



Article

Crystal-to-Crystal Transformation from $K_2[Co(C_2O_4)_2(H_2O)_2] \cdot 4H_2O$ to $K_2[Co(\mu-C_2O_4)(C_2O_4)]$

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Abstract: Crystal-to-crystal transformation is a path to obtain crystals with different crystal structures and physical properties. $K_2[Co(C_2O_4)_2(H_2O)_2] \cdot 4H_2O$ (**1**) is obtained from $K_2C_2O_4 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$ in H_2O with a yield of 60%. It is crystallized in the triclinic with space group $P\bar{1}$ and cell parameters: $a = 7.684(1) \text{ \AA}$, $b = 9.011(1) \text{ \AA}$, $c = 10.874(1) \text{ \AA}$, $\alpha = 72.151(2)^\circ$, $\beta = 70.278(2)^\circ$, $\gamma = 80.430(2)^\circ$, $V = 670.0(1) \text{ \AA}^3$, $Z = 2$ at 100 K. **1** is composed of K^+ , mononuclear anion $[Co(C_2O_4)_2(H_2O)_2]^{2-}$ and H_2O . Co^{2+} is coordinated by two bidentated oxalate anion and two H_2O in an octahedron environment. There is a hydrogen bond between mononuclear anion $[Co(C_2O_4)_2(H_2O)_2]^{2-}$ and H_2O . $K_2[Co(\mu-C_2O_4)(C_2O_4)]$ (**2**) is obtained from **1** by dehydration. The cell parameters of **2** are $a = 8.460(5) \text{ \AA}$, $b = 6.906(4) \text{ \AA}$, $c = 14.657(8) \text{ \AA}$, $\beta = 93.11(1)^\circ$, $V = 855.0(8) \text{ \AA}^3$ at 100 K, with space group in $P2_1/c$. It is composed of K^+ and zigzag $[Co(\mu-C_2O_4)(C_2O_4)]_n$ chain. Co^{2+} is coordinated by two bisbidentate oxalate and one bidentated oxalate anion in trigonal-prism. **1** is an antiferromagnetic molecular crystal. The antiferromagnetic ordering at 8.2 K is observed in **2**.

Keywords: oxalate; cobalt; crystal structure; magnetic property

1. Introduction

The change of the weak interaction of guest molecules, coordination geometry distortion, and coordination number in coordination compounds can effectively modulate the physical properties as magnetism, absorption, and chirality, so the dynamic molecular crystals have received great attention for their potential applications in molecular devices, as molecular sensors and switches become a powerful method for obtaining a specific compound with the yield of 100% by crystal-to-crystal transformation in crystal engineering [1–7]. The crystal-to-crystal transformations were observed between different dimensional coordination units as zero-dimensional (0D), one-dimensional chain (1D), two-dimensional (2D) layer, and three-dimensional (3D) coordination frameworks [8–10]. We are interested in dynamic crystals of $MX_2-(1,4\text{-dioxane})-H_2O$ system, and 0D to 2D, 1D to 2D, 1D to 3D crystal-to-crystal transformations were found [11–13]. Oxalate ($C_2O_4^{2-}$) is one of most popular used three-atoms ligands in the study of molecular-based magnet, its versatile abilities and intermediating efficient magnetic coupling among transition atoms have constructed 1D, 2D, and 3D magnetic materials [14–21]. However, the research on oxalate-based dynamic crystal is limited. Herein, we present a crystal-to-crystal transformation from 0D mononuclear compound $K_2[Co(C_2O_4)_2(H_2O)_2] \cdot 4H_2O$ (**1**) into a reported 1D coordination compound $K_2[Co(\mu-C_2O_4)(C_2O_4)]$ (**2**) accompanied by changes in crystal color, cell parameters, space group, coordination environment, crystal structure, and magnetic property.

2. Experiment and Discussion

1 was obtained from $\text{K}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in H_2O with yield of 60%.

When **1** was heated at an elevated temperature (at 120 °C for three minutes), it transferred to **2** after dehydration with a mass loss of 25.7%, crystal structure changed from mononuclear to one-dimensional chain (Scheme 1) and the crystal color changed from orange to pink. **2** remained stable until 300 °C (Figure 1). This is the second method to obtain **2** except the solvothermal method. The IR bands (Figure S1) between **1** and **2** is the strong broad band above 3000 cm^{-1} $\nu(\text{O-H})$ as from H_2O in **1**. The existence weak broad band above 3000 cm^{-1} means **2** is unstable to air as reported [17].

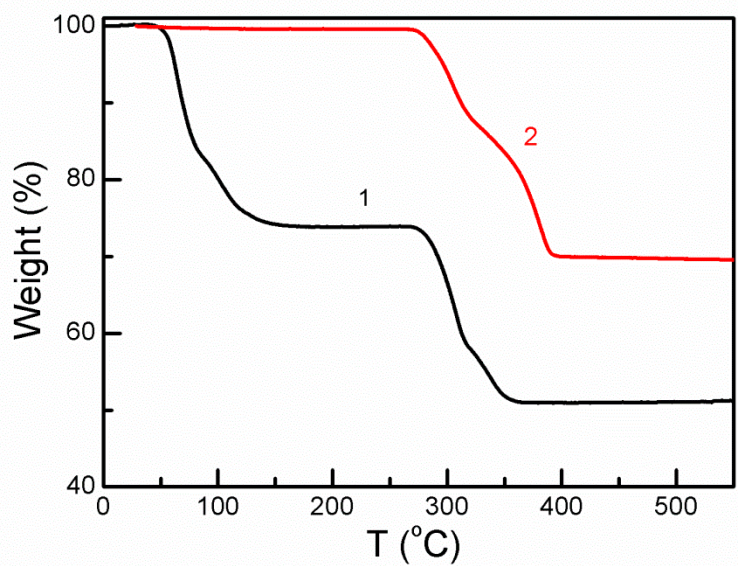


Figure 1. TGA plot of **1** (black) and **2** (red).

1 crystallizes in triclinic with space group of $P\bar{1}$: $a = 7.684(1)\text{ \AA}$, $b = 9.011(1)\text{ \AA}$, $c = 10.874(1)\text{ \AA}$, $\alpha = 72.151(2)^\circ$, $\beta = 70.278(2)^\circ$, $\gamma = 80.430(2)^\circ$, $V = 670.0(1)\text{ \AA}^3$, $Z = 2$. **1** is composed of K^+ , mononuclear coordination anion $\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^{2-}$ and H_2O (Figure 2a). There are two K^+ , one Co^{2+} , two oxalate ($\text{C}_2\text{O}_4^{2-}$), and six H_2O in an independent unit. K1 is surrounded by five O from three oxalato and four H_2O , K2 is surrounded by five O from three oxalato and four H_2O . K column formed by K1 and K2 host the vacancy of H-bond network formed by oxalate and H_2O along the b axis. $\text{K1} \cdots \text{K2}$ distances are $3.872(2)\text{ \AA}$ and $5.630(2)\text{ \AA}$ alternatively, and $\text{K1} \cdots \text{K1}$ and $\text{K2} \cdots \text{K2}$ distances are $9.011(1)\text{ \AA}$. Each Co^{2+} is coordinated by two oxalate anions with Co-O $2.078(2)\text{--}2.099(2)\text{ \AA}$ on the equatorial plane, and two H_2O with Co-O $2.114(4)\text{--}2.120(3)\text{ \AA}$ to fulfill the octahedron environment. O-Co-O angles are among $88.4(2)\text{--}92.3(1)^\circ$ from H_2O to equatorial plane and $176(1)^\circ$ between two H_2O atoms. Viewed along the b axis, $\text{Co} \cdots \text{Co}$ distances are of $9.011(1)\text{ \AA}$ and $7.684(2)\text{ \AA}$ alternatively along the a axis. There are hydrogen bonds between anions and coordinated H_2O : $\text{O9-H1} \cdots \text{O8}(-x,1-y,1-z)$ $2.839(5)\text{ \AA}/170^\circ$, $\text{O10-H4} \cdots \text{O1}(-x,2-y,-z)$ $3.178(5)\text{ \AA}/127^\circ$; between anions and solvent H_2O : $\text{O14-H12} \cdots \text{O1}$ $2.795\text{ \AA}/163^\circ$, $\text{O13-H9} \cdots \text{O6}(1-x,y,z)$ $2.740\text{ \AA}/169^\circ$, $\text{O9-H2} \cdots \text{O14}(-x,1-y,-z)$ $2.760\text{ \AA}/179^\circ$, $\text{O12-H8} \cdots \text{O2}(1-x,1-y,z)$ $2.820\text{ \AA}/167^\circ$, $\text{O11-H5} \cdots \text{O8}(-x,1-y,1-z)$ $2.826\text{ \AA}/156^\circ$, $\text{O10-H3} \cdots \text{O12}(-x,1-y,z)$ $2.755\text{ \AA}/176^\circ$, $\text{O11-H6} \cdots \text{O3}(-x,1-y,-z)$ $2.709\text{ \AA}/178^\circ$, $\text{O13-H10} \cdots \text{O7}$ $2.803\text{ \AA}/164^\circ$.

The crystal structure of **2** is the same as reported isostructural of $\text{K}_2[\text{Fe}(\mu\text{-C}_2\text{O}_4)(\text{C}_2\text{O}_4)]$ [17]. It consists of K^+ and zigzag chain $[\text{Co}(\mu\text{-C}_2\text{O}_4)(\text{C}_2\text{O}_4)_2]_n$ (Figure 2b). There are one and two half K^+ , one Co^{2+} , one and two half oxalato in an independent unit. Co^{2+} is trigonal-prismatic coordinated by three oxalate anions with Co-O distance $2.058(3)\text{--}2.151(4)\text{ \AA}$. K^+ is in the vacant formed by $\text{Co}(\text{C}_2\text{O}_4)_2^{2-}$ chain.

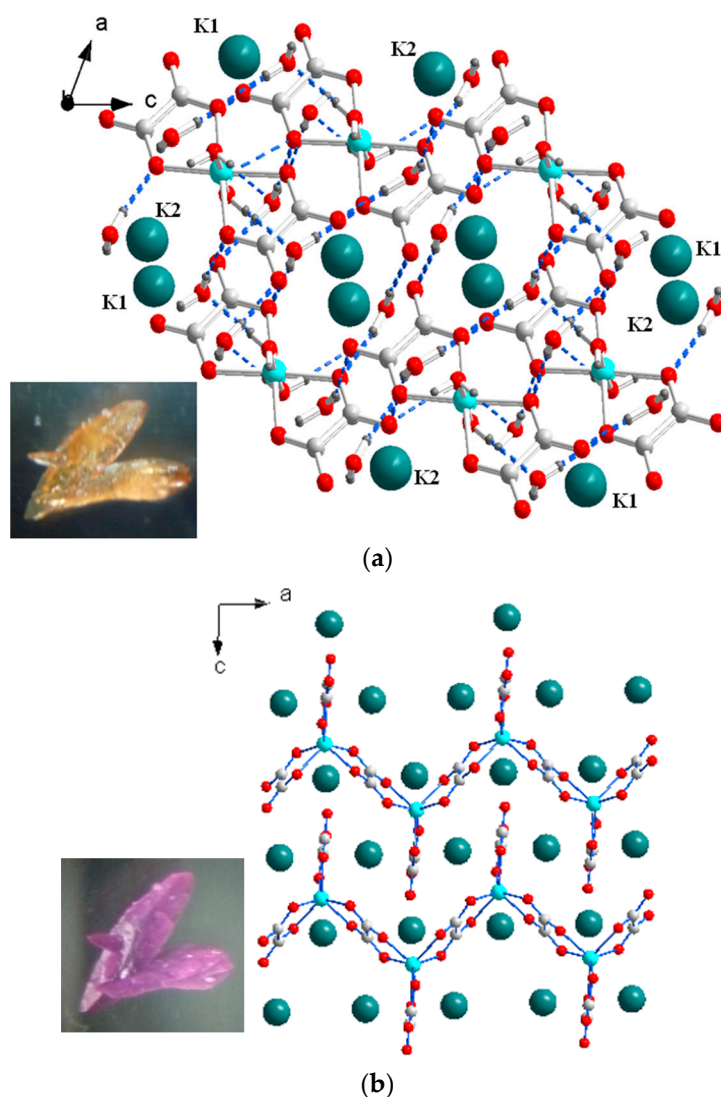


Figure 2. Crystal structure and appearance of **1** (a) and **2** (b). Color code: K, dark green; Co, cyan; C, light grey; O, red.; H, grey. Blue dashed lines are hydrogen bonds.

Depending on the extensive hydrogen bonds in **1** and zigzag chained structure of **2**, the magnetic properties of them were investigated. The transformation from **1** to **2** is irreversible. The sample was checked and remained the same before and after magnetic experiments.

1: χT is $3.41 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K. It is significantly larger than the value of $1.875 \text{ cm}^3 \text{ K mol}^{-1}$ expected for an isolated, spin-only ion with $S = 3/2$ and $g = 2.00$. This suggests a strong spin-orbit coupling. [20–22] The χT value decreased upon cooling and reached $1.30 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The susceptibility data above 50 K fit the Curie–Weiss law well, giving Curie and Weiss constants of $C = 3.613(6) \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -21.2(2) \text{ K}$, respectively, with $R = 3.74 \times 10^{-5}$ (Figure 3). The negative Weiss constant means the antiferromagnetic interaction between Co^{2+} ions through hydrogen bonds. At 2 K, the isothermal magnetization is $2.24 \text{ N}\beta$ at 65 kOe (Figure 4). No long-range magnetic ordering was observed in **1**.

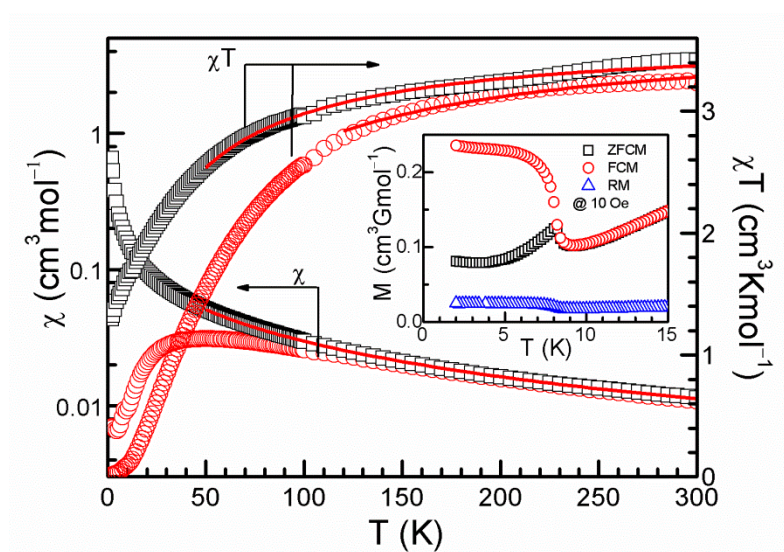


Figure 3. Magnetic susceptibility of **1** (black square) and **2** (red circle) under 1000 Oe. Inset: ZFCM/FCM/RM at 10 Oe of **2**. Red line: Curie-Weiss fitting.

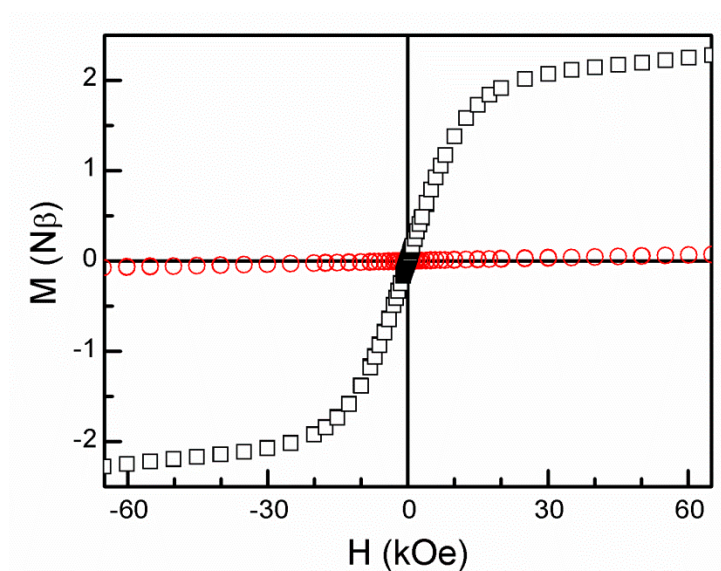


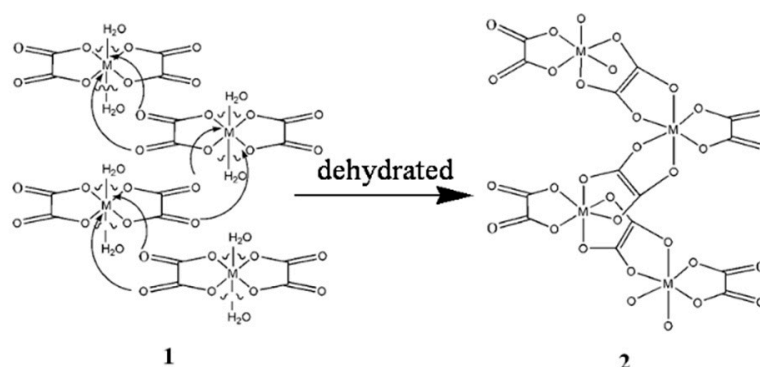
Figure 4. Isothermal magnetization of **1** (empty black square) and **2** (empty red circle) at 2 K.

2: On χ versus T plot, a broad maximum of $0.031 \text{ cm}^3 \text{ mol}^{-1}$ was observed around 50 K, which is similar to reported oxalate-bridged one-dimensional compounds [15,17,20]. Then χ value decreased upon cooling smoothly, it is $0.0070 \text{ cm}^3 \text{ mol}^{-1}$ at 2 K. At 300 K, χT is $3.24 \text{ cm}^3 \text{ K mol}^{-1}$, this means a strong spin-orbit coupling of Co^{2+} as **1**. The χT value decrease upon cooling and reach $0.014 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The data above 120 K were fitted with Curie-Weiss law, giving Curie and Weiss constant $C = 3.66(2) \text{ cm}^3 \text{ K mol}^{-1}$, $\theta = -35(1) \text{ K}$, $R = 4.96 \times 10^{-5}$. Field-cooled magnetization (FCM) and zero-field-cooled magnetization (ZFCM) measurements under a field of 10 Oe show a magnetic ordering at 8.2 K (Figure 3, inset). At 2 K, the isothermal magnetization increases smoothly and reaches $0.072 \text{ N}\beta$ at 65 kOe. The Hysteresis loop (H_c) is 500 Oe.

3. Conclusions

Orange **1** transfer to pink **2** by dehydration. **1** is composed of K^+ , mononuclear coordination anion $\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ and H_2O with extensive hydrogen bond between anion and H_2O , H_2O , and H_2O . **2** is consisted of K^+ and zigzag chain anion $[\text{Co}(\mu\text{-C}_2\text{O}_4)(\text{C}_2\text{O}_4)^{2-}]_n$.

The antiferromagnetic interaction in **1** from hydrogen bonds is weaker than oxalate-bridge in **2** [23]. **2** shows antiferromagnetic ordering at 8.2 K.



Scheme 1. Schematic drawing of the possible route of crystal-to-crystal transformation from **1** to **2**.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/magnechemistry7060077/s1>, sample preparation and characterization, Figure S1: IR spectra of **1** and **2**, Figure S2: Powder X-ray diffraction patterns of **1** and **2**.

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Data Availability Statement: Sample preparation, characterization, IR spectra and powder X-ray diffraction pattern of **1** and **2** are available on Supplementary Materials via. www.mdpi.com/xxx/s1.

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Conflicts of Interest: The authors declare no conflict of interest.

References

- Lim, S.H.; Olmstead, M.M.; Balch, A.L. Molecular accordion: Vapoluminescence and molecular flexibility in the orange and green luminescent crystals of the dimer, $\text{Au}_2(\mu\text{-bis}(\text{-diphenylphosphino)ethane})_2\text{Br}_2$. *J. Am. Chem. Soc.* **2011**, *133*, 10229–10238. [CrossRef] [PubMed]
- Huang, Y.; Schoenecker, B.; Mu, P.; Carson, C.G.; Karra, J.R.; Cai, Y.; Walton, K.S. A porous flexible homochiral SrSi_2 array of single-stranded helical nanotubes exhibiting single-crystal-to-single-crystal oxidation transformation. *Angew. Chem. Int. Ed.* **2011**, *50*, 436–440. [CrossRef] [PubMed]
- Chatterjee, P.B.; Audhya, A.; Bhattacharya, S.; Abtab, S.M.T.; Bhattacharya, K.; Chaudhury, M. Single crystal-to-single crystal irreversible transformation from a discrete Vanadium(V)-Alcoholate to an Aldehydic-Vanadium(IV) oligomer. *J. Am. Chem. Soc.* **2010**, *132*, 15842–15845. [CrossRef]
- Huang, Z.; White, P.S.; Brookhart, M. Ligand exchanges and selective catalytic hydrogenation in molecular single crystals. *Nature* **2010**, *465*, 598–601. [CrossRef]
- Kawasaki, T.; Hakoda, Y.; Mineki, H.; Suzuki, K.; Soai, K. Generation of absolute controlled crystal chirality by the removal of crystal water from achiral crystal of nucleobase cytosine. *J. Am. Chem. Soc.* **2010**, *132*, 2874–2875. [CrossRef]
- Allan, P.K.; Xiao, B.; Teat, S.J.; Knight, J.W.; Morris, R.E. In situ single-crystal diffraction studies of the structural transition of metal-organic framework copper 5-sulfaisophthalate, Cu-SIP-3. *J. Am. Chem. Soc.* **2010**, *132*, 3605–3611. [CrossRef]
- Thorarindottir, A.E.; Harris, T.D. Metal-Organic framework magnets. *Chem. Rev.* **2020**, *120*, 8716–8789. [CrossRef]
- Kaneko, W.; Ohba, M.; Kitagawa, S. A flexible coordination polymer crystal providing reversible structural and magnetic conversions. *J. Am. Chem. Soc.* **2007**, *129*, 13706–13712. [CrossRef]
- Zhang, Y.; Liu, T.; Kanegawa, S.; Sato, O. Reversible single-crystal-to-single-crystal transformation from achiral antiferromagnetic hexanuclears to a chiral ferrimagnetic double zigzag chain. *J. Am. Chem. Soc.* **2009**, *131*, 7942–7943. [CrossRef] [PubMed]
- Zhang, Y.; Liu, T.; Kanegawa, S.; Sato, O. Interconversion between a nonporous nanocluster and a microporous coordination polymer showing selective gas adsorption. *J. Am. Chem. Soc.* **2010**, *132*, 912–913. [CrossRef]

11. Duan, Z.; Zhang, Y.; Zhang, B.; Zhu, D. Crystal-to-Crystal transformation from antiferromagnetic chains into a ferromagnetic diamondoid framework. *J. Am. Chem. Soc.* **2009**, *131*, 6934–6935. [[CrossRef](#)]
12. Zhang, B.; Zhu, D.; Zhang, Y. Crystal-to-Crystal transformation from a mononuclear compound in a hydrogen-bonded three-dimensional framework to a layered coordination polymer. *Chem. Eur. J.* **2010**, *16*, 9994–9997. [[CrossRef](#)]
13. Shi, J.; Zhang, Y.; Zhang, B.; Zhu, D. Crystal-to-crystal transformation from a chain compound to a layered coordination polymer. *Dalton Trans.* **2016**, *45*, 89–92. [[CrossRef](#)]
14. Mathoniere, C.; Carling, S.G.; Yusheng, D.; Day, P. Molecular-based Mixed Valency Ferrimagnets $(XR_4)Fe^{II}Fe^{III}(C_2O_4)_3$ ($X = N, P$; $R = n$ -propyl, n -butyl, phenyl): Anomalous negative magnetisation in the tetra- n -butylammonium derivative. *J. Chem. Soc. Chem. Commun.* **1994**, 1551–1552. [[CrossRef](#)]
15. Clemente-Leon, M.; Coronado, E.; Marti-Gastaldo, C.; Romero, F.M. Multifunctionality in hybrid magnetic materials based on bimetallic oxalate complexes. *Chem. Soc. Rev.* **2011**, *40*, 473–497. [[CrossRef](#)]
16. Hernandez-Molina, M.; Lloret, F.; Ruiz-Perez, C.; Julve, M. Weak ferromagnetism in chiral 3-dimensional oxalate-bridged Cobalt(II) compounds. crystal structure of $[Co(bpy)_3][Co_2Ox_3]ClO_4$. *Inorg. Chem.* **1998**, *37*, 4131–4135. [[CrossRef](#)]
17. Hursthouse, M.B.; Light, M.E.; Price, D.J. One-dimensional magnetism in new anhydrous iron and cobalt ternary oxalates with rare trigonal prismatic metal coordination. *Angew. Chem. Int. Ed.* **2004**, *43*, 472–475. [[CrossRef](#)]
18. Coronado, E.; Galan-Mascaros, J.R.; Marti-Gastalo, C. Single chain magnets based on the oxalate ligand. *J. Am. Chem. Soc.* **2008**, *130*, 14987–14989. [[CrossRef](#)]
19. Glerup, J.; Goodson, P.A.; Hodgson, D.J.; Michelsen, K. Magnetic Exchange through Oxalate Bridges: Synthesis and Characterization of $(\mu$ -Oxalato)dimetal (II) Complexes of Manganese, Iron, Cobalt, Nickel, Copper and Zinc. *Inorg. Chem.* **1995**, *34*, 6255–6264. [[CrossRef](#)]
20. Garcia-Couceiro, U.; Castillo, O.; Luque, A. A new hydrated phase of cobalt(II) oxalate: Crystal structure, thermal behavior and magnetic properties of $[Co(-Ox)(H_2O)_2] \cdot 2H_2O$. *Inorg. Chim. Acta* **2004**, *357*, 339–344. [[CrossRef](#)]
21. Duan, Z.; Zhang, Y.; Zhang, B.; Zhu, D. $Co(C_2O_4)(HO(CH_2)_3OH)$: An antiferromagnetic neutral zigzag chain compound showing long-range-ordering of spin canting. *Inorg. Chem.* **2008**, *47*, 9152–9154. [[CrossRef](#)]
22. Duan, D.; Zhang, Y.; Zhang, B.; Pratt, F. Two homometallic antiferromagnets based on oxalato-bridged honeycomb assemblies: $(A)_2[M^{II}_2C_2O_4)_3]$ ($A =$ ammonium salt derived from diethylenetriamine; $M^{II} = Fe^{2+}, Co^{2+}$). *Inorg. Chem.* **2009**, *48*, 2140–2146. [[CrossRef](#)]
23. Desplanches, C.; Ruiz, E.; Rodrigue-Fortea, A.; Alvarez, S. Exchange coupling of transition-metal ions through hydrogen bonding: A theoretical investigation. *J. Am. Chem. Soc.* **2002**, *124*, 5197–5205. [[CrossRef](#)]