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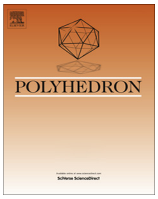

Copper(II)–azido complexes constructed from polypyridyl amine ligands

Franz A. Mautner [a,*], Masayuki Koikawa [b], Masahiro Mikuriya [c], Emily V. Harrelson [d], Salah S. Massoud [d,*]

[a] Institut für Physikalische and Theoretische Chemie, Technische Universität Graz, A-8010 Graz, Austria
[b] Faculty of Science and Engineering, Saga University, Saga 840-8502, Japan
[c] School of Sciences and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda 669-1337, Japan
[d] Department of Chemistry, University of Louisiana at Lafayette, P.O. Box 44370 Lafayette, LA 70504, USA

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ABSTRACT

A novel 1-D polymer Cu(II) complex bridged by perchlorate ions and azide ligand with the structural formula $[Cu(DPA)(N_3)(\mu O,O–ClO_4)]_n$ (**1**), $\{[Cu(L^{dpdmen})(\mu 1,3\text{-}N_3)]ClO_4\}_n$ (**2**), $\{[Cu_2(\mu\text{-}L^{py})(\mu\text{-}1,1,3\text{-}N_3)(\mu\text{-}1,3\text{-}N_3)](ClO_4)_2\}_n$ (**3**) and $\{[Cu_2(L^T)(\mu_2\text{-}1,3\text{-}N_3)(N_3)(H_2O)](ClO_4)_2.H_2O\}_n$ (**4**) where DPA = di(2-pyridylmethyl)amine, L^{dpdmen} = *N*,*N*′-bis(2-pyridylmethyl)-*N*,*N*′-dimethylethylenediamine and L^{py} = 2,6-bis[-bis(2-pyridylmethyl)aminomethyl]pyridine and L^T = 3,5-bis[bis(2-pyridylmethyl) aminomethyl]toluene were synthesized. The complexes were characterized by spectroscopic techniques (IR and visible) and by single crystal X-ray crystallography. The magnetic properties were also measured for **1**–**3** at variable temperatures (4.5–300 K). Compound **1** has the copper center in a 4+2 geometry with the equatorial plane formed through the three N-donors of the DPA and an azido group which acting as a monodentate ligand. The 1-D chain is generated *via* the axial O,O′-bridging perchlorato groups where the intra-chain Cu···Cu distance is 6.9416(16) Å. In complex **2**, the Cu center is ligated by the four N-donor atoms of L^{dpdmen} amine ligand and two N atoms of the EE bridging azido groups in a *cis*-coordinated asymmetric EE bonding fashion. The intra-chain Cu···Cu distance in this complex is 5.7949(15) Å.

1. Introduction

The azide ion N_3^- is a versatile ligand that can assemble and bridge paramagnetic divalent metal ions such Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} in a variety of ways. Aside from the fact that the azide ion can act as a simple terminal monodentate ligand [1–5], it can also bridge the metal ions in many different coordination bonding modes which include symmetric and assymetric double bridges $\mu_{1,3}$-N_3 (end-on-end, EE) [5–13] and $\mu_{1,1}$-N_3 (end-on, EO) [5,9–11,14–23], $\mu_{1,1,3}$-N_3, $\mu_{1,1,1}$-N_3, $\mu_{1,1,1,1}$-N_3, $\mu_{1,1,2,2}$-N_3, and $\mu_{1,1,1,3,3,3}$-N_3 [23–27]. The versatility of the coordination modes of this small ion and its effectiveness to propagate the magnetic interaction between the paramagnetic centers made this ligand an attractive target for extensive studies [1–27]. These bonding modes led to the formation of diverse polynuclear structures with different dimensionality (1D, 2D and 3D) and nuclearity (di-, tri-, tetra-, hexa- and poly-nuclear species) as well as interesting magnetic properties [5–33]. The coordination mode which can be adopted by a certain metal ion in the azido complexes depends largely on the nature of the coordinated co-ligands and the steric environments imposed onto their skeletons [5]. Also, it depends to some extent on the nature of the central metal ion; its oxidation state, the coordination number and geometry of the complex. Nowadays, it is well established that Cu(II) and Co(II) complexes that are derived from tripod tetradentate amine ligands lead to the isolation of mononuclear species [1–4] whereas polynuclear species are mainly produced with tri- and bi-dentate ligands [5,34].

The bridged azide ligand mediates the magnetic interaction between the paramagnetic metal centers. For example in bridged Cu(II)–azido complexes, symmetric double $\mu_{1,3}$-azido bonding are strongly antiferromagnetic whereas the corresponding $\mu_{1,1}$-azido are strongly ferromagnetic when the $Cu–N_{azide}–Cu$ angle is less than 108°. On the other hand asymmetric double $\mu_{1,3}$-azido bonding results in weak antiferromagnetic coupling whereas the corresponding $\mu_{1,1}$-azido bridges propagate moderately strong ferro- or anti-ferromagnetic interactions [5,9,10,15,16,19]. The Cu(II)–azido complexes are considered to be the most investigated systems compared to other metal(II)-azido compounds because of their diverse structures and applications as magnetic materials [35]. Moreover, in biological systems, the Cu–azide chemistry is of considerable interest because copper ions are found in the active sites of a large number of metalloproteins (hemocyanin, ascorbate oxidase, tyrosinase) and the function of these proteins is inhibited by the presence of azide ions [36].

Herein we report the structural and characterization of some Cu(II)–azide complexes that are derived from a variety of

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[*] Corresponding authors. Tel.: +43 316 4873 8234; fax: +43 316 4873 8225 (F.A. Mautner), tel.: +1 337 482 5672; fax: +1 337 482 5676 (S.S. Massoud).

E-mail addresses: mautner@ptc.tu-graz.ac.at (F.A. Mautner), ssmassoud@louisiana.edu (S.S. Massoud).

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polypyridyl amine ligands with different structural skeletons, such as those illustrated in Chart 1, to see how the ligand environment might affect the structure and the magnetic properties of these complexes.

2. Experimental

2.1. Materials and physical measurements

2-Chloromethylpyridine hydrochloride, 2,6-bis(bromomethyl)pyridine and 3,5-bis(bromomethyl)toluene, were purchased from Aldrich Chem. Comp., di(2-pyridylmethyl)amine (DPA) was obtained from TCI-America, *N,N′*-dimethylethylenediamine from Fluka. All other materials were reagent grade quality. 3,5-Bis[bis(2-pyridylmethyl)aminomethyl]toluene (L^T) was synthesized and characterized according to the published procedures Ref. [1b]. Infrared spectra were recorded on JASCO FT/IR-480 plus spectrometer as KBr pellets. Electronic spectra were recorded using Agilent 8453 HP diode UV–Vis spectrophotometer. ^1H and ^{13}C NMR spectra were obtained at room temperature on a Varian 400 NMR spectrometer operating at 400 MHz (^1H) and 100 MHz (^{13}C). ^1H and ^{13}C NMR chemical shifts (δ) are reported in ppm and were referenced internally to residual solvent resonances (DMSO-d$_6$: $\delta_H = 2.49$, $\delta_C = 39.4$ ppm). Elemental analyses were carried out by the Atlantic Microlaboratory, Norcross, Georgia USA. Magnetic susceptibilities of compounds were measured on polycrystalline powder at Kwansei Gakuin University and Saga University with a Quantum Design SQUID MPMS-XL susceptometer working in the range 4.5–300 K under external magnetic field of 0.5 T. Diamagnetic corrections were estimated from Pascal's Tables.

Caution: Salts of perchlorate and azide as well as their metal complexes are potentially explosive and should be handled with great care and in small quantities.

2.2. Synthesis of the compounds

2.2.1. Synthesis of *N,N′*-dimethyl-*N,N′*-bis(2-pyridylmethyl)ethylenediamine (L^{dpdmen})

A solution of *N,N′*-dimethylethylenediamine (1.72 g, 20 mmol) in dry tetrahydrofuran (60 mL) was treated with 2-chloromethylpyridine hydrochloride (6.604 g, 40 mmol) and triethylamine (8.093 g, 80 mmol) and the mixture was stirred under reflux for 18 h. The resulting mixture was cooled to in ice and the triethylamine hydrobromide was removed by filtration. The filtrate was then treated with 10 mL 15% NaOH solution and extracted with CH_2Cl_2 (3 × 40 mL). The combined extracts were dried over anhydrous $MgSO_4$. Removal of the solvent with rotary evaporator yielded dark brown oil which was chromatographed on alumina and eluted with 95/5 (v/v) mixture of ethyl acetate/MeOH ($R_f = 0.81$). The purified ligand was obtained as yellow viscous oil (yield: 4.2 g, 79%). Selected IR bands (cm^{-1}): ν(C–H) 3064 (w), 2949 (m), 2802 (m); pyridyl groups: 1592 (s), 1577 (m), 1474 (m), 1435 (s). ^1H NMR: 8.43 (m, 2H), 7.70 (m, 2H), 7.37 (m, 2H), 7.72 (m, 2H), 3.58 (s, 4H), 2.51 (s, 4H), 2.14 (s, 6H); ^{13}C NMR: 159.74 (2-py), 149.06 (6-py), 136.78 (4-py), 123.01 (3-py), 122.42 (5-py), 63.95 (N–CH_2-py), 35.40 (–CH_2–CH_2–N), 42.94 (CH_3–N), 40.60 (CH_3–N).

2.2.2. 2,6-Bis[bis(2-pyridylmethyl)aminomethyl]pyridine (L^{py})

A mixture of 2,6-bis(bromomethyl)pyridine (2.65 g, 10.0 mmol), di(2-pyridylmethyl)amine (4.00 g, 20.0 mmol), triethylamine (2.02 g, 20.0 mmol) and 80 mL anhydrous THF was magnetically stirred and gently refluxed under nitrogen gas for 4 days. The resulting brown mixture was cooled, filtered and solvent was removed by rotary evaporator. The resulting red-brown viscus oil was stirred with 60 mL of 15% NaOH, and then extracted with CH_2Cl_2 (3 × 30 mL). The organic phase was dried with anhydrous $MgSO_4$, filtered and solvent was removed. The ligand was purified by column chromatography on alumina using a mixture of ethyl acetate/MeOH (95/5, v/v) as eluent. Further purification on the column and evaporating the solvent yielded orange-brown solid which upon crystallization from CH_2Cl_2 with the aid of charcoal affords off white solid (yield: 2.8 g, 56%). Characterization: m.p. 109–110 °C, Elemental analysis: *Anal.* Calc. for $C_{31}H_{31}N_7$ (501.63 g/mol): C, 74.22; H, 6.23; N, 19.55. Found: C, 73.87; H, 6.20; N, 19.37%. Selected IR bands (cm^{-1}): ν(C–H): 3068 (w), 3012 (m), 2915 (w), 2882 (w), 2821 (s); pyridyl groups: 1590 (s), 1577 (m), 1475 (m), 1460 (m), 1437 (s). ^1H NMR: 8.44 (m, 4H), 7.70 (m, 2H), 7.70 (m, 5H), 7.54 (m, 4H), 7.40 (s, 2H), 7.19 (m, 4H), 3.73 (m, 8H), 2.48 (s, 4H); ^{13}C NMR: 159.48 (2′-py),158.70 (2-py, 6-py), 149.24 (6′-py), 136.93 (4-py), 122.99 (3′-py, 3-py, 5-py), 122.54 (5′-py), 121.25 (4′-py), 59.90 (N–CH_2-py).

2.2.3. Synthesis of $[Cu(DPA)(N_3)(\mu\text{-}ClO_4)]_n$ (**1**)

Copper(II) perchlorate hexahydrate (0.190 g, 0.5 mmol) and di(2-pyridylmethyl)amine (0.100 g, 0.5 mmol) were dissolved in 20 ml of H_2O. The solution was heated for 5 min, followed by the drop-wise addition of an aqueous solution sodium azide (0.036 g, 0.55 mmol in 5 mL H_2O). The violet-blue solution was heated on a steam-bath for 10 min, filtered through Celite while hot and allowed to crystallize at room temperature. After 2 h, the resulting large crystals of a violet compound which separated was collected by filtration, washed with absolute ethanol, ether and then air dried (overall yield: 192 mg, 95%). Well-shaped crystals of X-ray quality were obtained from dilute solutions. Characterization: Elemental analysis: *Anal.* Calc. for $C_{12}H_{13}N_6CuClO_4$: C, 35.65; H, 3.24; N, 20.79. Found: C, 35.81; H, 3.30; N, 21.06%. Selected IR bands (cm^{-1}): 2057 (s), 1092 (s), 1637 (vs), 1116 (m) and 1054 (m). Visible spectrum {λ_{max}, nm (ε_{max}, M^{-1}cm^{-1})} in H_2O: 643 (153), in DMSO: 642 nm (212) and in DMF 640 (264).

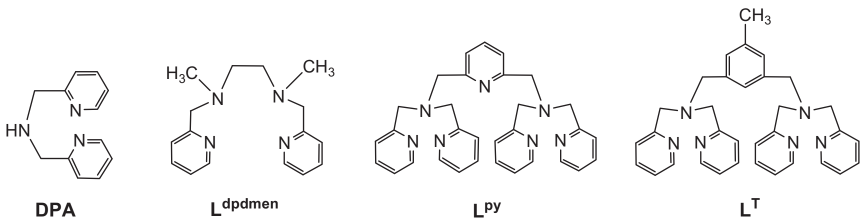

Chart 1. Structural relationship between the polypyridyl amine ligands used in this study. †Ligand abbreviations: DPA, bis(2-pyridylmethyl)amine; L^{dpdmen} *N,N′*-bis(2-pyridylmethyl)-*N,N′*-dimethylethylenediamine; L^{py}, 2,6-bis[bis(2-pyridylmethyl)aminomethyl]pyridine, L^T = 3,5-bis[bis(2-pyridylmethyl)aminomethyl]toluene.

2.2.4. Synthesis of $[Cu(L^{dpdmen})(ClO_4)]ClO_4$ (**2a**)

Copper(II) perchlorate hexahydrate (0.380 g, 1.0 mmol) was added to L^{dpdmen} (0.160, 1.0 mmol) dissolved in H_2O (20 mL). This solution was heated for 15 min on steam-bath and filtered through Celite and then allowed to crystallize at room temperature. After 2 weeks, the blue crystals which separated were collected by filtration, washed with propan-2-ol, followed by ether and air dried (overall yield: 0.340 g, 64%). Characterization: *Anal.* Calc. for $C_{16}H_{22}N_4Cl_2CuO_8$ (523.43 g/mol): C, 36.07; H, 4.16; N, 10.52. Found: C, 35.86; H, 4.13; N, 10.09%. Selected IR bands (KBr, cm^{-1}): ν(Cl–O) (ClO_4^-) at 1098 (vs). UV–Vis spectrum {λ_{max}, nm (ε_{max}, $M^{-1}cm^{-1}$)}: in H_2O: 634 (251).

2.2.5. Synthesis of $\{[Cu(L^{dpdmen})(\mu_{1,3}\text{-}N_3)]ClO_4\}_n$ (**2**)

To an aqueous solution of $[Cu(L^{dpdmen})(ClO_4)]ClO_4$ (0.260 g, 0.50 mmol in 10 mL H_2O), NaN_3 (0.046 g, 0.07 mmol) dissolved in H_2O (5 mL) was added drop-by-drop, during the addition the blue color turns green. The resulting solution was heated on a steam-bath for 5 min, filtered while hot through Celite and allowed to crystallize at room temperature. After 2 h, the green crystals which separated were collected by filtration, washed with propan-2-ol, followed by ether and then dried in air (overall yield: 0.215 g, 90%). Green needles suitable for X-ray analysis were obtained from dilute aqueous solutions. Characterization: Elemental analysis: *Anal.* Calc. for $C_{16}H_{22}N_7ClCuO_4$ (475.39 g/mol): C, 40.42; H, 4.66; N, 20.62. Found: C, 40.34; H, 4.64; N, 20.57%. Selected IR bands (cm^{-1}): 2060 (s), 2036 (s) 1087 (s). Visible spectrum {λ_{max}, nm (ε_{max}, $M^{-1}cm^{-1}$)} in H_2O: 629 (270) and CH_3CN (640 nm, 274).

2.2.6. Synthesis of $[Cu_2(L^{py})(N_3)_2](ClO_4)_2$ (**3**)

The ligand 2,6-bis[bis(2-pyridylmethyl)aminomethyl]pyridine (L^{py}) (0.0503 g, 0.100 mmol) dissolved in 5 mL of MeOH was added to an aqueous solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.075 g, 0.200 mmol/10 mL H_2O). The resulting blue solution was heated on a steam-bath for 5 min then treated with NaN_3 solution (0.014 g, 0.200 mmol/5 mL H_2O). This solution was heated for another 5 min, filtered through Celite and allowed to crystallize at room temperature. After, 4 days the green crystals which separated were collected, washed with cold absolute EtOH, ether and air dried (overall yield: 0.081 g, 89%). Single crystals were obtained from dilute solutions. Characterization: Elemental analysis: *Anal.* Calc. for $C_{31}H_{31}N_{13}Cl_2Cu_2O_8$ (911.78 g/mol): C, 40.84; H, 3.43; N, 19.97. Found: C, 40.65; H, 3.34; N, 19.84%. Selected IR bands (cm^{-1}): $\nu(N_3)$ 2079 (vs), 2052 (vs); ν(Cl–O) (ClO_4^-) 1120 (vs), 1091 (vs). UV–Vis spectrum {λ_{max}, nm (ε_{max} per Cu atom, $M^{-1}cm^{-1}$)} in H_2O: 380 (1605), 634 (244, br).

2.2.7. Synthesis of $[Cu_2(L^T)(\mu_2\text{-}1,3\text{-}N_3)(N_3)(H_2O)](ClO_4)_2{\cdot}H_2O$ (**4**)

The complex was isolated as dark bluish-green crystals using a similar procedure as that described above for complex **3** (overall yield: 56%). Single crystals were obtained from dilute solutions. Characterization: Elemental analysis: *Anal.* Calc. for $C_{33}H_{40}N_{12}Cl_2Cu_2O_{10}$ (960.74 g/mol): C, 41.25; H, 4.20; N, 17.50. Found: C, 41.33; H, 3.90; N, 17.43%. Selected IR bands (cm^{-1}): ν(OH) 3449 (H_2O); $\nu(N_3)$ 2067 (m), 2054 (vs); ν(Cl–O) (ClO_4^-) 1145 (m), 1119 (vs), 1089 (vs). UV–Vis spectrum {λ_{max}, nm (saturated solution)} in H_2O: 378, 648 (v br).

2.3. X-ray crystal structure analysis

The X-ray single-crystal data of the compounds **1** and **2** were collected on a Bruker-AXS SMART CCD diffractometer at 100(2) K. The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed in Table 1. The intensities were collected with Mo Kα radiation (λ = 0.71073 Å). Data processing, Lorentz-polarization and absorption corrections were performed using SMART, SAINT and the SADABS computer programs [37]. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2, using the SHELXTL [38] program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps, assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical constraints. In case of **2** split occupancies of 0.679(2) and 0.321(2) were applied for disordered oxygen atoms O(1), O(3), O(4) and O(5), O(6), O(7), respectively.

3. Results and discussion

3.1. Synthesis of the complexes

The four green azido complexes $[Cu(DPA)(N_3)(\mu_2\text{-}ClO_4)]_n$ (**1**), $\{[Cu(L^{dpdmen})(\mu_2\text{-}1,3\text{-}N_3)]ClO_4\}_n$ (**2**), $\{[Cu_2(\mu\text{-}L^{py})(\mu_3\text{-}1,1,3\text{-}N_3)(\mu_2\text{-}1,3\text{-}N_3)](ClO_4)_2{\cdot}nH_2O\}_n$ (**3**) and $[Cu_2(L^T)(\mu_2\text{-}1,3\text{-}N_3)(N_3)(H_2O)](ClO_4)_2{\cdot}H_2O$ (**4**) under investigation were synthesized in high yield by the reaction of an aqueous solution containing equimolar amounts of $Cu(ClO_4)_2{\cdot}6H_2O$ and a methanolic solution of the corresponding amine ligand (DPA, L^{dpdmen}, L^{py}, L^T: Chart 1) with an aqueous solution of sodium azide. Also, complex **2** was obtained *via* the reaction of $[Cu(L^{dpdmen})(ClO_4)]ClO_4$ with NaN_3. The synthesized complexes were structurally characterized by crystal structure, IR and UV–Vis spectra. The magnetic susceptibilities of the complexes were investigated at variable temperatures (4.5–300 K).

3.2. IR and electronic spectra of the complexes

The IR spectra of the azido complexes **1**–**3** reveal the presence of strong absorption bands at the frequency region 2060–2080 cm^{-1} attributed to the asymmetric stretching vibration, $\nu_{as}(N_3)$ of the azido group. Complexes **1** gave a single band at 2057 cm^{-1}, as expected for the monodentate azido group whereas two bands were observed in complexes **2**, **3** and **4** as a result of the existence of the bridging azido groups in two bonding modes (see Section 2). The Cl–O of the ClO_4^- group displayed strong vibration band around 1090–1150 cm^{-1} region, and the split of this band into two or three components in the perchlorato complexes **1** and **4**. In this complex, the split of this band results from the reduction of the symmetry of

Table 1
Crystallographic data and processing parameters.

Compound	1	2
Empirical formula	$C_{12}H_{13}ClCuN_6O_4$	$C_{16}H_{22}ClCuN_7O_4$
Formula mass	404.28	475.41
System	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.6451(17)	12.262(3)
b (Å)	13.093(3)	18.888(4)
c (Å)	13.765(3)	8.8122(18)
α (°)	90	90
β (°)	101.70(3)	107.45(3)
γ (°)	90	90
V (Å^3)	1525.7(6)	1947.0(8)
Z	4	4
μ (mm−1)	1.639	1.299
D_{calc} (Mg/m^3)	1.760	1.622
Crystal size (mm)	0.27 × 0.23 × 0.16	0.35 × 0.30 × 0.18
θ_{max} (°)	26.37	26.37
Data collected	11968	14497
Unique reflection/R_{int}	3127/0.0551	3975/0.0523
Parameters/restraints	251/1	264/0
Goodness-of-fit (GOF) on F^2	1.101	1.031
R_1/wR_2 (all data)	0.0446/0.1120	0.0403/0.0986
Residual extrema (e/Å^3)	1.056/−0.496	0.556/−0.317

the ClO_4^- group to C_{2v} due to its coordination to the Cu^{2+} ion or its involvement in hydrogen bonding (see next section).

The visible spectra of the azido complexes **1**–**4** and **2a** in H_2O display a single broad band over the wavelength range 650–630. Moreover in complex **1**, the position of this band did not show any significant change when the spectrum was measured in DMSO or DMF. The spectral feature of the complexes is most likely consistent with tetragonally distorted six-coordinate geometry for Cu(II) complex.

3.3. Description of the structures

*3.3.1. [Cu(DPA)(N$_3$)(ClO4)]$_n$ (**1**)*

A perspective view of **1** together with the atom numbering scheme is presented in Fig. 1, and relevant bond parameters are summarized in Table 2. Cu(1) is six-coordinated in a 4 + 2 fashion by three N-donor atoms of the DPA ligand, and one N atom of a terminal azido group [Cu(1)–N from 1.948(2) to 2.013(2) Å] in basal positions; and the *trans*-axial sites are occupied by oxygen atoms of perchlorate bridging ligand with semi-coordinative Cu(1)–O bond lengths ranges from 2.605(2) to 2.840(2) Å. The μ-O,O-bridging perchlorate anions connect the Cu polyhedra to a polymeric chain oriented along the *c*-axis of the monoclinic unit cell. The intra-chain Cu···Cu distance is 6.9416(16) Å, and the shortest inter-chain Cu···Cu separation is 6.8400(16) Å.

*3.3.2. {[Cu(L^{dpdmen})(μ1,3-N$_3$)](ClO4)}$_n$ (**2**)*

A perspective view of **2** together with the atom numbering scheme is presented in Fig. 2, and selected bond parameters are given in Table 2. The structure consists of polymeric $[Cu(L^{dpdmen})(-N_3)]_n^{n+}$, cationic chains oriented along the *c*-axis of the monoclinic unit cell, and perchlorate counter ions. The Cu(1) center is ligated by four N atoms of the L^{dpdmen} amine ligand and two N atoms of the EE bridging azido group. The Cu(1)–N(L2) bond distances vary from 2.008(2) to 2.089(2) Å, whereas the *cis*-coordinated asymmetric EE azido bridge has Cu(1)–N(11) of 2.008(2) and Cu(1)–N(13′) of 2.606(3) Å. The N(11)–N(12) and N(12)–N(13) bond distances are 1.198(3) and 1.155(3) Å, respectively. The Cu–N–N and N–N–N bond angles are 122.48(9)°, 115.02(13)° and 176.6(3)°, respectively. The intra-chain metal···metal distance is 5.7949(15) Å, and the shortest inter-chain Cu···Cu separation is 8.146(2) Å.

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

Compound **1**			
Cu(1)–N(11)	1.948(2)	Cu(1)–N(3)	1.981(2)
Cu(1)–N(1)	1.988(2)	Cu(1)–N(2)	2.013(2)
Cu(1)–O(2′)	2.605(2)	Cu(1)–O(1)	2.642(3)
Cu(1)–O(6)	2.840(2)	N(12)–N(13)	1.155(3)
N(11)–N(12)	1.198(3)	-	-
N(11)–Cu(1)–N(3)	96.86(9)	N(11)–Cu(1)–N(1)	97.98(9)
N(3)–Cu(1)–N(1)	164.79(8)	N(11)–Cu(1)–N(2)	179.40(9)
N(3)–Cu(1)–N(2)	82.64(8)	N(1)–Cu(1)–N(2)	82.51(8)
N(12)–N(11)–Cu(1)	122.48(19)	N(13)–N(12)–N(11)	176.6(3)
O(2′)–Cu(1)–O(6)	153.91(18)	O(2′)–Cu(1)–O(1)	173.34(9)
*Compound **2***			
Cu(1)–N(1)	2.008(2)	Cu(1)–N(11)	2.008(2)
Cu(1)–N(2)	2.028(2)	Cu(1)–N(3)	2.086(2)
Cu(1)–N(4)	2.089(2)	N(11)–N(12)	1.194(3)
Cu(1)–N(13′)	2.606(3)	N(12)–N(13)	1.166(3)
N(1)–Cu(1)–N(11)	90.19(9)	N(4)–Cu(1)–N(13′)	162.01(9)
N(11)–Cu(1)–N(12)	89.61(9)	N(1)–Cu(1)–N(2)	178.17(9)
N(11)–Cu(1)–N(3)	171.52(9)	N(1)–Cu(2)–N(3)	81.60(9)
N(1)–Cu(1)–N(4)	104.01(9)	N(2)–Cu(1)–N(3)	98.53(9)
N(2)–Cu(1)–N(4)	77.81(9)	N(11)–Cu(1)–N(4)	100.74(9)
N(12)–N(11)–Cu(1)	121.99(19)	N(3)–Cu(1)–N(4)	83.40(8)
N(13)–N(12)–N(11)	177.8(3)	-	-

Symmetry code: (‘) *x*, −*y* + 1/2, *z* − 1/2.

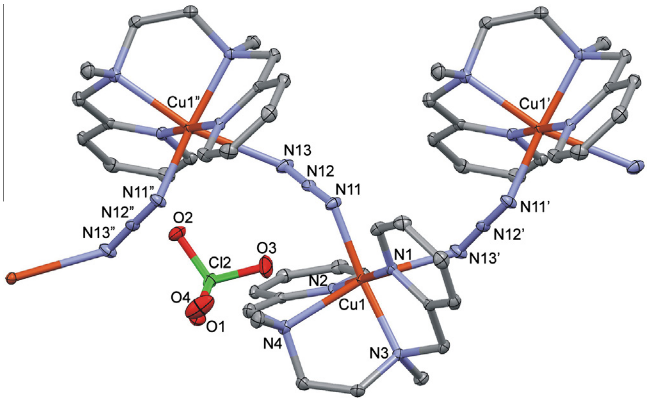

Fig. 2. Perspective view (50% probability ellipsoids) of **2** together with the atom numbering scheme. Symmetry code: (‘) *x*, −*y* + 1/2, *z* − 1/2; (“) *x*, −*y* + 1/2, *z* + 1/2.

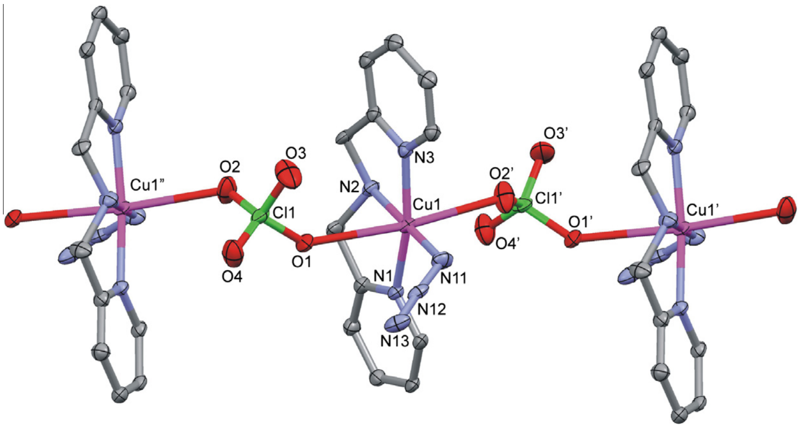

Fig. 1. Perspective view (50% probability ellipsoids) of **1** together with the atom numbering scheme. Symmetry code: (‘) *x*, −*y* + 1/2, *z* − 1/2; (“) *x*, −y + 1/2, *z* + 1/2. Disordered oxygen atoms with minor occupancy are omitted.

3.3.3. Attempts to solve structures of compounds **3** and **4**

Full structure determinations of compounds **3** and **4** failed due to low single crystal quality. However, preliminary structural results clearly show the polymeric chain core systems of the compounds **3** and **4** (see Supplementary section).

3.4. Magnetic properties

The magnetic data of complex **1** are shown in Fig. 3 in the form of χ_A and μ_{eff} versus T plots, where χ_A is the magnetic susceptibility per Cu unit, μ_{eff} is the magnetic moment per Cu unit, and T is the absolute temperature. At 300, the magnetic moment of **1** is 1.88 μ_B which is a little bit higher than the spin-only value for copper(II) $S = ½$ ion. The magnetic moment exhibits a continuous slight decrease with lowering temperature and reaches 1.70 μ_B at 4.5 K, which suggests the presence of a weak antiferromagnetic interaction between the copper(II) ions. Considering the crystal structure of **1**, the magnetic data were analyzed by the Boner–Fisher model for an isolated Heisenberg 1D chain [39]:

$$\chi_A = (Ng^2\beta^2/kT)(0.25 + 0.14995x + 0.30094x^2)/(1.0 + 1.9862x + 0.68854x^2 + 6.0626x^3) + N\alpha \qquad (1)$$

where $x = |J|/kT$ and $N\alpha$ is the temperature-independent paramagnetism, which was set to 60×10^{-6} cm^3 mol^{-1} for each copper(II) ion. The best-fitting parameters are $g = 2.13$ and $J = -0.41$ cm^{-1}. The magnetic interaction is negligibly small because of the very poor overlap of the equatorial magnetic orbital and the axial bridging perchlorate ion. The magnetic behavior observed in this complex is similar to that found in the bridging μ1,5-dicyanamido complex {[Cu(MeDPA)(μ1,5-dca)]ClO$_4$}$_n$, where MeDEPA = *N*-methylbis[2-(2-pyridylethyl)]amine [40].

The temperature dependence of magnetic susceptibility of **2** was measured in the temperature range of 4.5–300 K under an external magnetic field of 0.5 *T*. Fig. 4 shows the plots of χ_A versus T and μ_{eff} versus T. The μ_{eff} versus T plot of **2** (2.01 μ_B at 300 K) shows a slight decrease with lowering the temperature over the range 70–300 K and an increase on lowering the temperature from 70 to 4.5 K, reaching 2.37 μ_B at 4.5 K. The increase of the μ_{eff} value indicates a ferromagnetic interaction between two adjacent Cu(II) centers *via* the azido groups. The magnetic data were analyzed by the series expansion (2) for the Heisenberg model for ferromagnetically coupled $S = ½$ ions which was derived by Baker et al. [41].

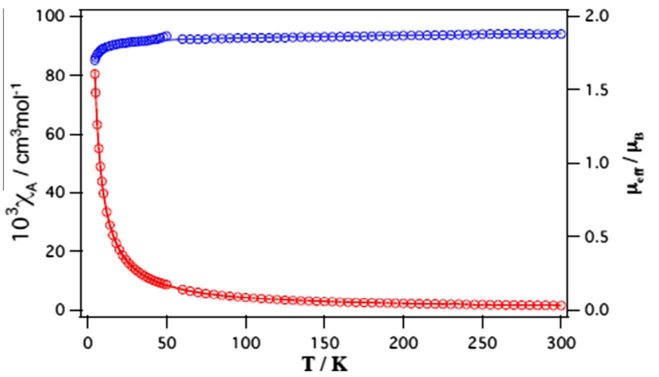

Fig. 3. Temperature dependence of magnetic susceptibilities (red circles) and effective magnetic moments (blue circles) for complex **1**. The solid lines represent the theoretical curves derived from Eq. (1) with the parameters of $g = 2.13$ and $J = -0.41$ cm^{-1}. (Color online.)

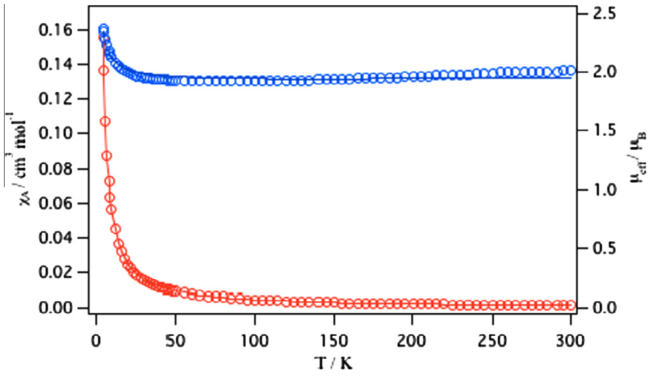

Fig. 4. Temperature dependence of magnetic susceptibilities (red circles) and effective magnetic moments (blue circles) for complex **2**. The solid lines represent the theoretical curves derived from Eq. (2) with the parameters of $g = 2.20$ and $J = 1.68$ cm^{-1}. (Color online.)

$$\chi_A = (Ng^2\mu_B^2/4kT)[(1.0 + 5.7979916x + 16.902653x^2 + 29.376885x^3 + 29.832959x^4 + 14.036918x^5)/(1.0 + 2.7979916x + 7.0086780x^2 + 8.6538644x^3 + 4.5743114x^4)]^{2/3} + N\alpha \qquad (2)$$

where $x = J/2kT$. The solid line in Fig. 4 shows the calculated curve with best-fitting parameters of $g = 2.20$ and $J = 1.68$ cm^{-1}.

The temperature dependence of magnetic susceptibility of **3** was measured in the temperature range of 2.0–4.5 K under external field of 0.5 T. The plots of χ_M versus T and μ_{eff} versus T. are shown in Fig. S2. The μ_{eff} versus T plot of **3** (2.98 μ_B at 300 K) shows a slight decrease with lowering the temperature over the range 45–300 K followed by an increase on lowering the temperature from 45 to 10 K, and then decreasing again to 2.53 μ_B at 2.0 K. Based on the structure, the spin-exchange Hamiltonian can be described as $H = -2(2J_1S_{Cu2}\cdot S_{Cu1} + J_2S_{Cu1}\cdot S_{Cu1})$ where $J_1 = J_{Cu2Cu1} = -J_{Cu2'Cu1'}$, $J_2 = J_{Cu1Cu1}$, due to the inversion center symmetry of the linear tetra-nuclear (Cu2–Cu1–Cu1′–Cu2′) unit, assuming $J_{Cu2Cu1'} = J_{Cu2'Cu1} = 0$, $J_{Cu2Cu2'} = 0$, $J_{Cu2Cu1} = J_{Cu2'Cu1'}$. The susceptibility Eq. (3) as derived from the van Vleck equation [42],

$$\chi_{tet}(4\mathrm{Cu}) = (2Ng^2\beta^2/kT)[5\exp(-E_1/kT) + \exp(-E_2/kT) + \exp(-E_3/kT) + \exp(-E_4/kT)]/[5\exp(-E_1/kT) + 3\exp(-E_2/kT) + 3\exp(-E_3/kT) + 3 \times \exp(-E_4/kT) + \exp(-E_5/kT) + \exp(-E_6/kT)] + 4N\alpha \qquad (3)$$

was used to fit the experimental data. The best fitted parameters are $g = 2.28$, $J_1 = -0.63$ cm^{-1}, $J_2 = 2.8$ cm^{-1}. The J_1 value describes the magnetic interaction via the end-to-end (μ$_2$-1,3) bridging of N_3^- being antiferro-magnetic, and J_2 is the interaction via the end-on (μ$_2$-1,1) of the N_3^- being ferro-magnetic. This is in harmony with the magnetic interaction in most azido-bridged copper(II) complexes.

4. Conclusion

We report the synthesis and characterization of four Cu(II)–azide complexes that derived from a variety of polypyridyl amine ligands with different structural skeletons, namely [Cu(DPA)(N$_3$)(μ$_2$-ClO$_4$)]$_n$ (**1**), {[Cu(L^{dpdmen})(μ$_2$-1,3-N$_3$)]ClO$_4$}$_n$ (**2**), {[Cu$_2$(μ-L^{py})(μ$_3$-1,1,3-N$_3$)(μ$_2$-1,3-N$_3$)](ClO$_4$)$_2$·*n*H$_2$O}$_n$ (**3**) and [Cu$_2$(L^T)(μ$_2$-1,3-N$_3$)(N$_3$)(H$_2$O)](ClO$_4$)$_2$·H$_2$O (**4**). The common structural feature of this series of four complexes is the formation of polymeric chain systems. The magnetic properties of compounds **1**–**3** exhibit very weak magnetic coupling between the Cu^{2+} centers with antiferromagnetic interaction in complex **1** ($J = -0.41\ cm^{-1}$) ferro-magnetic interactions in complex **2** ($J = 1.68\ cm^{-1}$) and ferro-magnetic and antiferro-magnetic interactions in complex **3** ($J = 2.8$ and $-0.63\ cm^{-1}$).

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Appendix A. Supplementary data

CCDC 918734, and 918735 contains the supplementary crystallographic data for complexes **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.04.033.

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