Inorganic Chemistry Communications 33 (2013) 138–141

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

X-ray single-crystal structure and magnetic properties of $KMn(H_2O)_5Ru_2(CO_3)_4 \cdot 5H_2O$: A layered soft magnet

Dan Wang, Bin Liu *, Jin Jin, Xue-Mei Liu, Yan-Yan Jia, Gang-Lin Xue

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Xi'an 710069, PR China

ARTICLE INFO

Article history:
Received 24 February 2013
Accepted 17 April 2013
Available online 29 April 2013

Keywords:
Heterometallic
Diruthenium
Manganese
Structure
Magnetism

ABSTRACT

The temperature manipulation induces the aggregation of $Ru_2(CO_3)_4^{3-}$ paddle-wheel precursors and Mn^{2+} ions in lower temperature ~10 °C forming layer structural complex, $K[Mn(H_2O)_4Ru_2(CO_3)_4]\cdot 5H_2O$ (**1**). It composes of new negative layer $\{Mn(H_2O)_5Ru_2(CO_3)_4\}_n^{\ n-}$, and magnetic exchanges between spin centers result in ordering below 3.8 K. The observed critical temperature is like the previously reported 3D heterometallic carbonates $H_{0.3}K_{0.7}Mn[Ru_2(CO_3)_4](H_2O)_{5.5}$, which demonstrates that it is independent of the interlayer connecting in such heterometallic complexes based on square-grid layer $\{Ru_2(CO_3)_4\}_n^{\ 3n-}$.

Molecule materials derived from paramagnetic building blocks Ru_2^{n+} have been shown to develop a growing area of contemporary materials chemistry research.[1–3] Significantly, the magnetic properties can be tuned and improved by virtue of chemical control and modification. To obtain molecular magnetic materials, it is fundamental to use the bridging ligands, such as CN^- [4] and TCNQR [5], that could effectively transmit magnetic coupling. As far as the substituted groups (R = methyl and *tert*-butyl) of carboxylate-bridged paddlewheel diruthenium are concerned, 3D and 2D complexes, showing cubic interpenetrating-lattice and layer structure, exhibit ferrimagnetic ordering with the highest ordering temperature of 37.5 K. [4a].

In the past few years, the D_{4h} symmetry $Ru_2(CO_3)_4^{3-}$, as an intriguing building block, has attracted special attention for the design and synthesis of molecule-based magnets, and recent works indicate that the carbonate group, CO_3^{2-}, is an efficient ligand bridge mediating ferromagnetic coupling interaction between spin carriers. [6] $Ru_2(CO_3)_4^{3-}$ used in the assembly with transitional metal ions by J. S. Miller group forms heterometallic complexes $K_xH_{1-x}[M(H_2O)_4Ru_2(CO_3)_4]\cdot nH_2O$ (M = Mg, Mn, Fe, Co, Ni) [6b]. In these complexes, Ru_2 units are cross-linked by carbonate groups forming a square grid layer $[Ru_2(CO_3)_4]_n^{\ 3n-}$, and $M(H_2O)_4^{2+}$ ions bridging neighboring layers $[Ru_2(CO_3)_4]_n^{\ 3n-}$ in a *cis* mode form these 3D framework structures. Recently, we obtained a new bimetallic carbonates soft ferromagnet, $Mn_4(H_2O)_{16}H[Ru_2(CO_3)_4]_2[Ru_2(CO_3)_4(H_2O)_2]11H_2O$ [7], composed of both *cis* and *trans* fashion $Mn(H_2O)_4^{2+}$ ions linking the new (4,4) layers $[Ru_2(CO_3)_4]_n^{\ 3n-}$ forming a novel 3D structure. In this paper, the X-ray structure and magnetic properties of a new 2D structural complex $K[Mn(H_2O)_5Ru_2(CO_3)_4]\cdot 5H_2O$ (**1**) that contains new negative layer $\{Mn(H_2O)_5Ru_2(CO_3)_4\}_n^{\ n-}$ are reported. Meanwhile, the simultaneous assembly of $Ru_2(CO_3)_4^{3-}$ and Mn^{2+} in aqueous solution leading to the diverse dimensional structures may be manipulated by the introduction of different reactants ratio as well as temperature conditions, and this layer structural complex exhibits ferromagnetism between spin centers both $Ru_2^{II,III}$ and Mn^{II} with a Curie temperature of 3.8 K.

Compound **1** was synthesized by mixing 6 mL of an aqueous solution of $K_3Ru_2(CO_3)_4\cdot 5H_2O$ [8] (0.02 mmol) with 4 mL of an aqueous solution of $MnSO_4\cdot H_2O$ (0.04 mmol) at 10 °C, which produced dark-brown column crystals after several weeks with a yield of 34% (based on Ru). The IR spectrum shows a series of strong bands between 1450 and 700 cm^{-1}, characteristic of the fundamental or splitting vibration of the carbonate groups CO_3^{2-} [9].

Single-crystal X-ray diffraction studies [10] reveal that complex **1** crystallizes in the monoclinic space group $P2_1$. The asymmetric unit consists of one $Ru_2(CO_3)_4^{3-}$, one $Mn(H_2O)_5^{2+}$, one K^+ and five lattice water molecules (Fig. 1). Each Ru_2 moiety has four CO_3^{2-} ligands, which chelate and bridge Ru—Ru bond forming the paddle-wheel geometry. The Ru1—Ru2 bond length is 2.2606(11) Å, comparable to the 2.25 Å length reported for the starting material [8], and 2.258 and 2.265 Å observed for the heterometalic carbonate diruthenium [6]. The Ru—O bond lengths fall in the range of 2.015(6)–2.279(7) Å, comparable to those in other related complexes [11,12]. The axial positions of Ru1Ru2 moiety are terminated by oxygen atoms from neighboring Ru2 units forming a square-grid layer $[Ru_2(CO_3)_4]_n^{\ 3n-}$ (Fig. 2). The Ru1A—O9—C3 and Ru2D—O12—C4 angles are 134.2(7)° and 134.0(6)°, respectively. Mn(1) shows a distorted octahedral environment, and it can be considered as one corner of $\{Mn(H_2O)_6\}^{2+}$ substituted by carbonate oxygen donor O(3) from the $Ru_2(CO_3)_4^{3-}$

---

* Corresponding author. Tel./fax: +86 29 88302304.
E-mail address: liubin@nwu.edu.cn (B. Liu).

1387-7003/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.inoche.2013.04.027

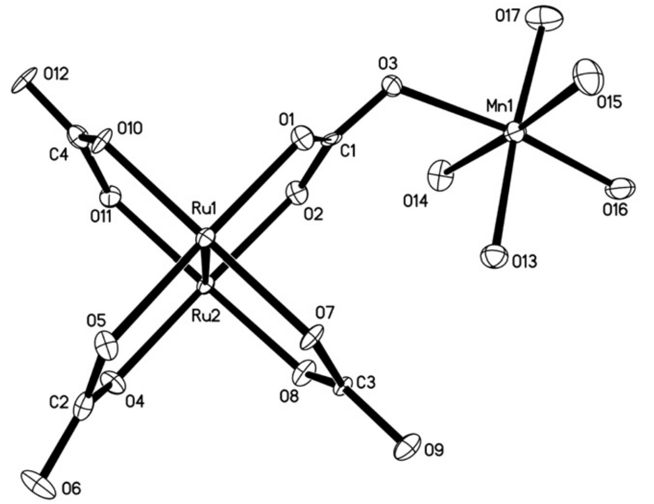

Fig. 1. A fragment of the $Mn(H_2O)_5Ru_2(CO_3)_4^-$ in compound **1** with the atomic labeling scheme (thermal ellipsoids shown at 30% probability). All H atoms are omitted for clarity.

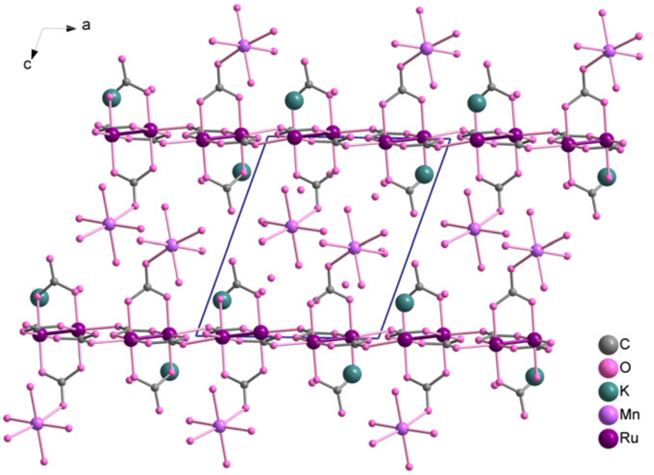

Fig. 3. Packing diagram of **1** projected down the b-axis.

dimer forming a new negative layer $[Mn(H_2O)_5Ru_2(CO_3)_4]_n^{n-}$ (Fig. 3). The bond lengths of Mn(1)—O are in the range of 2.158(6)–2.241(7) Å, and the Mn(1)—O(3)—C(1) angle is 121.7(5)°. The K(1) atom is located at a general position within the layer, and lattice water fill the intra- and interlayer spaces. This is different from the observed complexes $K_{0.7}H_{0.3}Mn(H_2O)_4[Ru_2(CO_3)_4]\cdot zH_2O$ [5b], in which two positions of six-coordinate environment Mn are substituted by carbonate oxygen atoms, thus bridging neighboring $[Ru_2(CO_3)_4]_n^{3n-}$ layers in the *cis* mode forming a 3D framework structure.

Magnetic measurements were carried out on crystalline sample of compound **1**. At room temperature, the $\chi_M T$ value is 6.81 cm^3 K mol^{-1} per $MnRu_2$, close to the expected spin-only value for $Ru_2^{II,III}$ ($S = 3/2$, $g = 2$) and Mn^{II} ($S = 5/2$, $g = 2$) (Fig. 4). As the temperature is lowered, the $\chi_M T$ monotonically increases and then increases abruptly up to a maximum value of 38.02 cm^3 K mol^{-1} at 3.5 K, followed by a drop to 27.78 cm^3 K mol^{-1} at 1.8 K. Commonly, the large positive zero-field splitting *D* of mixed-valent Ru₂(II,III) makes the $\chi_M T$ decreasing *via* cooling, here in the monotonic increase in $\chi_M T$ suggests that significant ferromagnetic coupling is mediated between spin centers in compound **1**. The abrupt increase of $\chi_M T$ with decreasing temperature at ~10 K indicates a possible magnetic ordering. Above 15 K, the susceptibility data can be analyzed by the following equation containing the zero-field splitting *D* parameter based on the spin ground state $S = 3/2$: [4a]

$$\chi = \chi_{Ru_2} + \chi_{Mn},$$

where

$$\chi_{Mn} = \frac{N g_{Mn}^2 \beta^2}{3k(T-\theta)} S(S+1)$$

and

$$\chi_{Ru_2} = \frac{N g_{Ru}^2 \beta^2}{k(T-\theta)} \left[\frac{1}{3} \frac{1+9e^{-2D/kT}}{4\left(1+e^{-2D/kT}\right)} + \frac{2}{3} \frac{1+(3kT/4D)\left(1-e^{-2D/kT}\right)}{1+e^{-2D/kT}} \right]$$

where the Weiss constant θ roughly accounts for the magnetic interactions between the paramagnetic centers. The best fit (fixed $g_{Mn} = 2.0$), shown as the solid line in Fig. 4, gives parameters $g_{Ru} = 2.26$, $D = 56.3$ cm^{-1} and $\theta = 5.0$ K. The positive θ value also confirms the presence of ferromagnetic exchanges between spin centers.

The FC and ZFC plots at an applied field of 10 Oe show plateau value and diverge below ca. 3.8 K (Fig. 5). This may imply the presence of

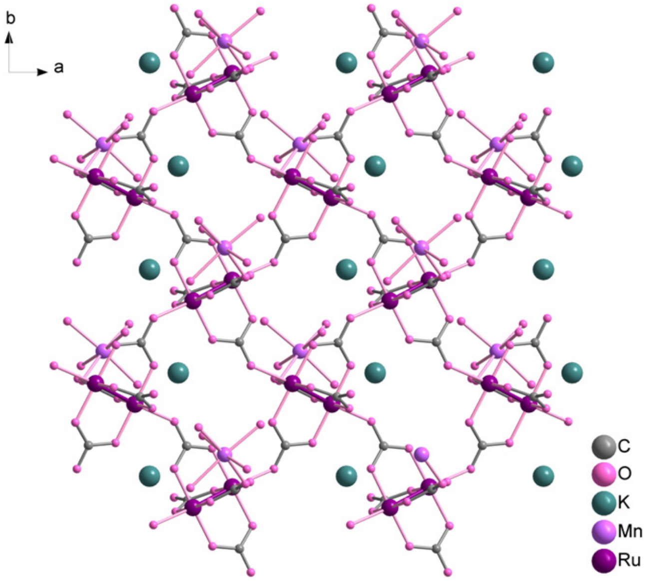

Fig. 2. Square-grid layer structure $[Mn(H_2O)_5Ru_2(CO_3)_4]_n^{n-}$ viewed in *ab* plane.

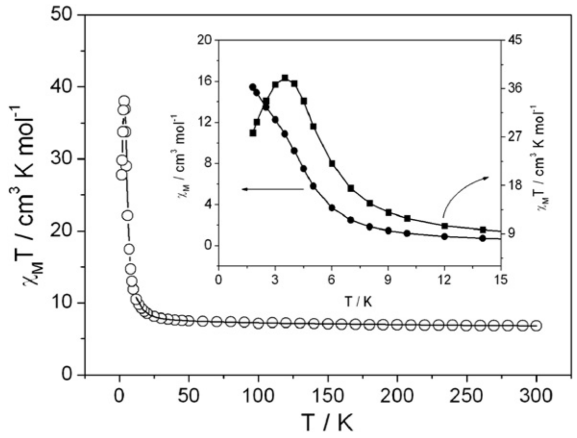

Fig. 4. $\chi_M T$ vs. T plot for compound **1**, inset: $\chi_M T$ and χ_M plots below 15 K.