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Non-interpenetrating honeycomb-like 2D [6,3] network built by a novel trigonal metalloligand†

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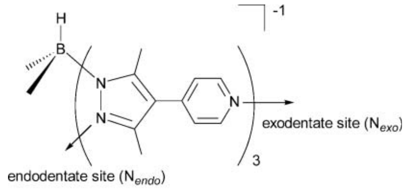
The combination of a novel trigonal metalloligand and linear linker affords the large non-interpenetrating honeycomb-like 2D [6,3] network in spite of the large hexagon lattice dimension.

Judicious fabrication of polytopic ligands and metal corners has afforded a variety of topologies of coordination networks in the realm of the crystal engineering.[1] Recently, a new approach[2] of metalloligands has been investigated to control the assembly of building blocks that possess second coordination sphere comprising *exo*-oriented donor atoms. The geometry of metalloligands depends on the preferred geometry of metal ions and the nature of the ligand bearing the functional groups. Despite of great potential in fabricating specific topologies, only a few metalloligands have been as yet reported, for examples, linear,[3] trigonal[4] and square planar.[5] The development of well-designed metalloligands is most challenging in the study of specific topologies of coordination polymers in current advances. In our quest for novel metalloligands and their application in new structural features, here we report a novel C_3 silver trigonal metalloligand (**1**) bearing a tripodal borate ligand (**L**) and its accommodation to non-interpenetrating honeycomb-like 2D [6,3] network (**2**).



L

We obtained potassium hydrotris(3,5-dimethyl-4-(4-pyridyl)-pyrazolyl)borate (**KL**) by molten methods applied in general synthesis of tripodal borate ligand. A characteristic band of B–H stretch appears at 2442 cm^{-1}. **L** has the exodentate pyridyl nitrogen (N$_{exo}$) atoms and endodentate pyrazolyl (N$_{endo}$) nitrogen atoms in a similar environment as in the hydrotris(1,2,4-triazolyl)borate ligand.[6] Among numerous polypyrazolylborate ligands[7] known, the 4-position of the pyrazole ring has rarely been modified by organic functional groups to be utilized for extended architectures.[8] Although two polypyrazolylborate ligands bearing 4-cyanopyrazole rings were reported the resultant metalloligands turned to be disadvantageous as building blocks due to a very weak coordinating ability of the nitrile group. To the best of our knowledge, **L** is the first polypyrazolylborate ligand to exhibit strong coordinating ability by introducing pyridyl groups into the 4-position of pyrazole rings. Supposing that three N$_{endo}$ atoms bite a metal center to complete the first coordination sphere, we will be able to fabricate diverse metalloligands as building blocks with free N$_{exo}$ atoms (second coordination sphere) to participate in multidimensional coordination polymers.

As a neutral building block, [Ag(**L**)(PPh$_3$)] (**1**)† was obtained by the reaction of Ag$^+$ ion with **L** in the presence of triphenylphosphine in methanol. A characteristic B–H stretch band appears at 2529 cm^{-1}. Recrystallizaion of **1** from acetone gives colorless crystals as formula of **1**·0.5acetone. X-ray analysis‡ of **1**·0.5 acetone reveals that the bulky **L** and PPh$_3$ ligands allow of a strongly distorted tetrahedral environment around silver center (Fig. 1). All the N$_{endo}$ atoms of **L** chelate the Ag^I ion in terdentate mode. Therefore, three facial pyridylpyrazole arms with free N$_{exo}$ atoms spread out in trigonal orientation. The disparity of bond lengths of Ag–N and B–N causes the direction of pyridylpyrazole arms to deviate from a precise trigonal plane and, therefore, to point toward the boron center to some degree. The proton NMR data are also consistent with the structural properties of **1** as well as with the evidence of the ^{31}P–{^{1}H} NMR. The Ag–P coupling is resolved at room temperature as values for Ag isotopes, which sharpens to a doublet of doublets consistent with the abundance for ^{107}Ag and ^{109}Ag with the coupling constant of 584 Hz and 675 Hz at 18.2 ppm at room temperature. This indicates that there is no dissociation of **1** in CHCl$_3$ even at room temperature.[9] As a result, the structural property of **1** in CHCl$_3$ solution is consistent with the crystal structure.

To confirm the function of **1** as metalloligand for construction of coordination polymers, the reaction† of **1** with Rh$_2$(OAc)$_4$ 2pyridine with stoichiometric mole ratio of 1:1.5 was carried out. We obtained the 2D coordination polymer as formula of $[[(\mathbf{1})(\mathrm{Rh_2(OAc_4)})_{1.5}]\cdot x\mathrm{CHCl_3}]_n$ ($\mathbf{2}\cdot x\mathrm{CHCl_3}$). A characteristic B–H stretch band appears at 2532 cm^{-1}. The combination of trigonal metalloligand (**1**) and linear linker gives the honeycomb-like 2D [6,3] network (Fig. 2). The structural features of **2** are that the tetrahedral environment of **1** remains intact and all three N$_{exo}$ atoms are utilized in the coordination of the axial sites of Rh$_2$(OAc)$_4$ moieties which function as linear linkers.

Owing to the intrinsic deviation of **1** from flat trigonal orientation,

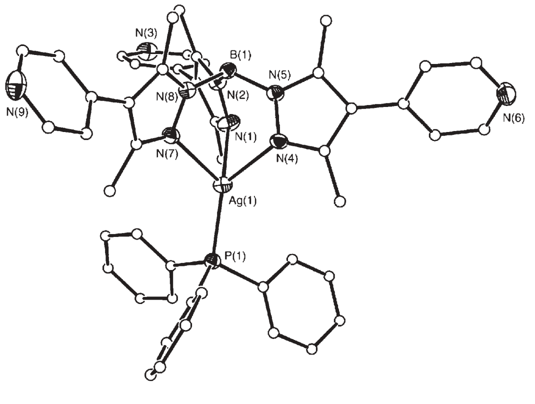


Fig. 1 The crystal structure of metalloligand **1**. Selected bond lengths/Å and angles/°, Ag(1)–N(1) 2.3683(2), Ag(1)–N(4) 2.2973(2), Ag(1)–N(7) 2.3500(2), Ag(1)–P(1) 2.3403(6); N(4)–Ag(1)–N(7) 82.36(7), N(4)–Ag(1)–N(1) 80.54(7), N(7)–Ag(1)–N(1) 84.56(7), P(1)–Ag(1)–N(1) 125.62(5), P(1)–Ag(1)–N(4) 136.93(5), P(1)–Ag(1)–N(7) 128.51(5).

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† Electronic supplementary information (ESI) available: Experimental conditions and structural details. See http://www.rsc.org/suppdata/cc/b4/b409596k/

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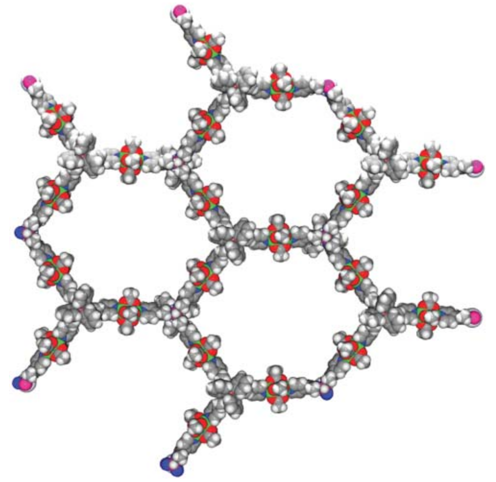

Fig. 2 The honeycomb-like 2D [6,3] network of **2** with a view along with the crystallographic *a*-axis.

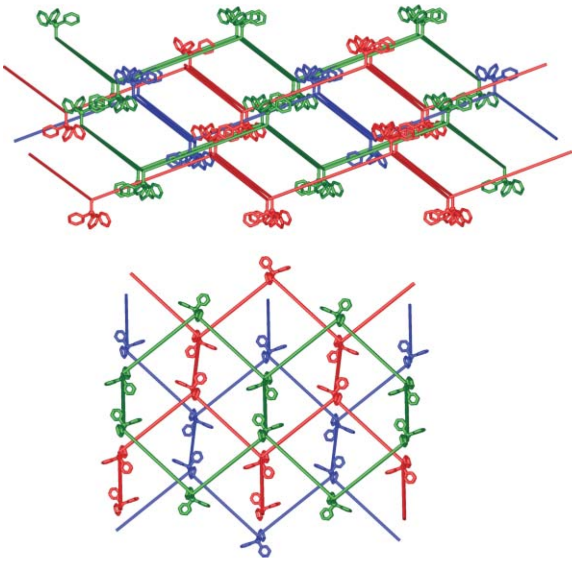

Fig. 3 The corrugated 2D layer architectures with PPh_3 ligands of **2** (top) and parallel stacking in ABC alternations along the crystallographic *a*-axis (bottom) depicted by OLEX.[11]

2 appears as a corrugated 2D layer architecture in which silver centres locate at the vertices of a chair-like structure. PPh_3 ligands occupy the axial positions of the silver vertices in an up and down pattern (Fig. 3, top). To the best of our knowledge, **2** shows the largest 2D hexagon lattice dimension (23.9 Å × 23.8 Å × 23.9 Å) in non-interpenetrating 2D [6,3] nets. It is a very rare case that, despite the large honeycomb dimension, 2D layers of **2** do not interpenetrate one another.[10] 2D hexagonal layers are stacked in parallel in ABC alternations along the crystallographic *a*-axis (Fig. 3, bottom).

2 might be considered as the inter-sustaining framework in which the hexagon lattice void of one layer is filled with the large PPh_3 ligands of the above and below layers. The remaining room is occupied by $CHCl_3$ molecules. **2** loses its own crystallinity outside the mother liquor since the included $CHCl_3$ molecules escape from the void easily. The whole framework of dried solid collapses, according to the XRPD pattern.

In conclusion, a novel tripodal ligand (**L**) terdentates the silver(I) center to complete the first coordination sphere by three N_{endo} atoms. Therefore, resultant trigonal metalloligand (**1**) possesses second coordination sphere comprising three free N_{exo} atoms to be utilized in the extended architectures. The facile fabrication of 2D [6,3] network (**2**) reveals that **1** has a great potential in the field of coordination polymers as a promising trigonal building block.

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Notes and references

‡ Experimental conditions and structural details are given in the ESI.† Crystal data for **1**·0.5 acetone: $C_{49.50}H_{49}AgBN_9O_{0.50}P$, $M = 927.63$, Triclinic, $a = 12.9830(1)$, $b = 14.0920(1)$, $c = 14.6710(4)$ Å, $\alpha = 115.702(1)$, $\beta = 100.030(5)$, $\gamma = 102.110(6)^\circ$, $V = 2255.12(4)$ Å^3, $T = 150(1)$ K, space group $P\bar{1}$ (No. 2), $Z = 2$, μ(Mo–Kα) = 0.529 mm^{-1}, 29 652 reflections measured, 10 331 unique ($R_{int} = 0.0595$) which were used in all calculation, $R_1 = 0.0384$, w$R_2 = 0.0925$ [$I > 2\sigma(I)$] and $R_1 = 0.0547$, w$R_2 = 0.1009$ for all data. CCDC 241372. Crystal data for **2**·xCHCl$_3$: $[C_{60}H_{64}AgBN_9O_{12}PRh_3]\cdot xCHCl_3$, $M = 1561.58$, Monoclinic, $a = 18.4633(2)$, $b = 36.227(3)$, $c = 21.1806(2)$ Å, $\beta = 107.750(2)^\circ$, $V = 13492.5(2)$ Å^3, $T = 233(2)$ K, space group $P2_1/n$ (No.14), $Z = 4$, μ(Mo–Kα) = 0.547 mm^{-1}, 122 313 reflections measured, 32 406 unique ($R_{int} = 0.1870$) which were used in all calculations, $R_1 = 0.0981$, w$R_2 = 0.2281$ [$I > 2\sigma(I)$] and $R_1 = 0.2364$, w$R_2 = 0.2592$ for all data. As usual in crystals containing large voids, diffraction appears weakly and the solvents or anions are disordered in the large voids in the lattice. There are more than six disordered $CHCl_3$ molecules per unit formula (**2**·xCHCl$_3$) in the voids of the framework. So, the molecular weight corresponds to the **2** framework instead of **2**·xCHCl$_3$. They are removed using "SQUEEZE" in PLATON program[12] to obtain a good framework geometry. CCDC 241373. See http://www.rsc.org/suppdata/cc/b4/b409596k/ for crystallographic data in .cif or other electronic format.

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