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Axial ligands of Ru_2 tuning Zn^{2+} rearrangement to form a new heterometallic carbonate: Synthesis, structure and magnetic properties

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ABSTRACT

The self-assembly of $Ru_2(CO_3)_4^{3-}$ and Zn^{2+} in neutral aqueous solution forms heterometallic carbonate $ZnHRu_2(CO_3)_4(H_2O)_2\cdot 2H_2O$ (**1**). X-ray crystallographic analysis and magnetic investigation show that **1** behaves as 2D antiferromagnetic layers. It is different from those light transitional metal d^{1-9} centers (Mn, Co, and Ni), which merely exhibit octahedral MO_6 environment and *trans*- or *cis*-mode link Ru_2 dimers to form 2D and 3D frameworks, the production of **1** shows Zn^{2+} adopting tetrahedral environment. Compared with Zn^{2+} adopting octahedral environment in $KZn(H_2O)_6[Zn(H_2O)_2Ru_2(CO_3)_4Cl_2]\cdot 4H_2O$, it proves that the axial position ligands (L) of Ru_2 dimers account for the tetrahedral ZnO_4 (L = H_2O) or octahedral ZnO_6 (L = Cl^-) environments, and this is also due to the d^{10} electronic configuration of Zn^{2+} with the equivalent crystal field energy of the tetrahedral ZnO_4 and octahedral ZnO_6 symmetry.

Extended coordination polymers that are derived from paramagnetic dimetal building blocks containing M–M bonds have been constructed and gained increasing attention because of their structural diversities [1], unusual properties [2], and their magneto–structural correlations [3]. Mixed-valent diruthenium(II,III) centers are chelated/bridged by tetracarboxylates [4] and non-carboxylate-type *O,O′*-donor bridging ligands [5], including SO_4^{2-}, PO_4^{3-} and $hedp^{4-}$, to form paddle–wheel building block, and these structures exhibit a $S = 3/2$ high-spin ground state with a $\sigma^2\pi^4\pi^{*2}\delta^{*1}$ valence electronic configuration, which is attributed to the near degeneracy of π* and δ* orbitals. Two axial ligands of Ru_2 dimer have been received, which provides building blocks to construct 1D, 2D or 3D structural assemblies, and recent works have focused on the expanded frameworks that possess a high Curie temperature T_c [6].

Studies show that $Ru_2(CO_3)_4^{3-}$ potentially functions as a building block to construct magnetic materials as isomorphic and magnetically ordered systems $H_xK_{1-x}M^{II}[Ru^{II/III}{}_2(CO_3)_4](H_2O)_y(MeOH)_z$ (M = Mn, Fe, Co, Ni, and Mg) [7], in which the octahedral M ions link to $Ru_2(CO_3)_4^{3-}$ units in a *cis* mode to form a 3-D structure, but reveal a 2D magnetic ordering [8]. We have synthesized a series of molecule-based magnets with different topological structures by simultaneous assembly of $Ru_2(CO_3)_4^{3-}$ and M^{2+} (M = Mn, Co, Cu) in an aqueous solution, and reveal that the temperature, templates, reactant ratio, and solvents influence the formation of structural diversity [9]. Especially, the reaction temperatures selected have been found to be changing the coordination environment of the Cd^{2+}, for which a lower temperature (5 °C) accounts for the eight-coordinate and a higher (25 °C) for six-coordinate environment of Cd^{2+} [9b]. Recently, we obtained the single-crystal structure of a 2D heterometallic carbonate $KZn(H_2O)_6[Zn(H_2O)_2Ru_2(CO_3)_4Cl_2]\cdot 4H_2O$ (**2**), in which each six-coordinate Zn^{2+} ion shows an octahedral environment and links to $[Ru_2(CO_3)_4Cl_2]^{5-}$ in a cross mode and vice versa giving a negative layer of $[Zn(H_2O)_2Ru_2(CO_3)_4Cl_2]_n^{3n-}$ [9e]. In this paper, we report that the axial ligands of Ru_2 dimer play a key role in the assembly of Zn–$Ru_2(CO_3)_4$ systems in aqueous solutions, and without Cl^- in the presence, a new layered structural complex with the formula $ZnHRu_2(CO_3)_4(H_2O)_2\cdot 2H_2O$ is obtained, in which Zn^{2+} with tetrahedral environment directs the final products with given topologies of the layer. As we are known, diruthenium carbonate units that are linked by tetrahedral M^{2+} have never been reported so far.

During the synthesis, the organic solvents and temperature significantly affect the isolation of the title complex. For example, the increasing temperature (>25 °C) or adding some organic solvents, such as $(CH_3)_2CO$, CH_3OH, C_2H_5OH and CH_3CN, cannot yield the target complex **1**. Additionally, the self-assembly of $Ru_2(CO_3)_4^{3-}$ units and Zn^{2+} in the presence of Cl^- results in a heterometallic carbonate **2** [9e]. IR spectrums of complex **1** exhibit a series of strong bands between 600 and 1600 cm^{-1}, which are characteristic of the stretching vibrations of carbonate groups [10] (Fig. S1). TG analysis for complex **1** shows a weight loss of 5.1% in the temperature range of 30–220 °C, corresponding to the release of two lattice water molecules (5.2%). The fast mass loss occurs above 220 °C due to the decomposition of main structure. The weight loss 36.7% for **1** in the range of 220–500 °C is in agreement with the calculated decomposition value (release of four CO_2 and two coordination water molecules, 36.6%) (Fig. S3).

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Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in orthorhombic space group *Pccm*. The asymmetric unit comprises a quarter $[Ru_2(CO_3)_4(H_2O)_2]^{3-}$ dimer, a quarter Zn^{2+}, and disordered water O6, O7 and O8 (Fig. 1. a). Four equivalent CO_3^{3-} groups chelate/bridge two equivalent Ru atoms to form the paddlewheel dimer of $Ru_2(CO_3)_4^{3-}$, which is similar to that in the starting materials [5k]. Each Ru atom possesses a distorted octahedral environment, and four equatorial positions are occupied by four carbonate oxygen [O(1), O(2), O(1A), O(2A)] from the equivalent CO_3^{2-} groups. The axial positions are filled with an equivalent Ru atom and a water oxygen O(3). The Ru(1)–Ru(1A) distances of 2.2599(13) Å for **1** is shorter than the Ru–Ru bond lengths of the Ru(1)–Ru(1A) [2.2652(11) Å] and Ru(2)–Ru(2C) [2.2701(11) Å] for complex **2** [9e], which demonstrates that the axial position Cl^- ligands weaken the Ru–Ru bond more than H_2O. It has also been found for $[Ru_2(hedp)_2L_2]^{n-}$ [hedp = 1-hydroxyethylidenediphosphonate, $CH_3C(OH)(PO_3)_2^{4-}$] with the Ru–Ru bond weakening ability of $H_2O < Br^- < Cl^- < \mu$-$NCS^- < \mu$-$NC^- < \mu$-SCN^- [5g]. Ru–O bond lengths of 2.024(5)–2.303(8) Å for **1** are in agreement with those in some other O′O-donor ligands that chelate/bridge the mixed-valent Ru_2 dimer, including $Ru_2(RCO_2)_4^+$ [1a], $Ru_2(HPO_4)_4^{3-}$ [5k], $Ru_2(SO_4)_4^{3-}$ [5h,i], and $Ru_2(hedp)_2^{3-}$ [5a–g]. Fig. 1. b reveals that Zn is surrounded by carbonate oxygen atom O4 and its equivalents O(4D), O(4E), and O(4F) giving Zn(1)–O(4) bond lengths of 1.959(5) Å. While oxygen atom O2 and its equivalents give a long Zn…O distance of 2.922 (1) Å. The O(4)–Zn–O(4) angles range from 97.23(19)° to 123.33(19)°. The marked angular deviations indicate that Zn possesses a pseudo-tetrahedral environment instead of a distorted planar geometry. Consequently, the paddle–wheel units of $Ru_2(CO_3)_4^{3-}$ connect the neighboring Zn ions in a cross mode and vise versa (Fig. 1. c), and yield a square grid layer structure in the *bc* plane (Figs. 1. c and S4, ESI). Table S2 lists the selected bond lengths and angles of the complex **1**. We unsuccessfully synthesized 3D isomorphous Zn–Ru_2CO_3 that are similar to $H_xK_{1-x}M[Ru_2(CO_3)_4](H_2O)_y(MeOH)_z$ (M = Mn, Fe, Co, Ni, Mg). Some light transitional metal d^{1-9} centers (Mn, Co, and Ni) merely exhibit octahedral environments and *cis* mode link to Ru_2 dimers to form 3D frameworks. However, Zn^{2+} adopting both tetrahedral MO_4 and octahedral MO_6 environments in the Zn–$Ru_2(CO_3)_4$ assemblies could attributed to the d^{10} electronic configuration with the equivalent crystal field energy of the tetrahedral MO_4 and octahedral MO_6 symmetry. The distorted $\{ZnO_4\}$ tetrahedral coordination has also been observed in $(CH_6N_3)_2[Zn(CO_3)_2]$, in which Zn center acts as the pseudo-tetrahedral node of the diamond net [11]. ICP elemental analysis of complex **1**, in which the Zn–Ru–K ratio is 1:2:0, indicates that one H^+ must be present to balance the charge. The result has also been observed in the structure of $Mn_4(H_2O)_{16}H[Ru_2(CO_3)_4]_2[Ru_2(CO_3)_4(H_2O)_2]\cdot 11H_2O$ [9a]. The lattice water molecules are disordered and stabilized between the layers through hydrogen bonding (Figs. 1. d and S5, ESI). Because of the disordered lattice water molecules, the product of $ZnHRu_2(CO_3)_4$

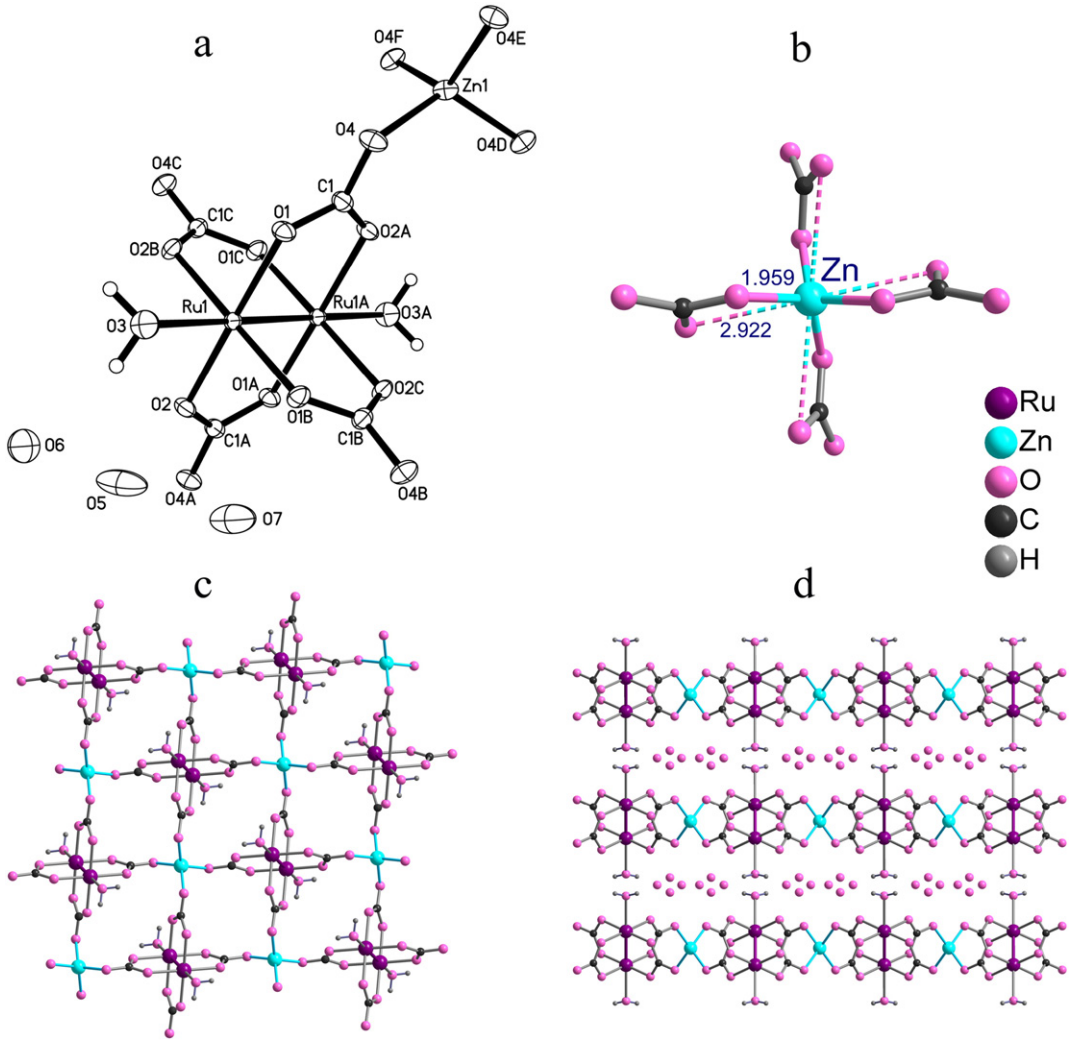

Fig. 1. a. Building unit of **1** with atomic label scheme (50% probability); b. local coordination geometry of Zn^{2+}; c. the layer $\{ZnHRu_2(CO_3)_4(H_2O)_2\}_n$ viewed along the a-axis; d. packing diagram of **1** projected down the b-axis.