms except CH_3 groups and C=O, Cu–O and some CH_3 groups correspondingly. Band gap has been used as a simple indicator of kinetic stability and it could indicate the reactivity pattern of the structure [43]. Band gap of the complex is about 4.646 eV and this large value implies high kinetic stability and low chemical reactivity. Further, with regard to energies of the frontier orbitals, the chemical hardness, electrophilicity index and electronegativity of the complex are calculated as 2.323 eV, 3.838 and 3.171 eV, respectively.

Interaction sites and bonding properties were analyzed based on NBO calculations. Acceptor-donor interactions can be described using NBO results [44]. In Table 2, it is seen that Mulliken and NBO charges suggest the formation of acceptor-donor couples between Cu, N and O atoms in the examined complex. WBI and FBO can be used to evaluate the degree of covalent bonding [45,46]. In this study, if the calculated MBO, WBI and FBO values are examined in Table 2, it is seen that covalent bond characters between Cu and O atoms are higher than the values of Cu and N atoms.

4.3. Magnetic properties

For the magnetization–temperature (M–T) measurements, at 300 K, χT has a value as 0.45 cm^3 K mol^{-1} which is slightly higher than the expected value for a Cu atom magnetically independent based on g = 2.0. χT gradually decreases while temperature lowers (Fig. 5). Interactions in chain are antiferromagnetic and dominant. As seen from Fig. SI4, dihedral angle between planes containing two adjacent Cu atoms is of the order of 117.75° which explains the antiferromagnetic exchange interactions within these channels [47].

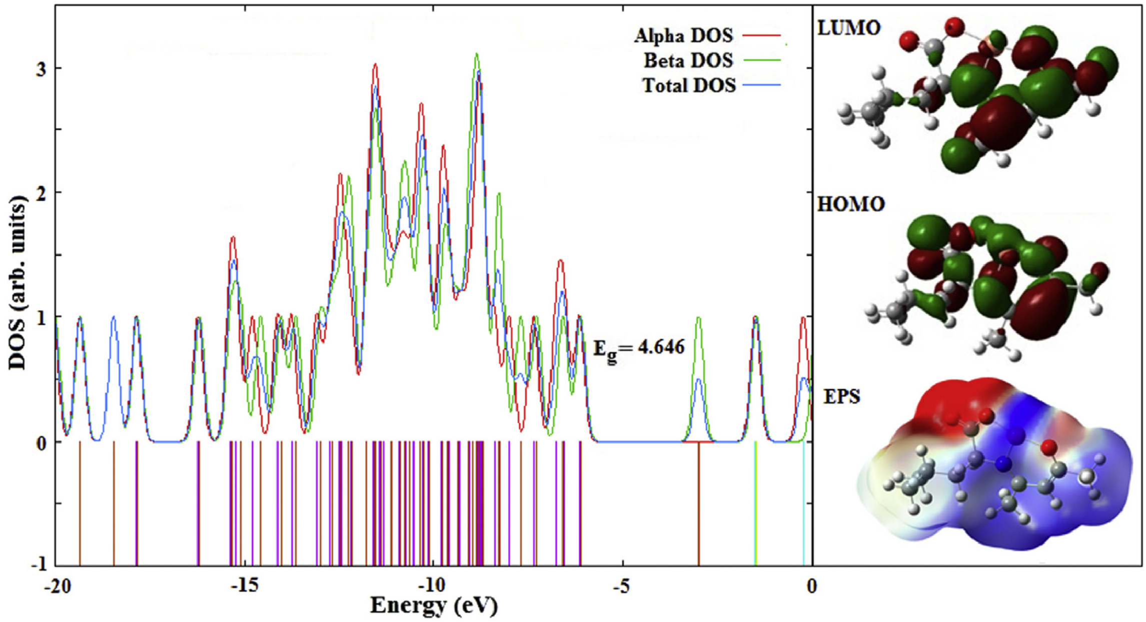

Fig. 4. DOS and EPS graphs of the complex.

Table 2
Population analysis of some atoms for the investigated structure.

Atom	Valence number	Mulliken charge	NBO charge	MBO	WBI	FBO
Cu	2.667	0.827	1.123			
N	3.050	−0.641	−0.616	0.555	0.697	1.127
O1	1.986	−0.639	−0.727	0.604	0.790	1.278
O2	1.948	−0.622	−0.722	0.641	0.807	1.296
O3	2.006	−0.488	−0.614			

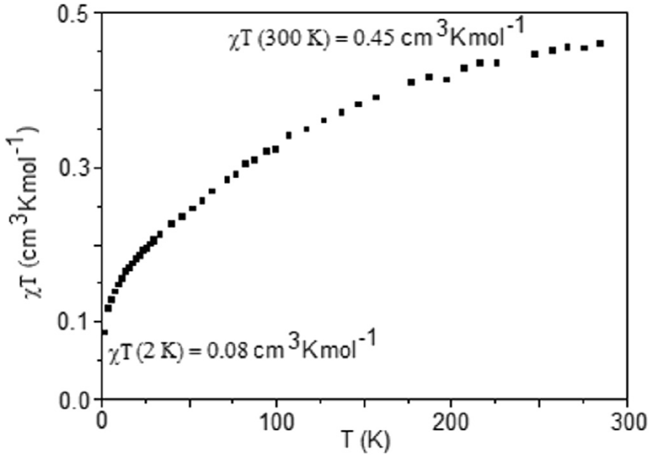

Fig. 5. Temperature dependence of χT.

5. Conclusion

A new CP was obtained by the use of an original chiral ligand and Cu(II). We have conducted crystallographic study, theoretical analyses and measurement of magnetic susceptibilities. Each copper coordinates three ligands at the same time and is surrounded by five donor atoms. Coordination sphere of Cu atoms shows deformation due to the Jahn–Teller effect. Covalent bond characters between Cu and N atoms are lower than values between Cu and O atoms. The compound is kinetically very stable with the large gap energy. There are predominant antiferromagnetic interactions and non-centrosymmetric structures, so it can be of interest to scientists working in the field of nonlinear optics.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2017.02.046.

References

[1] B.F. Hoskins, R. Robson, Infinite polymeric frameworks consisting of three dimensionally linked rod-like segments, J. Am. Chem. Soc. 111 (1989) 5962–5964.

[2] C. Di Nicola, E. Forlin, F. Garau, A. Lanza, M.M. Natile, F. Nestola, L. Pandolfo, C. Pettinari, Coordination polymers based on trinuclear and mononuclear copper-pyrazolate building moieties connected by fumarate or 2-methylfumarate ions, J. Organomet. Chem. 714 (2012) 74–80.

[3] J.B. De Coste, G.W. Peterson, Metal–organic frameworks for air purification of toxic chemicals, Chem. Rev. 114 (2014) 5695–5727.

[4] B.V. de Voorde, B. Bueken, J. Denayerb, D.D. Vos, Adsorptive separation on metal–organic frameworks in the liquid phase, Chem. Soc. Rev. 43 (2014) 5766–5788.

[5] M. Roy, S. Sengupta, S. Bala, S. Bhattacharya, R. Mondal, Systematic study of mutually inclusive influences of temperature and substitution on the coordination geometry of Co(II) in a series of coordination polymers and their properties, Cryst. Growth Des. 16 (2016) 3170–3179.

[6] H. Zhang, C. Lin, T. Sheng, S. Hu, C. Zhuo, R. Fu, Y. Wen, H. Li, S. Su, X. Wu, A luminescent metal–organic framework thermometer with intrinsic dual emission from organic lumophores, Chem. Eur. J. 22 (2016) 4460–4468.

[7] E.D. Bloch, W.L. Queen, M.R. Hudson, J.A. Mason, D.J. Xiao, L.J. Murray, R. Flacau, C.M. Brown, J.R. Long, Hydrogen storage and selective, reversible O_2 adsorption in a metal–organic framework with open chromium(II) sites, Angew. Chem. Int. Ed. 55 (2016) 8605–8609.

[8] J. Hong, L. Huo, Y. Wang, R. Long, C. Zheng, Syntheses, crystal structures and properties of two coordination polymers derived from flexible dicarboxylate and N-donor ligands, Inorg. Chim. Acta 455 (2017) 81–87.

[9] D. Reinares-Fisac, L.M. Aguirre-Díaz, M. Iglesias, N. Snejko, E. Gutiérrez-Puebla, M.Á. Monge, F. Gándara, A mesoporous indium metal–organic framework: remarkable advances in catalytic activity for strecker reaction of ketones, J. Am. Chem. Soc. 138 (2016) 9089–9092.

[10] M. Deng, P. Yang, X. Liu, B. Xia, Z. Chen, Y. Ling, L. Weng, Y. Zhou, J. Sun, End-end connection pattern of trinuclear-triangular copper cluster for construction of two metal–organic frameworks: syntheses, structures, magnetic and gas adsorption properties, Cryst. Growth Des. 15 (2015) 1526–1534.

[11] Y.W. Dong, R.Q. Fan, X.M. Wang, P. Wang, H.J. Zhang, L.G. Wei, W. Chen,

Y.L. Yang, (E)-N-(Pyridine-2-ylmethylene)arylamine as an assembling ligand for Zn(II)/Cd(II) complexes: aryl substitution and anion effects on the dimensionality and luminescence properties of the supramolecular metal–organic frameworks, Cryst. Growth Des. 16 (2016) 3366–3378.

[12] J. Ferrando-Soria, D. Cangussu, M. Eslava, Y. Journaux, R. Lescouëzec, M. Julve, F. Lloret, J. Pasan, C. Ruiz-Pérez, E. Lhotel, C. Paulsen, E. Pardo, Rational enantioselective design of chiral heterobimetallic single-chain magnets: synthesis, crystal structures and magnetic properties of oxamato-bridged $M^{II}Cu^{II}$ chains (M = Mn, Co), Chem. Eur. J. 17 (2011) 12482–12494.

[13] O. Sato, Optically switchable molecular solids: Photoinduced spin-crossover, photochromism, and photoinduced magnetization, Acc. Chem. Res. 36 (2003) 692–700.

[14] Y. Arimoto, S. Ohkoshi, Z.J. Zhong, H. Seino, Y. Mizobe, K. Hashomoto, Photoinduced magnetization in a two-dimensional cobalt octacyanotungstate, J. Am. Chem. Soc. 125 (2003) 9240–9241.

[15] G. Li, T. Akitsu, O. Sato, Y. Einaga, Photoinduced magnetization of the cyano-bridged 3d–4f heterobimetallic assembly $Nd(DMF)_4(H_2O)_3(\mu\text{-}CN)Fe(CN)_5 \cdot H_2O$ (DMF = N,N-dimethylformamide), J. Am. Chem. Soc. 125 (2003) 12396–12397.

[16] K. Inoue, K. Kikuchi, M. Ohba, H. Okawa, Titelbild: structure and magnetic properties of a chiral two-dimensional ferrimagnet with T_C of 38 K, Angew. Chem. 115 (2003) 4857–4983.

[17] K. Inoue, H. Imai, P.S. Ghalsasi, K. Kikuchi, M. Ohba, H. Okawa, J.V. Yakhmi, A three-dimensional ferrimagnet with a high magnetic transition temperature (T_C) of 53 K based on a chiral molecule, Angew. Chem. 113 (2001) 4372–4374.

[18] E. Coronado, J.R. Galan-Mascaros, C.J. Gomez-Garcia, J.M. Martinez-Agudo, Molecule-based magnets formed by bimetallic three-dimensional oxalate networks and chiral tris(bipyridyl) complex cations. The series $[Z^{II}(bpy)_3][ClO_4][M^{II}Cr^{III}(ox)_3]$ (Z^{II} = Ru, Fe, Co, and Ni; MII = Mn, Fe, Co, Ni, Cu, and Zn; ox = Oxalate dianion), Inorg. Chem. 40 (2001) 113–120.

[19] O. Mamula, A. von Zelewsky, T. Bark, H. Stoeckli-Evans, A. Neels, G. Bernardinelli, Predetermined chirality at metal centers of various coordination geometries: a chiral cleft ligand for tetrahedral (T-4), square-planar (SP-4), trigonal-bipyramidal (TB-5), square-pyramidal (SPY-5), and octahedral (OC-6) complexes, Chem. Eur. J. 6 (2000) 3575–3585.

[20] C. Train, R. Gheorghe, V. Krstic, L.M. Chamoreau, N.S. Ovanesyan, G.L.J.A. Rikken, M. Gruselle, M. Verdaguer, Strong magneto-chiral dichroism in enantiopure chiral ferromagnets, Nat. Mater. 7 (2008) 729–734.

[21] G.L.J.A. Rikken, E. Raupach, Observation of magneto-chiral dichroism, Nature 390 (1997) 493–494.

[22] M.M. Turnbull, T. Sugimoto, L.K. Thompson, Molecule-based Magnetic Materials, ACS, Washington, 1996.

[23] Y.C. Lo, Y.J. Chang, P.M. Chhetri, W.J. Huang, J.D. Chen, Construction of coordination polymers based on bis-pyridyl-bis-amide and dicarboxylate ligands, Polyhedron 117 (2016) 777–787.

[24] S.K. Seth, Exploration of supramolecular layer and bi-layer architecture in M(II)–PPP complexes: structural elucidation and Hirshfeld surface analysis [PPP = 4-(3-Phenylpropyl)pyridine, M = Cu(II), Ni(II)], J. Mol. Struct. 1070 (2014) 65–74.

[25] S. Baral, A. Chakravorty, New trinuclear copper(II) species, Inorg. Chim. Acta 39 (1980) 1–8.

[26] R.J. Butcher, C.J. O'Connor, C.J.E. Sinn, Synthesis and relation between magnetism and structure of a trinuclear copper(II) hydroxo complex [Cu3OHL3(ClO4)]ClO4 and a hexanuclear copper(II) oxo complex [Cu3OL'3(-ClO4)]2(LH=3-(phenylimino)butanone 2-oxime, L'H=1,2-diphenyl-2-(methylimino)ethanone 1-oxime), Inorg. Chem. 20 (1981) 537–545.

[27] Y. Agnus, R. Louis, B. Metz, C. Boudon, J.P. Gisselbrecht, M. Gross, Trinuclear copper(II) hydroxo and hexanuclear copper(II) oxo complexes with the ligand 3-(benzylimino)butanone 2-oxime. Syntheses and spectral, structural and redox characteristics, Inorg. Chem. 30 (1991) 3155–3161.

[28] P.A. Angaridis, P. Baran, R.R. Boca, F.C. Lee, W. Haase, G. Mezei, R.G. Raptis, R. Werner, Synthesis and structural characterization of trinuclear Cu^{II}–pyrazolato complexes containing μ_3-OH, μ_3-O, and μ_3-Cl Ligands. Magnetic susceptibility study of $[PPN]_2[(\mu_3\text{-}O)Cu_3(\mu\text{-}pz)_3Cl_3]$, Inorg. Chem. 41 (2002) 2219–2228.

[29] X. Liu, M.P. de Miranda, E.J.L. McInnes, C.A. Kilner, M.A. Halcrow, Antisymmetric exchange in two tricopper(II) complexes containing a $[Cu_3(\mu_3\text{-}OMe)]^{5+}$ core, J. Chem. Soc. Dalton Trans. (2004) 59–64.

[30] S. Ferrer, J.G. Haasnoot, J. Reedijk, E. Muller, M.B. Cingi, M. Lanfranchi, A.M. Lanfredi, J. Ribas, Trinuclear N,N-bridged copper(II) complexes involving a Cu_3OH core: $[Cu_3(\mu_3\text{-}OH)L_3A(H_2O)_2]A \cdot (H_2O)x$ {L = 3-Acetylamino-1,2,4-triazolate; A = CF_3SO_3, NO_3, ClO_4; x = 0, 2} synthesis, X-ray structures, spectroscopy, and magnetic properties, Inorg. Chem. 39 (2000) 1859–1867.

[31] S. Ferrer, F. Lloret, I. Bertomeu, G. Alzuet, J. Borras, S. Garcıa-Granada, M. Liu-Gonzalez, J.G. Haasnoot, Cyclic trinuclear and chain of cyclic trinuclear copper(II) complexes containing a pyramidal $Cu_3O(H)$ core. Crystal structures and magnetic properties of $[Cu_3(\mu_3\text{-}OH)(aaat)_3(H_2O)_3](NO_3)_2 \cdot H_2O$ [aaat = 3-Acetylamino-5-amino-1,2,4-triazolate] and $\{[Cu_3(\mu_3\text{-}OH)(aat)_3(\mu_3\text{-}SO_4)] \cdot 6H_2O\}n$ [aat = 3-Acetylamino-1,2,4-triazolate]: new cases of spin-frustrated systems, Inorg. Chem. 41 (2002) 5821–5830.

[32] B. Sarkar, M.S. Ray, M.G.B. Drew, A. Figuerola, C. Diaz, A. Ghosh, Trinuclear Cu(II) complexes containing peripheral ketonic oxygen bridges and a μ_3-OH core: steric influence on their structures and existence, Polyhedron 25 (2006) 3084–3094.

[33] M.S. Ray, S. Chattopadhyay, M.G.B. Drew, A. Figuerola, J. Ribas, C. Diaz, A. Ghosh, Trinuclear Cu^{II} complexes containing peripheral ketonic oxygen bridges and a μ_3-OH core: syntheses, crystal structures, spectroscopic and magnetic properties, Eur. J. Inorg. Chem. 22 (2005) 4562–4571.

[34] B. Le Guennic, S. Petit, G. Chastanet, G. Pilet, D. Luneau, N. Ben Amor, V. Robert, Antiferromagnetic behavior based on quasi-orthogonal MOs: Synthesis and characterization of a Cu_3 oxidase model, Inorg. Chem. 47 (2008) 572–577.

[35] M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, SIR2004: an improved tool for crystal structure determination and refinement, J. Appl. Cryst. 38 (2005) 381–388.

[36] G.M. Sheldrick, SHELXL97, University of Göttingen, Germany, 1997.

[37] L.J. Farrugia, WinGX suite for small-molecule single-crystal crystallography, J. Appl. Cryst. 32 (1999) 837–838.

[38] M.J. Frisch, G.W. Trucks, H.B. Schlegel, et al., Gaussian 09, Revision A.1, Gaussian Inc., Wallingford, CT, 2009.

[39] R.D. Dennington, T.A. Keith, J.M. Millam, GaussView 5.0.8, Gaussian Inc., 2008.

[40] N.M. O'Boyle, A.L. Tenderholt, K.M. Langner, Cclib: a library for package-independent computational chemistry algorithms, J. Comput. Chem. 29 (2008) 839–845.

[41] T. Lu, F. Chen, Multiwfn: a multifunctional wavefunction analyzer, J. Comput. Chem. 33 (2012) 580–592.

[42] A.W. Addison, T. Rao, T.N. Rao, J. Reedijk, J. Van Rijn, G.C. Verschoor, Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen–sulphur donor ligands; the crystal and molecular structure of aqua [1,7-bis(N-methylbenzimidazol-2′-yl)-2,6-dithiaheptane]copper(II) perchlorate, J. Chem. Soc. Dalton Trans. (1984) 1349–1356.

[43] S.K. Seth, G.C. Maity, T. Kar, Structural elucidation, Hirshfeld surface analysis and quantum mechanical study of para-nitro benzylidene methyl arjunolate, J. Mol. Struct. 1000 (2011) 120–126.

[44] F. Hassani, H. Tavakol, A DFT, AIM and NBO study of adsorption and chemical sensing of iodine by S-doped fullerenes, Sens. Actuat. B Chem. 196 (2014) 624–630.

[45] Z. Mahdavifar, M. Poulad, Theoretical prediction of ozone sensing using pristine and endohedral metalloboron B_{80} fullerenes, Sens. Actuat. B Chem. 205 (2014) 26–38.

[46] J. Du, X. Sun, C. Zhang, The hydrogen storage on heptacoordinate carbon motif CTi_7^{2+}, Int. J. Hydrogen Energy 41 (2016) 11301–11307.

[47] J. Wieemann, Y. Pascal, J. Chuche, Relation entre la structure et les propriétés physiques, Masson et Cie éditeurs, 1965.