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Planar Copper and Nickel Triangles with a Guanidine-derived Ligand

Takuto Matsumoto, Yamato Sato, Takuya Shiga* and Hiroki Oshio*

A novel guanidine-derived ligand with three tetradentate N_4 coordination sites and its trinuclear copper and nickel complexes, $[Cu_3]$ and $[Ni_3]$, were synthesized. X-ray structural analyses of $[Cu_3]$ and $[Ni_3]$ reveals the complexes to have planar triangular structures with pseudo C_3 symmetry. Magnetic measurements for $[Cu_3]$ and $[Ni_3]$ complexes indicate that antiferromagnetic interactions are operative in both complexes with intratriangle exchange coupling constants of g = 2.08(1), J = -130(1) cm^{-1} for $[Cu_3]$, and g = 2.18(1), J = -14.9(1) cm^{-1} for $[Ni_3]$. $[Cu_3]$ has a doublet spin ground state at low temperature, while the magnetic susceptibility data and magnetization curve suggest that the ground state of $[Ni_3]$ is spin singlet.

Introduction

Odd-membered antiferromagnetic rings continue to attract great interest due to their potential to exhibit spin frustration, non-colinear spin states and spin chirality.[1] There remain, however, relatively few reports concerning three-, five-, and seven- membered antiferromagnetic ring systems, whereas there are many studies on even-membered rings.[2] Of the reported odd-membered systems, magnetically isolated three membered rings are the most widely studied, while examples of five- and seven- nuclear systems are rare. We reported the synthesis of a seven-membered antiferromagnetic vanadyl ring based on a cyclodexytrin template that exhibited unusual stepped magnetization,[3] but the scarcity of suitable templates renders the rational synthesis of five- and seven- membered rings challenging.[4] On the other hand three-membered ring complexes can self-assemble from simple building blocks to yield clusters whose magnetic interactions can be studied to shed light on the fundamentals of quantum spins.[5] In particular, the magnetic properties of odd-membered antiferromagnetic rings with S = 1/2 spins have been extensively studied for three-membered rings, which is simplest system and close to a real quantum spin model. In one such example, half step magnetization and hysteresis curves originating from spin chirality were observed in the antiferromagnetically coupled $[Cu^{II}_3]$ polyoxometalate sandwich complex $Na_9[Cu_3Na_3(H_2O)_9(\alpha\text{-}AsW_9O_{33})_2]$.[6] The magnetization curve collected by the application of a rapidly

pulsed field showed asymmetry between the positive and negative field regions. Motivated by interest in quantum spin systems, several $[Cu_3]$-type molecules have been synthesized by molecular design, and their magnetic behaviour studied.[7]

One-dimensional frustrated spin models have unique and diverse properties. In contrast to higher dimensional spin systems, quantum spin chains have no long-range order. In the absence of frustration, such as in an antiferromagnetic ladder with an even number of legs, S = 1/2 systems are expected to have an excitation gap.[8] When frustration is present, the Lieb-Schultz-Mattis theorem suggests that the spin gap must be accompanied with at least doubly degenerate ground states.[9] Three-leg spin tubes have a triangular column type structure, and antiferromagnetic interactions are operative between the spins. Although the theory of spin tubes is well studied and the expected physical properties are interesting from a fundamental viewpoint, there are only few examples of compounds with triangular column type structures.[10] The first example of a three-leg spin tube with S = 3/2, the inorganic chromium inorganic ($CsCrF_4$, Cr^{3+}; S = 3/2) was reported in 2009,[11] with a space group of $P\bar{6}$ 2m, and a columnar superstructure where identical Cr_3 equilateral triangles are stacked without rotation along the c axis. The distance between Cr ions in the equilateral triangle is 3.741 Å, while that along the c axis is 3.857 Å. The magnetic susceptibility data shows that antiferromagnetic interactions are operative between the chromium ions, and the Weiss temperature is -143 K. The specific heat capacity shows there is no magnetic phase transition below 4 K. The heat capacity curve tends to a non-zero value at 0 K, and suggests that this compound has a gapless spin-liquid state, a so-called Tomonaga–Luttinger liquid.

A spin tube with divalent copper ions, $[Cl(CuCl_2tachH)_3]^{2+}$ (tach = cis, trans-1,3,5-triamino-cyclohexane), was reported in 2004 by Cronin et al. and the physical properties have been

a. Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tennnodai 1-1-1, Tsukuba 305-8571, Japan.
E-mail: oshio@chem.tsukuba.ac.jp; Fax: +81 29 853 4238; Tel: +81 29 853 4238

well studied. [12] This Cu$_3$ spin tube shows weak antiferromagnetic interactions between Cu(II) ions in the intra-triangular units, and has moderate antiferromagnetic interactions between Cu(II) ions of neighbouring Cu$_3$ triangle units. Therefore, the spin system can be regarded as weakly antiferromagnetic-coupled three-leg chains. Magnetization measurements at low temperature suggest this system has a gapless Tomonaga-Luttinger liquid ground state, although the theoretical prediction did indicate the existence of a spin gap. In order to access a novel quantum phase, fine-tuning of the magnetic interactions and spin topology is important.

In another example, a dabco (= 1,4-diazabicyclo[2.2.2]octane) bridged-type copper spin tube structure *catena*-[Cu$_3$(L1)$_3$(dabco)$_3$]·3Et$_2$O (H$_2$L1 = 1,1-(1,4-phenylene)-bis(4,4-dimethylpentane-1,3-dione)) was reported in 2006 by Lindoy et al.[13] The planar triangular moiety consists of three copper(II) ions and three bis-β-diketone type bridging ligands, and the trinuclear metallocycles are bridged by dabco moieties. Although this three-leg spin tube is not a twisted structure, the space group is $P2_1/m$, i.e. it has no crystallographic C_3 axis. In this system, the physical properties appear likely to be very interesting but to date only the structure was reported. From the view point of molecular design of magnetic system, the planar complex may be a useful building unit for the spin tube.

Towards the development of experimental spin tube models, it is important to construct triangular trinuclear complexes as building units through the use of appropriate planar bridging ligands whose coordination sites describe an equilateral triangle.

In this paper, the rational synthesis and magnetic properties of triangular metal complexes with highly planar structures were studied. A new guanidine-derived ligand, H$_2$L·HCl (= 1,2,3-tris[(6-(1H-pyrazol-1-yl)pyrid-2-ylmethylene)amino]guanidinium chloride), was prepared and its copper and nickel complexes were synthesized. The ligand has three planar tetra-dentate N$_4$ coordination sites and can coordinate the equatorial positions of transition metal ions, suggesting that it may be a useful building block for planar triangle complexes in line with findings with a similar guanidine-type ligand.[14]

Experimental section

Materials and general characterization

All chemicals were used without further purification except when noted. Diethyl ether was distilled over calcium hydride then sodium/benzophenone. The precursors **1**-**3** of the guanidine-derivative ligand were prepared by modified versions of published methods according to Scheme 1.[9-11]
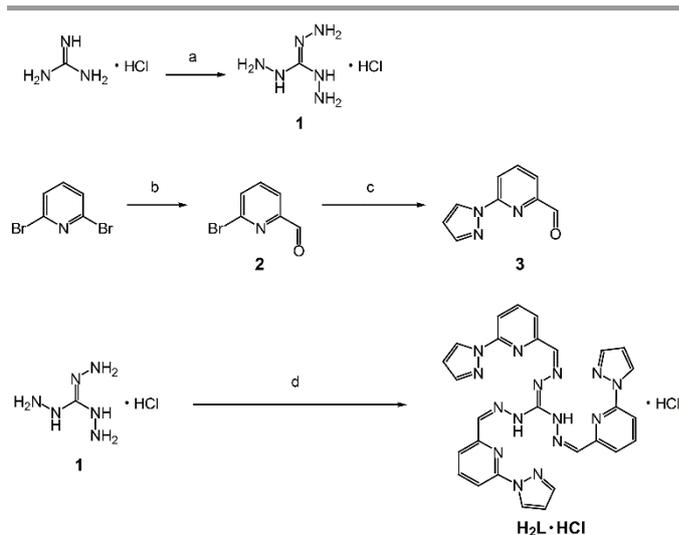
Scheme 1. Synthesis of **H$_2$L·HCl**. a) Hydrazine monohydrate, 1,4-dioxane. b) *n*-BuLi, DMF, Et$_2$O. c) Pyrazole, 1,10-phenanthroline monohydrate, CuI, K$_2$CO$_3$, toluene. d) **3**, EtOH.

Preparation of 1,2,3-triaminoguanidinium chloride (1).[15] To a suspension of guanidinium chloride (1.91 g, 20 mmol) in 1,4-dioxane (10 mL) was added hydrazine monohydrate (3.41 g, 68 mmol) with stirring. The mixture was heated under reflux for two hours. After the mixture cooled to ambient temperature, the product was collected by filtration, washed with 1,4-dioxane, and dried to give 1,2,3-triaminoguanidinium chloride (**1**) as a white crystalline solid.

Preparation of 6-bromo-2-pyridinecarboxaldehyde (2).[16] 2,6-dibromopyridine (19.0 g, 80.0 mmol) was dissolved in anhydrous diethyl ether (150 mL) under a nitrogen atmosphere. The solvent was cooled down to -78 °C and *n*-buthyl lithium (2.6 M in hexane) (30.7 mL, 80.0 mmol) was added slowly, while ensuring that the temperature did not rise above -60 °C. After addition, the reaction mixture was allowed to warm to -40 °C for fifteen minutes, and cooled down to -78 °C again. Anhydrous N,N-dimethylformamide (6.74 mL, 88.0 mmol) was added, ensuring that the reaction temperature did not exceed -70 °C. The mixture was stirred for two hours at -78 °C, before the reaction was quenched by the addition of 6 M hydrochloric acid. (30 mL). The organic phase was collected and dried over anhydrous magnesium sulfate. After evaporating the solvent, the residue was purified by column chromatography on a silica gel (eluting with dichloromethane) to give 6-bromo-2-pyridinecarboxaldehyde (**2**) (10.1 g, 54.3 mmol, 68 % yield) as a crystalline white solid: ^{1}H-NMR (CDCl$_3$) δ 10.01 (s, 1H), 7.93 (dd, 1H, J = 6.4 Hz, 1.8 Hz), 7.76 (dd, 1H, J = 8.0 Hz), 7.73 (dd, 1H, J = 7.8 Hz, 1.8Hz).

Preparation of 6-(1H-pyrazol-1-yl)-2-pyridinecarboxaldehyde (3).[17] A mixture of **2** (5.58 g, 30.0 mmol), pyrazole (2.66 g, 39.0 mmol), 1,10-phenanthroline monohydrate (1.19 g, 6.00 mmol), CuI (1.25g, 3.00 mmol), and K$_2$CO$_3$ (4.56 g, 30.0 mmol) was suspended in toluene (120 mL) and refluxed for one day. After cooling to room temperature, the mixture was filtered through celite, the solvent was removed *in vacuo*, and the residue was purified by silica gel chromatography (eluting with

dichloromethane/ethyl acetate = 40:1) to give 6-(1H-pyrazol-1-yl)-2-pyridinecarboxaldehyde (**3**) (4.08 g, 23.6 mmol, 79 % yield) as a white solid: ^{1}H-NMR (CDCl$_3$) δ 10.05 (s, 1H), 8.68 (d, 1H, J = 6.6 Hz), 8.23 (d, 1H, J = 8.4 Hz), 7.99 (dd, 1H, J = 8.0 Hz), 7.84 (d, 1H, J = 7.4 Hz), 7.78 (s, 1H), 6.52 (dd, 1H, J = 2.6 Hz, 2.2 Hz). Anal. (calc.) for C$_9$H$_7$N$_3$O (**3**): C, 62.68 (62.42); H, 4.15 (4.07); N, 24.26 (24.26) %.

Preparation of 1,2,3-tris[(6-(1H-pyrazol-1-yl)pyrid-2-ylmethylene)amino]guanidinium chloride (H$_2$L·HCl). **1** (469 mg, 0.33 mmol) was dissolved in water (5 mL) and ethanol solution (50 mL). **3** (1.90 g, 1.10 mmol) was added into the aqueous solution, resulting in the production of white precipitate. The suspension was stirred for three hours at room temperature and the precipitate was collected by filtration, washed with ethanol and diethyl ether, and dried to give H$_2$L·HCl (2.32 g) as a pale yellow powder. The crude product was used for complexation without further purification.

Preparation of [Cu$_3$LCl$_3$]Cl·n(solv.) ([Cu$_3$]). H$_2$L·HCl (80 mg, 0.13 mmol) in water (10 mL) was added into CuCl$_2$·2H$_2$O (70 mg, 0.41 mmol) in water (5 mL). After two weeks, brown needle crystals of [Cu$_3$LCl$_3$]Cl·5H$_2$O (**[Cu$_3$]**) suitable for single crystal X-ray crystallography were obtained. These crystals were collected by filtration, affording [Cu$_3$LCl$_3$]Cl·7H$_2$O (48 mg, 0.047 mmol, 37 % yield). Anal. (calc.) for C$_{28}$H$_{35}$N$_{15}$Cl$_4$Cu$_3$O$_7$ ([Cu$_3$LCl$_3$]Cl·7H$_2$O): C, 32.78 (32.77); H, 3.28 (3.44); N, 20.29 (20.48) %.

Preparation of [Ni$_3$L(solv.)$_6$](BF$_4$)$_4$·n(solv.) ([Ni$_3$]). H$_2$L·HCl (20 mg, 0.033 mmol) and Ni(BF$_4$)$_2$·6H$_2$O (34 mg, 0.10 mmol) were dissolved in methanol (5 mL). The mixture was heated and stirred for ten minutes, then cooled to ambient temperature. Diisopropyl ether was allowed to diffuse into the solution, resulting in the formation of yellow block-like crystals of [Ni$_3$L(CH$_3$OH)$_5$(H$_2$O)](BF$_4$)$_4$·CH$_3$OH (**[Ni$_3$]**) suitable for X-ray analysis. These crystals were collected by filtration, affording {Ni$_3$L(CH$_3$OH)(H$_2$O)$_5$}(BF$_4$)$_4$·CH$_3$OH after air-drying and solvent molecules exchange (28.5 mg, 0.0219 mmol, 66 % yield). Anal. (calc.) for C$_{29}$H$_{35}$N$_{15}$B$_4$Ni$_3$F$_{16}$O$_6$ ([Ni$_3$L(CH$_3$OH)(H$_2$O)$_5$](BF$_4$)$_4$·CH$_3$OH): C, 28.55 (28.72); H, 3.12 (2.91); N, 17.64 (17.32) %.

X-ray Crystallography

A single crystal was removed from the mother liquor, mounted on a glass rod and intensity data was collected using a Bruker SMART or SMART APEX II CCD systems with Mo-$K\alpha$ radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-square techniques on F^2 using SHELXTL.

Magnetic Measurements

Magnetic susceptibility data with an applied magnetic field of 500 Oe were collected using a Quantum Design MPMS-5S SQUID magnetometer. Magnetic data were corrected for the diamagnetism of the sample holder and for the diamagnetism of the sample using Pascal's constants.

NMR measurements

^{1}H-NMR spectra were measured on a Bruker AVANCE400 spectrometer at room temperature. Chemical shifts in NMR were reported in ppm (δ), relative to the internal standard of tetramethylsilane (TMS). The signals observed were described as s (singlet), d (doublet), t (triplet), m (multiplets). The number of protons (n) for a given resonance is indicated as nH. Coupling constants are reported as J in hertz.

Elemental analysis

Elemental analyses were performed using a Perkin Elmer 2400 element analyser.

Results and Discussion

Structures

[Cu$_3$] crystallized in the $P2_1/n$ space group and the structural data were collected at 100 K.[18] [Cu$_3$] has a planer trinuclear triangular core, consisting of three copper ions (Figure 1). The asymmetric unit includes one ligand, three copper ions, three coordinated chloride ions, one uncoordinated chloride ion and five water molecules. All copper ions have square pyramidal geometry with N$_4$Cl donor sets and show elongated-type Jahn-Teller distortion with the elongated axis lying perpendicular to the ligand plane. The coordination bond lengths, charge balance and coordination geometries of the copper ions suggest that all are divalent. Three chloride ions coordinate the copper ions as axial ligands, and the remaining chloride ion is free in the crystal lattice. The ligand, L^{2-}, coordinates the equatorial positions of all copper ions, acting as a bridge between all three centres. The distances between the copper ions are Cu1-Cu2 = 4.8360(16) Å, Cu2-Cu3 = 4.8026(15) Å and Cu3-Cu1 = 4.8353(16) Å, respectively. The structure suggests that strong antiferromagnetic interactions are operative between the copper ions, through Cu-N-N-Cu magnetic pathways and the magnetic orbitals on equatorial planes. The Cu-N-N-Cu torsion angles are close to linear, ranging from 173.10° to 177.71°. Hydrogen bonds exist between the trinuclear complex cations, forming a columnar structure.

The three copper ions and all atoms of the ligand L^{2-} lie on the same plane with a deviation of 0.422(2) Å from the least-squares planes defined by all atoms. The Cu1, Cu2 and Cu3 ions deviate from the equatorial plane defined by four donor atoms (N1, N3, N4, N15), (N5, N6, N8, N9) and (N10, N11, N13, N14) by -0.081(4), -0.243(4), 0.052(4) Å, respectively. There are some hydrogen bonding interactions between chloride ions and water molecules, forming a one-dimensional network along the b axis. π-π interactions are observed between neighbouring triangles, expanding the one-dimensional ribbon along the a axis. The shortest intermolecular metal-metal distances is 6.7814(15) Å, through a translational operation along the b axis.

(a)

(b)
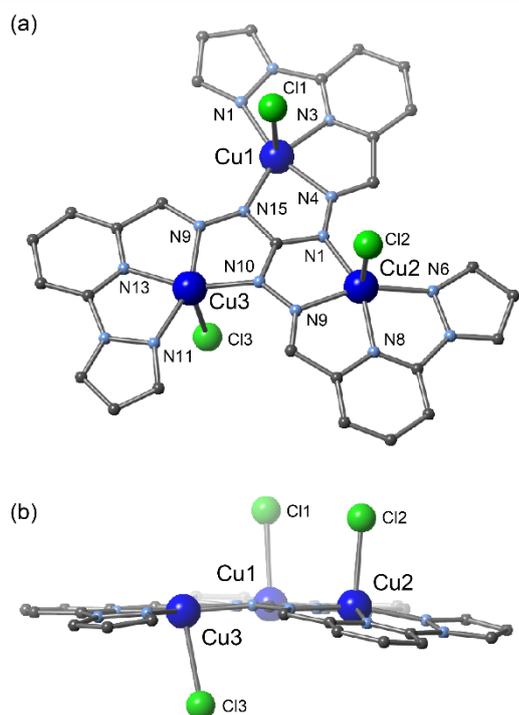
Figure 1. Molecular structure of [Cu₃]. (a) Top view. (b) Side view. Counter anions, hydrogen atoms and solvent molecules have been omitted for clarity.

(a)

(b)
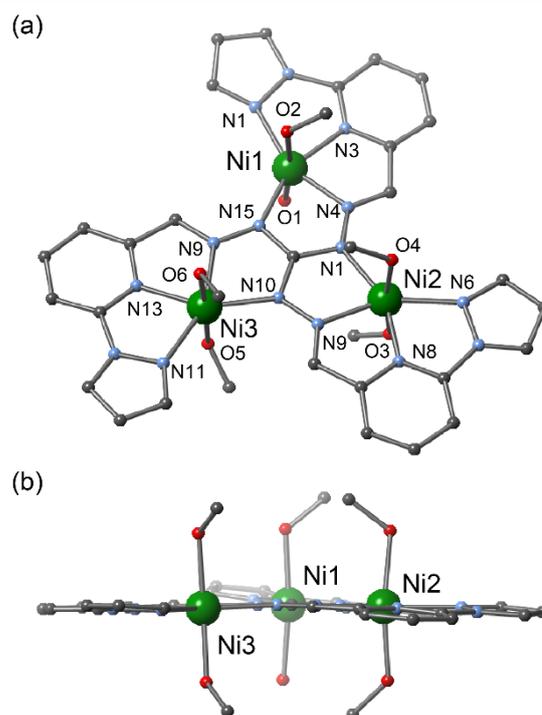
Figure 2. Molecular structure of [Ni₃]. (a) Top view. (b) Side view. Counter anions, hydrogen atoms and solvent molecules have been omitted for clarity.

[Ni₃] crystallized in the $P\bar{1}$ space group and the structural data were collected at 100 K.[19] [Ni₃] has a similar trinuclear triangular core, consisting of one ligand, three nickel ions, five coordinated methanol moieties and one water molecule, with four tetrafluoroborate ions included in the crystal lattice as counter anions (Figure 2). The distances between the nickel ions are Ni1-Ni2 = 4.9599(12) Å, Ni2-Ni3 = 4.9877(12) Å and Ni3-Ni1 = 4.9957(12) Å, respectively. All nickel ions have six-coordinate octahedral coordination geometries suggesting that all nickel ions are divalent and in their HS state (S = 1). All nickel centres are coordinated in a meridional fashion by the N-donor atoms of the ligand and by two oxygen atoms from solvent molecules. The Ni1 ion is coordinated by one water and one methanol molecule in the apical positions, while Ni2 and Ni3 ions are coordinated by two methanol molecules.

[Ni₃] has a planar structure similar to [Cu₃]. All atoms of the ligand and the three nickel ions lie on the same plane with deviation of less than 0.35 Å. The Ni1, Ni2 and Ni3 ions deviate from the equatorial plane defined by their four donor atoms (N1, N3, N4, N15), (N5, N6, N8, N9) and (N10, N11, N13, N14) by -0.027(3), -0.006(3), -0.023(3) Å, respectively. The shortest intermetallic separations of Ni3-Ni3#1 ions between neighboring triangular units is 9.5053(17) Å (symmetry operation #1: -x+1, -y, -z+1).

Overall, the guanidine derivative ligand, H₂L·HCl, was shown to support [M₃L]ⁿ⁺ (M; metal ion) type structure, acting as a -2 anionic ligand. Guanidine has two single bonds and one double bond between the nitrogen and carbon atoms. In this system, the bond lengths between the centre carbon atom (C28) and nitrogen atoms are C28-N5 = 1.345(10) Å, C28-N10 = 1.360(10) Å, and C28-N15= 1.373(10) Å for [Cu₃] and C28-N5 = 1.359(8) Å, C28-N10 = 1.376(8) Å, and C28-N15= 1.368(8) for [Ni₃], respectively. These bond lengths are intermediate between single and double bonds, and show that the C=N double bond in both complexes is delocalized between the four atoms. Therefore, all carbon and nitrogen atoms form sp²-like hybrid orbitals, and complexes with highly planar structures were produced.

Magnetic properties

DC magnetic susceptibility data of [Cu₃] and [Ni₃] were measured in the temperature range of 1.8 - 300 K under an applied magnetic field of 500 Oe and the $\chi_m T$ versus T plots are shown in Figure 3.

The $\chi_m T$ value of [Cu₃] at 300 K was 0.622 emu mol⁻¹ K, which is smaller than the expected value of three magnetically isolated S = 1/2 spins (1.125 emu mol⁻¹ K (g = 2.00)), and decreased with cooling to reach a plateau blow 130 K. The $\chi_m T$ value of [Cu₃] at 100 K was 0.411 emu mol⁻¹ K, close to the spin only value of 0.375 emu mol⁻¹ K (g = 2.00), expected for the isolated spin of one Cuᴵᴵ ion (S = 1/2). The $\chi_m T$ value of [Ni₃] at 300 K was 3.20 emu mol⁻¹ K, slightly larger than the spin only value of 3.00 emu mol⁻¹ K (g = 2.00), calculated from the sum of the uncorrelated spins of three Niᴵᴵ ions (S = 1). The

$\chi_m T$ value also showed a decrease with lowered temperature. The $\chi_m T$ value at 1.8 K was 0.039 emu mol^{-1} K, suggesting that the spin ground state of [Ni$_3$] at low temperature is spin singlet. The triangular spin Hamiltonian model of H = -2J($S_1·S_2 + S_2·S_3 + S_3·S_1$), where J represents the exchange of coupling constant between metal ions, was used to analyse the magnetic susceptibility data of [Cu$_3$] and [Ni$_3$] (the schematic spin model is shown inset in Figure 5). The solid lines are the least square fits and the parameters for [Cu$_3$] are g = 2.08(1), J = -130(1) cm^{-1}, and for [Ni$_3$] are g = 2.18(1), J = -14.9(1) cm^{-1}, showing that strong antiferromagnetic interactions are operative between the metal ions, respectively. In the case of [Cu$_3$], the magnetic exchange interactions between copper ions are operative through N-N bonds and involve the overlapping of the magnetic equatorial orbitals of the copper ions, thus promoting strong interactions. We recently reported the magnetic behaviour of a linear trinuclear copper complex with a planar structure, which shows similarly strong magnetic interactions J = -194 cm^{-1} between neighbouring copper ions when bridged by pyrazole groups.[20] In both cases the magnetic pathways are mediated by similar sp^2-type N-N bridges, indicating that the strength of the magnetic interaction in [Cu$_3$] is reasonable from a structural viewpoint.
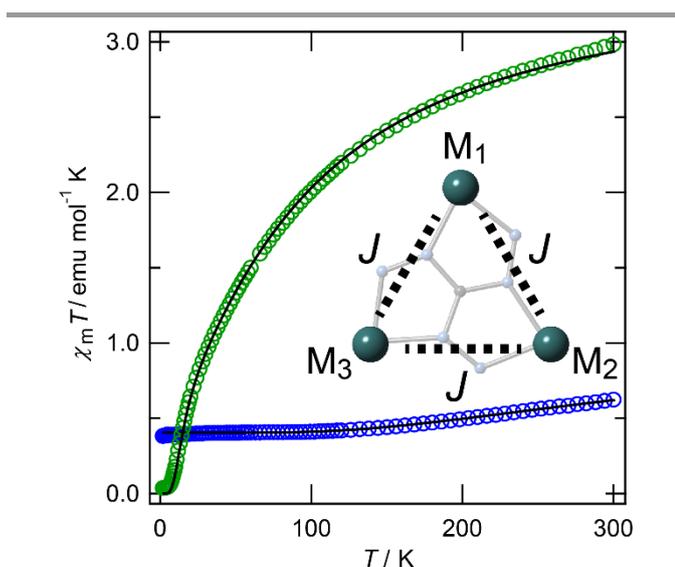
Figure 3. Temperature dependences of magnetic susceptibilities for [Cu$_3$] (blue circle) and [Ni$_3$] (green circle). The solid lines indicate theoretical curve (see text). The schematic drawing in the inset is the spin model for fitting of magnetic data.

The field-dependence of magnetization data for [Cu$_3$] and [Ni$_3$] at 1.8 K is shown in Figure S1. The magnetic moment of [Cu$_3$] at 5 T reached 0.974 $N\beta$, suggesting that the ground state of [Cu$_3$] is S_T = 1/2. The magnetization curve was analysed using an S = 1/2 Brillouin function and the estimated curve is shown as a solid line. The observed data are slightly lower than the estimated curve across the majority of the applied magnetic fields, suggesting that weak antiferromagnetic interactions are likely to be operative between neighbouring triangular molecules at low temperature. Calculated magnetization curves of [Cu$_3$] at 1.8 K, estimated from a regular triangle model with the above-mentioned g and J values are shown in Figure S2. At low magnetic fields, the ground state S_T = 1/2 is strongly stabilized and the next level crossing point (to S_T = 3/2) is estimated to occur at 280 T. The magnetic moment of [Ni$_3$] at 5 T was 0.068 $N\beta$, showing that the ground state of [Ni$_3$] is S_T = 0 (Figure S1). The calculated magnetization curves of [Ni$_3$] at 1.8 K showed that level crossing is estimated to occur at 19.6 T (S_T = 0 → 1), 41.2 T (S_T = 1 → 2), and 61.8 T (S_T = 2 → 3) (Figure S3). In order to observe spin flipping under pulsed magnetic field, the strength of the magnetic interactions should be weak. Further study on spin frustration and spin chirality will require detailed EPR experiments. We are currently applying our learning from the presented systems to aid in the construction of spin tubes.

Conclusions

A novel guanidine derivative and its tri-nuclear metal complexes were synthesized. The ligand can coordinate three metal ions in its N$_4$ binding positions, forming planar triangular structures. The exchange coupling constants were g = 2.08(1), J = -130(1) cm^{-1} for [Cu$_3$], and g = 2.18(1), J = -14.9(1) cm^{-1} for [Ni$_3$], suggesting that antiferromagnetic interactions are operative between the metal ions in both complexes. The ground spin state of [Cu$_3$] at low temperature is spin doublet, while in the case of [Ni$_3$], the magnetic susceptibility data and magnetization curve suggest that its ground state is spin singlet. The synthesized guanidine derivative ligand has proven itself useful in the construction of antiferromagnetic triangle units with planar molecular structures, however, in this example, the counterions and solvent molecules precluded the formation of supramolecular spin-tube type arrangements. Further work will attempt to connect the units to form extended structures. The presented complexes are 4+ cations, a fact that may be used to their advantage by employing anionic bridging units to link them into extended systems. These results will shed light on the molecular design of planar triangular building blocks and extended spin-tubes.

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18 Crystallographic data for [Cu$_3$] (C$_{28}$H$_{31}$N$_{15}$Cl$_4$Cu$_3$O$_5$ = 990.10 g mol^{-1}): monoclinic, $P2_1/n$, a = 11.665(3) Å, b = 6.7814(15) Å, c = 48.532(11) Å, β = 94.167(4)°, V = 3828.8(15) Å^3, Z = 4, D_{calcd} = 1.718 g cm^{-3}, R1 = 0.0907 (I > 2σ(I)), wR2 = 0.2438 (all data) (CCDC1403544).

19 Crystallographic data for [Ni$_3$] (C$_{34}$H$_{47}$N$_{15}$B$_4$F$_{16}$Ni$_3$O$_7$ = 1301.23 g mol^{-1}): triclinic, $P\bar{1}$, a = 10.0521(8) Å, b = 11.4299(9) Å, c = 22.6136(18) Å, α = 77.6660(10)°, β = 83.379(2)°, γ = 83.524(2)°, V = 2510.9(3) Å^3, Z = 2, D_{calcd} = 1.721 g cm^{-3}, R1 = 0.0861 (I > 2σ(I)), wR2 = 0.2276 (all data) (CCDC1403545).

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