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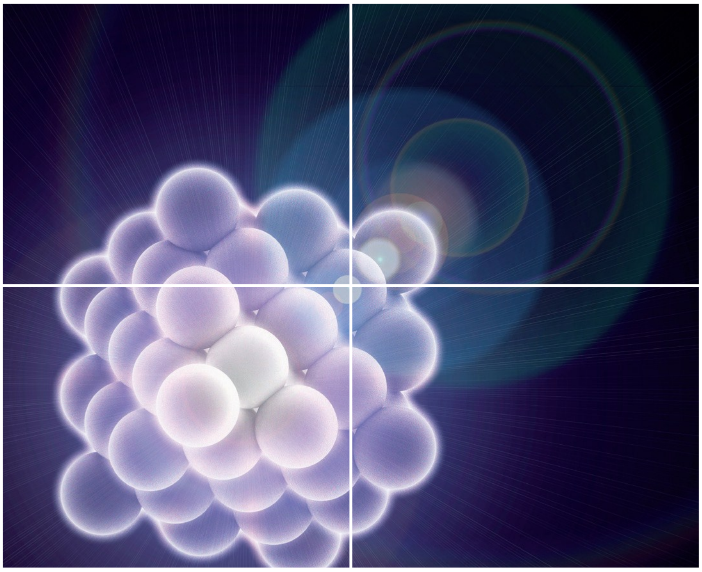

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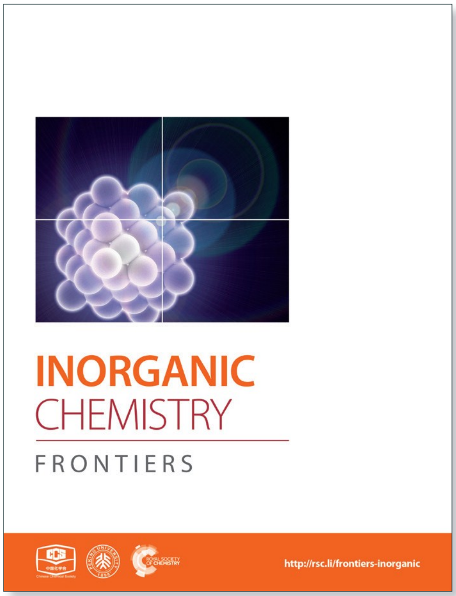

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Planar trinuclear complexes with linear arrays of metal ions

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Two trinuclear complexes, $[Cu^{II}_3(L)_2](BF_4)_2$ (1) and $[Ni^{II}_3(L)_2(MeOH)_4](BF_4)_2$ (2), supported by the multidentate ligand L^{2-} (H_2L =5,5'-pyridyl-3,3'-bi-1H-pyrazole) were obtained and their structures determined. Both complexes have linear trinuclear structures composed of two ligands and three metal ions. Cryomagnetic studies reveal both complexes to show intramolecular antiferromagnetic interactions between metal ions.

Coordination architectures with varied topologies can be constructed through the self-assembly of transition metals and multidentate ligands, and their structure-dependent physical properties and functionalities have been intensively investigated.[1] The assembly of metal ions into specific shapes, structures and arrays can be achieved through the considered choice of 'pre-programmed' ligands with clearly defined binding sites and orientations.[2] When using rigid ligands with linear bridging coordination modes, network compounds are commonly formed. For example, metal-organic-frameworks (MOFs) are often constructed from rigid ligands, which can linearly connect between metal ions.[1a] In contrast, flexible bridging ligands can effectively form discrete polynuclear cluster complexes, such as oxo-bridged polynuclear clusters which can be supported by multidentate alkoxo ligands.[3] Polynuclear complexes with regular arrays of metal ions are of particular interest to the chemist due to the synergy between their physical properties and their clearly defined specific structures.[4] For example, molecular wires composed from metal ions with metal-metal bonds were investigated,[1c] and may have applications in molecular nano-electronics, while triangle and grid-like cluster molecules exhibit specific electronic structures and spin ground states.[5,6]

To date, we have studied ring, helix, and grid molecules supported by rigid and planar multidentate ligands.[7] Based on our previous research, it is clear that pyridine-pyrazolate ligands can be very useful for the construction of multinuclear complexes through self-assembly based on their preprogrammed transition metal bridging behaviour and propensity for supramolecular π-π stacking interactions. We previously reported the synthesis and characterization of a [3 × 3] grid-like nonanuclear cobalt single-molecule magnet and multiredox active [3 × 3] copper grids.[7b] The complexes are constructed using a pyridine-pyrazolate ligand with one tridentate and two bidentate binding sites. Ligands with such defined coordination abilities have great possibilities for the formation of coordination architectures with predictable, stable structures and tuneable physical properties. As a result we are now extending our study of the complex structures accessible with planar and rigid multidentate ligands.

In this work, we use a pyridine-pyrazolate ligand H_2L (=5,5'-pyridyl-3,3'-bi-1H-pyrazole)[8] with two types of bidentate binding site. Two novel complexes with bridging ligand L^{2-}, $[Cu^{II}_3(L)_2](BF_4)_2$ (**1**), and $[Ni^{II}_3(L)_2(MeOH)_4](BF_4)_2$ (**2**) are isolated, their structures determined by single-crystal X-ray structural analyses and their magnetic properties investigated.

The planar multidentate pyridine-pyrazole ligand H_2L was synthesized by a modified version of a previously reported synthetic method.[8] Reactions of the planar ligand H_2L with metal sources afford the linear trinuclear complexes **1** and **2**.[9,10] X-ray structural analyses reveal that both complexes have linear trinuclear structures composed of two L^{2-} ligands and three metal ions arranged to form planar molecules. The three metal ions can be categorized into two types: terminal metal ions located at the edge of the molecule with four nitrogen donor atoms from two pyridine and two pyrazole donor groups; and central metal ions with four nitrogen donors from four pyrazole groups.

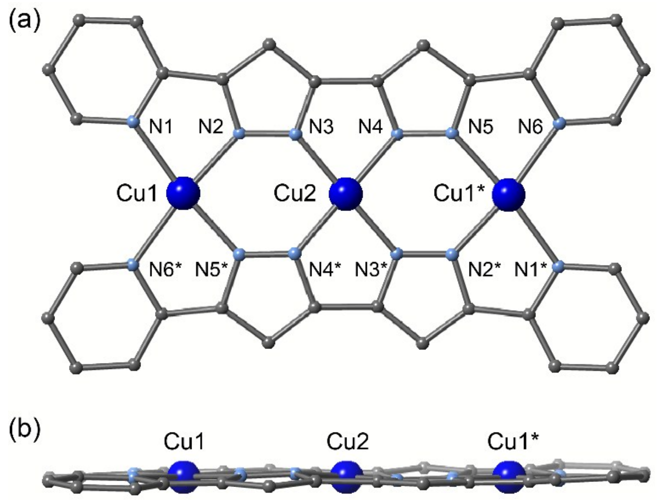

Figure 1 Molecular structure of **1**. (a) Top view (b) Side view. (symmetry code *: -x, -y, -z)

1 crystalized in the monoclinic space group $P2_1/n$,[11] with an inversion centre on the Cu2 ion. All copper ions have the same square-planar four-coordinate geometry without any solvent coordination, and their equatorial planes lie on the plane described by the two supporting ligands. The BF_4^- counterion weakly interacts with the Cu1 ion in its apical position. While Cu2 in the central coordination site has an average bond length of 1.884(7) Å, the Cu1 ions have an average bond distance of 2.026(8) Å. The Cu1 ion deviates from the equatorial plane defined by N1, N2, N5*, and N6* atoms by 0.030(4) Å, while the Cu2 ion lies on the N3, N4, N3*, and N4* plane. Significant π-π stacking interactions can be observed, and a one-dimensional columnar structure is formed (Figure S1). The intramolecular metallic separations of Cu1···Cu2, and Cu1···Cu1* are 3.865(5), 7.731(11) Å, respectively. The shortest intermolecular metal-metal distance (Cu1···Cu2$^{\#1}$) is 3.756(4) Å (symmetry code #1: +x+1, +y, +z).

2 crystalized in the monoclinic space group $P2_1/c$,[12] with an inversion centre located on the central Ni2 ion. The Ni2 ion is coordinated by four N-donating pyrazole moieties, resulting in square-planar geometry, and an average bond length of 1.843(4) Å. The Ni1 ions in the terminal sites have distorted octahedral geometries, with four nitrogen donors from the ligands in the equatorial sites and two oxygen donors from solvent methanol molecules in the apical sites, and an average bond length of 2.073(5) Å. Complex **2** has a similar planar structure to that of **1**, but the π-systems of neighbouring complexes are prevented from overlapping due to the coordination of the axial methanol molecules. The intracluster Ni1···Ni2 and Ni2···Ni2* metal-metal separations are 3.9491(14), 7.898(3) Å, respectively, while the shortest intermolecular metal-metal distance is 8.004(3) Å, for Ni1$^{\#1}$···Ni1$^{\#2}$ (symmetry code #1: -x, -y, -z, #2: +x+1, +y, +z). Elemental analyses for air-dried samples of **1** and **2** gave compositions of $[Cu_3(L)_2](BF_4)_2 \cdot 1.5H_2O$ (**1′**) and $[Ni_3(L)_2(MeOH)_2(H_2O)_2](BF_4)_2 \cdot 2H_2O$ (**2′**), respectively. The formula changes arise from solvent exchange and moisture absorption on the crystal surfaces. As no crystal colour changes were observed, the following magnetic studies were discussed based on the assumption that no significant changes in coordination geometry had occurred.

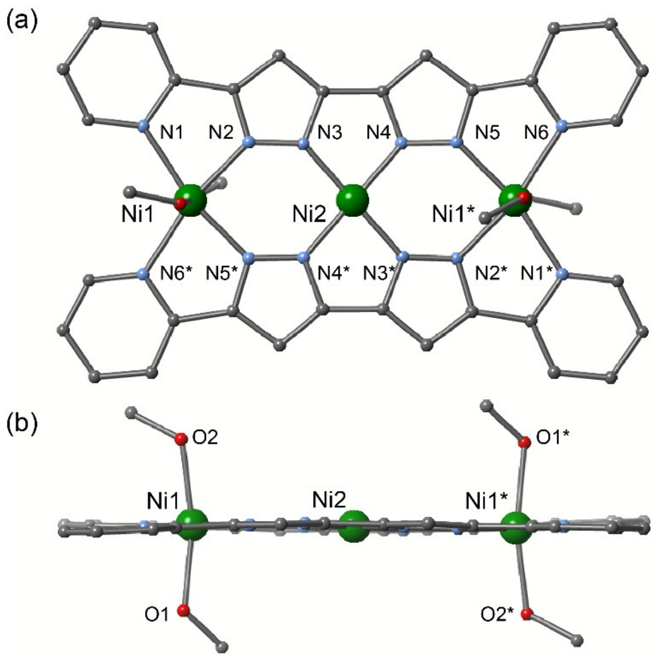

Figure 2 Molecular structure of **2**. (a) Top view (b) Side view.

Magnetic susceptibility data for **1′** and **2′** are shown in Figures 3 and 4, respectively. The $\chi_m T$ values of both compounds decrease as temperature is lowered, indicating the occurrence of antiferromagnetic interactions between metal ions in both species.

In **1′**, all copper ions lie on the molecular plane defined by the two ligands, and share their equatorial planes. The strong overlap of magnetic orbitals on the molecular plane ensures that substantial coupling constants can be expected. A spin model of the linear trinuclear core was applied to the magnetic analyses,[13] and the data fitted to give intramolecular coupling constants of J_1 = -194 cm^{-1} and J_2 = -4.5 cm^{-1} with g_{Cu} = 2.09, and an intermolecular component of zJ' = -0.178 cm^{-1}.

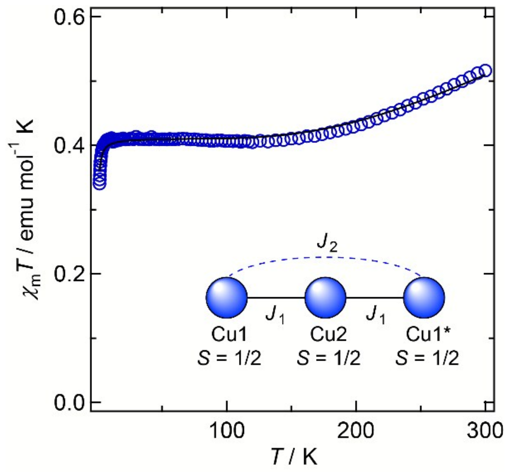

Figure 3 $\chi_m T$ versus T plots of **1'**. Inset: spin model used by magnetic analyses.

Considering the coordination geometry of **2'**, it is suggested that the central Ni2 ion is diamagnetic, while the terminal Ni1 (and Ni1*) ions are paramagnetic. The magnetic behaviour of **2'** can therefore be analysed using a dinuclear spin model[14], in which J_1 can be fixed to zero, to give J_2 = -1.01 cm^{-1} and g = 2.06.

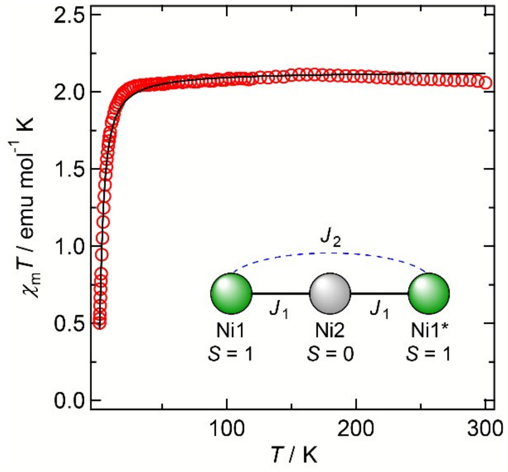

Figure 4 $\chi_m T$ versus T plots of **2'**. Inset: spin model used in magnetic analyses.

In summary, two planar trinuclear complexes, $[\mathrm{Cu^{II}_3(L)_2}](\mathrm{BF_4})_2$ (**1**) and $[\mathrm{Ni^{II}_3(L)_2(MeOH)_4}](\mathrm{BF_4})_2$ (**2**), were synthesized and their structures and magnetic properties studied. The synthesis of planar clusters is important for the development novel functional molecules.

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† Electronic Supplementary Information (ESI) available: [Synthesis of ligand, packing diagrams and crystallographic details. CCDC 1020899 (**1**) and 1020900 (**2**)]. See DOI: 10.1039/c000000x/

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9 Synthesis of $[\mathrm{Cu^{II}_3(L)_2}](\mathrm{BF_4})_2$ (**1**): To a methanolic solution (20 mL) of $\mathrm{Cu(BF_4)_2{\cdot}nH_2O}$ (286 mg, 0.90 mmol) was added a methanolic suspension (15 mL) of H_2L (43.0 mg, 0.15 mmol) and Et_3N (41.3 μL, 0.30 mmol). After stirring for several minutes, 35 mL of acetonitrile was added to the reaction mixture. Resulting brown

solution was filtered and the filtrate was diffused by diethyl ether. Yellow needles of $[Cu^{II}_3(L)_2](BF_4)_2$ (**1**) were crystalized. The crystals were collected *in vacuo* and exposed by air to obtain $[Cu^{II}_3(L)_2](BF_4)_2 \cdot 1.5H_2O$ (**1'**). Yield: 27 mg (39 %). Anal. calcd for **1'** $[Cu_3(L)_2](BF_4)_2$ $1.5H_2O$ ($C_{32}H_{23}N_{12}B_2F_8O_{1.5}Cu_3$) (%) : C, 39.88; H, 2.41; N, 17.44. Found (%) C, 39.90; H, 2.21; N, 17.25.

10 Synthesis of $[Ni^{II}_3(L)_2(MeOH)_4](BF_4)_2$ (**2**): To an methanolic solution (7.5 mL) of $Ni(BF_4)_2 \cdot 6H_2O$ (61 mg, 0.18 mmol) was added a methanolic suspension (5 mL) of H_2L (8.6 mg, 0.03 mmol) and Et_3N (8.3 μL, 0.06 mmol). The resulting green solution was filtered and the filtrate was diffused by diethyl ether. Green needles of $[Ni^{II}_3(L)_2(MeOH)_4](BF_4)_2$ (**2**): were crystalized. The crystals were collected *in vacuo* and exposed by air to obtain $[Ni^{II}_3(L)_2(MeOH)_2(H_2O)_2](BF_4)_2 \cdot 2H_2O$ (**2'**). Yield: 21.5 mg (28 %). Anal. calcd for **2'** $[Ni^{II}_3(L)_2(MeOH)_2(H_2O)_2](BF_4)_2 \cdot 2H_2O$ ($C_{34}H_{36}N_{12}B_2F_8O_6Ni_3$) (%) : C, 38.58; H, 3.43; N, 15.88. Found (%) C, 38.78; H, 3.38; N, 16.15.

11 Crystallographic data for **1** ($C_{32}H_{20}N_{12}B_2F_8Cu_3$ = 936.84 gmol^{-1}): monoclinic, $P2_1/n$, a = 6.262(11) Å, b = 23.89(4) Å, c = 11.132(19) Å, β = 104.46(3)°, V = 1612(5) Å^3, Z = 2, D_{calcd} = 1.930 g cm^{-3}, $R1$ = 0.0868 ($I > 2\sigma(I)$), $wR2$ = 0.2268 (all data) (CCDC 1020899)

12 Crystallographic data for **2** ($C_{36}H_{32}N_{12}B_2F_8O_4Ni_3$ = 1046.48 gmol^{-1}): monoclinic, $P2_1/c$, a = 9.771(4) Å, b = 14.196(6) Å, c = 14.513(6) Å, β = 90.374(8) °, V = 2013.1(15) Å^3, Z = 2, D_{calcd} = 1.726 g cm^{-3}, $R1$ = 0.0827 ($I > 2\sigma(I)$), $wR2$ = 0.299 (all data) (CCDC 1020900)

13 Spin Hamiltonian of $\{Cu_3\}$ system: $\mathbf{H} = 2J_1(\mathbf{S}_{Cu1}\mathbf{S}_{Cu2}+\mathbf{S}_{Cu1^*}\mathbf{S}_{Cu2})+2J_2(\mathbf{S}_{Cu1}\mathbf{S}_{Cu1^*})$

14 Spin Hamiltonian of $\{Ni_3\}$ system: $\mathbf{H} = 2J_1(\mathbf{S}_{Ni1}\mathbf{S}_{Ni2}+\mathbf{S}_{Ni1^*}\mathbf{S}_{Ni2})+2J_2(\mathbf{S}_{Ni1}\mathbf{S}_{Ni1^*})$