One-Dimensional Coordination Polymers of Dihydrobis(1,2,4-triazol-1-yl)borate Ruthenium(II) Complex

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Increasing interest in coordination and organometallic polymers lies in the various intriguing properties of well-designed inorganic polymer materials.[1] A variety of attempts have been made to synthesize multidentate ligands which can bridge various metal centers. Ambidentate poly(triazolyl)borate ligands $[H_nB(tz)_{4-n}]^-$ (n = 1 and 2, tz = 1,2,4-triazol-1-yl)[2,3] are good candidates for multidimensional network topologies.[4,5] It was revealed that both the exodentate (4-position) and endodentate (2-position) nitrogen atoms of the triazolyl rings have comparable electron density to coordinate competitively to metal centers from the theoretical calculation and the ^{15}N NMR study.[6] It was frequently observed that the poly(triazolyl)borate ligands induce metal ions to form multidimensional coordination polymers through the coordinations of exodentate N atoms whose electron density is higher than the endodentate N atoms. However, in the case of $[HB(tz)_3]^-$, tridentate chelated monomers $M[\eta^3\text{-}HB(tz)_3]_2$ (M = Fe^{2+}, Co^{2+}, Cu^{2+} and Zn^{2+})[3] are exclusively isolated, and these results are explained by a combination of chelate and kinetic effect.[5] Discrete Ag^I and Cu^I complexes bearing a bidentate dihydrobis(1,2,4-triazolyl)borate through endodentate coordination such as $Cu(L)_n[\eta^2\text{-}H_2B(tz)_2]$ (L = aryl phosphines, n = 1 or 2), $Ag(L)_2[\eta^2\text{-}H_2B(tz)_2]$ (L = aryl phosphines), Ag(dppf)$[\eta^2\text{-}H_2B(tz)_2]$ (dppf = 1,10-bis(diphenylphosphino)ferrocene) and their polymeric derivatives were recently reported.[7] In these cases, however, the dihydrobis(1,2,4-triazolyl)borate ligands coordinate to the same type of ions to constitute 1D homometallic polymer networks.

In order to develop efficient heterometallic polymeric systems whose physicochemical properties can be systematically tuned, we are pursuing to prepare discrete mononuclear complexes bearing anionic dihydrobis(1,2,4-triazolyl)borate ligands through endodentate coordinations instead of exodentate coordinations. Discrete complexes having a ligand (or ligands) through a bidentate coordination of the two endodentate N atoms could potentially serve as metalloligands for the engineering of 1D modular structure through additional coordinations of the exodentate N atoms to two other transition metal moieties. Recently we were able to prepare discrete mononuclear $Fe[HB(tz)_3]_2\cdot ClO_4$ and Ag(L)-(PPh_3) (L = hydrotris(3,5-dimethyl-4-(4-pyridyl)pyrazolyl)-borate) to use them as building blocks for novel 3D or 2D functional networks.[8] On the other hand, the reaction between $Mn(TPP)\cdot ClO_4$ and $K[H_2B(tz)_2]$ only afforded a discrete mononuclear $Mn(TPP)(H_2O)[\eta^1\text{-}H_2B(tz)_2]$ instead of 1D polymeric structures because of a steric bulk of TPP ligand (TPP is 5,10,15,20-tetraphenylporphine).[9]

Here we report a new metalloligand having a dihydrobis-(1,2,4-triazolyl)borate, $RuH(CO)(PPh_3)_2[\eta^2\text{-}H_2B(tz)_2]$ (**1**) and its successful applications to 1D supramolecular systems through self-assembly. Because **1** might have catalytic activities for the hydrogenation of ketones and aldehydes under hydrogen atmosphere, the 1D polymers of **1** could be used as recyclable heterogeneous catalysts. The compound **1** was obtained in good yield from the reaction of RuHCl-$(CO)(PPh_3)_3$[10] with $K[H_2B(tz)_2]$[2] (Figure 1). The compound **1** was fully characterized by ^{1}H and $^{31}P\{^1H\}$ NMR, IR, and elemental analysis. A triplet resonance signal of the hydride ligand from ^{1}H NMR and a singlet peak of two P atoms from $^{31}P\{^1H\}$ NMR clearly indicate that the proposed structure of **1** which is an ideal geometry as a metalloligand. The entire coordination environment is same to the crystallographically characterized $RuH(CO)[P(p\text{-Tolyl})_3]_2[\eta^2\text{-}H_2B(tz)_2]$ and $RuH(CO)(AsPh_3)_2[\eta^2\text{-}H_2B(pz)_2]$ (pz is pyrazol-1-yl).[11]

Unlike other insoluble dihydrobis(triazolyl)borate derivatives, the monomer **1** shows a good solubility in halogenated hydrocarbon solvents. The reactions of **1** with 1 or 2 equivalent $Cu(OAc)_2\cdot H_2O$ afford well-defined 1D heterometallic polymers $\{[Cu_2(OAc)_4][\mathbf{1}][Cu(\eta^1\text{-}OAc)_2][\mathbf{1}]\}_n$ (**2**) and $\{[\mathbf{1}][Cu_2(OAc)_4]\cdot(CH_2Cl_2)_2\}_n$ (**3**), respectively, which contain lantern-type dicopper moieties, $Cu_2(OAc)_4$.[12] Single crystal x-ray crystallographic studies of **2** and **3** confirm the

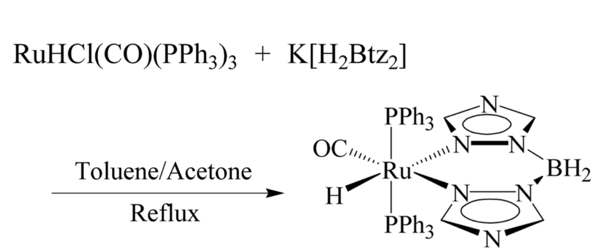

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Figure 1. Reaction scheme of $RuHCl(CO)(PPh_3)_3$ and $K[H_2B(tz)_2]$.

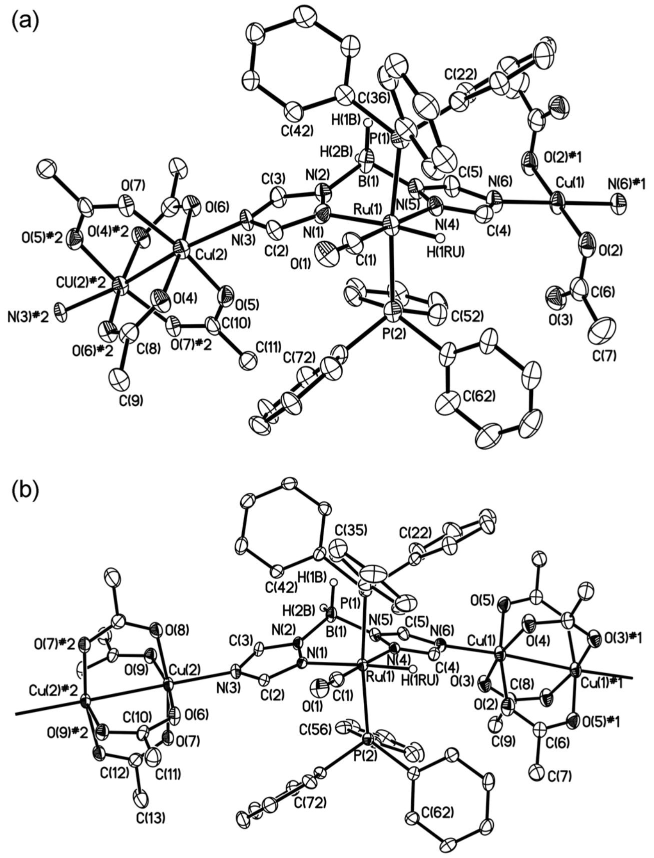

Figure 2. (a) Repeating unit of 1D coordination polymer **2**. Selected bond distances (Å) and angles (°): Cu(1)-N(6) 1.983(8), Cu(1)-O(2) 1.959(8), Cu(2)-N(3) 2.174(8), Cu(2)···Cu(2)b 2.639(3), Ru(1)-N(1) 2.190(9), Ru(1)-N(4) 2.126(8), N(1)-Ru(1)-N(4) 89.4(3), P(1)-Ru(1)-P(2) 173.09(10). Symmetry codes a: –x+1, –y–1, z, b: –x+1, –y–2, –z. (b) Crystal structure of 1D coordination polymer **3**. Cu(1)-N(6) 2.156(4), Cu(1)···Cu(1)a 2.6436(13), Cu(2)-N(3) 2.156(4), Cu(2)···Cu(2)b 2.6303(12), Ru(1)-N(1) 2.187(4), Ru(1)-N(4) 2.149 (4), N(1)-Ru(1)-N(4) 87.88(15), P(1)-Ru(1)-P(2) 173.34(5). Symmetry codes a: –x+1, –y+1, z, b: –x+1, –y, –z. Hydrogen atoms except for H(1Ru) and methylenechloride solvates are omitted for clarity.

proposed structure of **1** and show that **1** indeed behaves as a good building block to connect other metal centers because of the vacant exodentate N atoms. As shown Figure 2(a), **2** is consisted of alternating $Cu_2(OAc)_4$ and $Cu(OAc)_2$ units connected by **1**. Therefore, **2** contains an unique unsymmetrical repeating unit. Two different exodentate N(6) atoms are bound to Cu(1) atom which is further coordinated by two acetate ligands in η^1-mode with Cu(1)-O(2) distance of 1.959 (8) Å. The interaction between Cu(1) and O(3) is very weak with the distance of 2.661 (8) Å. The equatorial positions of $Cu_2(OAc)_4$ are occupied by other exodentate N(3) atoms with the length of 2.174(8) Å which is in the range of bonding distances between dicopper complex and typical N donor atoms (2.12-2.25 Å).[13] Figure 2(b) shows the crystal structure of **3**. Unlike **2**, the repeating unit of **3** has 1 : 1 ratio of **1** and $Cu_2(OAc)_4$. The corresponding 1D polymer is relatively linear compared with **2**. Exodentate N atoms (N(3) and N(6)) of **1** coordinate dicopper units in the length of 2.156(4) Å and which are slightly shorter than those of **2**. It is interesting to note that two different 1D modular structures were obtained by a simple control of the reactant ratio. Reaction of **1** with $Rh_2(O_2CMe)_4{\cdot}2MeOH$ in boiling acetone solution rapidly produced pink-colored 1D polymer $\{[\mathbf{1}][Rh_2(O_2CMe)_4]\}_n$ (**4**). Reactions between **1** and $Mo_2(O_2CCF_3)_4$ also lead to the formation of yellow 1D polymer $\{[\mathbf{1}][Mo_2(O_2CCF_3)_4]\}_n$ (**5**). Both **4** and **5** have a similar structure like **3** based on elemental analysis. However, we were unable to grow X-ray quality crystals.

In summary, the discrete mononuclear complex **1** serves as a good building block for heterometallic 1D coordination polymers with various lantern-type dimers. The different molar ratio of **1** with $Cu(OAc)_2{\cdot}H_2O$ afforded structurally unique **2** and **3**, respectively. Both $\{[\mathbf{1}][Rh_2(O_2CMe)_4]\}_n$ and $\{[\mathbf{1}][Mo_2(O_2CCF_3)_4]\}_n$ were also obtained as stable solids. This unique modular approach enabled us to prepare well defined 1D coordination polymers in which two different transition metal moieties were preserved as a form of single strand. In order to expand this strategy, we are investigating other functional complexes containing dihydrobis(1,2,4-triazolyl)borate ligands.

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