

K10[Co₄(H₂O)₂(B- α -SiW₉O₃₄H)₂] · 21H₂O : a sandwich polyoxometalate based on the magnetically interesting element cobalt

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$\text{K}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-SiW}_9\text{O}_{34}\text{H})_2] \cdot 21\text{H}_2\text{O}$: A sandwich polyoxometalate based on the magnetically interesting element cobalt

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Abstract

The magnetism of a sandwich tetracobalt(II) substituted tungstosilicate $\text{K}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-SiW}_9\text{O}_{34}\text{H})_2] \cdot 21\text{H}_2\text{O}$ has been studied based on an isotropic Heisenberg model supplemented by a zero-field splitting term.

Keywords: Cobalt(II); Sandwich; Polyoxometalate; Magnetism

As the largest subclass of transitional metal substituted polyoxometalates (TMSPs), sandwich-type compounds have received increasing interest for their magnetism in recent years [1]. Though their structures containing more than one paramagnetic transition metal ion in close proximity may exhibit exchange-coupled spins leading to large spin ground states, these compounds often display the weak magnetism because the magnetic sites are encapsulated in a diamagnetic molecular metal oxide cluster [1c,1d]. As a matter of fact, the special use of these compounds in magnetism area is that they offer ideal structural supports for the study of the interactions between paramagnetic metal atoms [2,3] as well as between delocalized electrons and paramagnetic metal atoms [4].

On the other hand, it is to be noted that the interaction between orbitally degenerate ions, as for example high-spin cobalt(II) in octahedral sites, remains an essentially unsolved problem [5]. The high symmetry of sandwich-type TMSPs and the small distortion of the octahedral CoO_6 sites should facilitate the theoretical treatment required to give a quantitative explanation of the cobalt–cobalt magnetic interaction.

Herein, we report the synthesis, structure and magnetism of a sandwich TMSPs based on the magnetically interesting element Co.

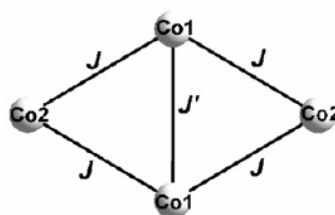
Reaction of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.048 g) and $\text{Na}_9[\beta\text{-SiW}_9\text{O}_{34}\text{H}] \cdot 23\text{H}_2\text{O}$ [6] (0.1 mmol, 0.28 g) in 10 mL of KAc buffer (pH 4.8) at 80 °C for 1 h followed by slow evaporation at room temperature resulted in red single crystals (0.15 g, yield 54%) [7]. X-ray analyses [8] reveal the compound, crystallized as $\text{K}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-SiW}_9\text{O}_{34}\text{H})_2] \cdot 21\text{H}_2\text{O}$ (**1**), belongs to monoclinic system. The dimeric polyoxoanion $[\text{Co}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-SiW}_9\text{O}_{34}\text{H})_2]^{10-}$ consists of two lacunary $[\text{B-}\alpha\text{-SiW}_9\text{O}_{34}\text{H}]^{10-}$ Keggin moieties linked by four Co^{2+} ions, leading to a sandwich-type structure with idealized C_{2v} symmetry (Fig. 1). The central belt of **1** is composed of a rhombic Co_4O_{16} group consisting of four coplanar CoO_6 octahedral sharing edges (Fig. 2). The distances of $\text{Co} \cdots \text{Co}$ along the sides of the rhombus are 3.18 Å while along the diagonal of the rhombus are 3.30 Å and 5.44 Å, respectively. There is a narrow variation in the Co-O-Co angles, with an average value of 95.8°. These values for the metal-metal separation and the geometry of the bridging unit are very similar to that found in the phosphorus-containing polyanion $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ which is the first example of sandwich TMSPs as well as of cobalt-based sandwich TMSPs reported by Weakley et al. [9].

Although silicon-containing analogues SiMn_2W_9 , SiCu_2W_9 , and SiZn_2W_9 had been well reported by Kortz et al., [1c] which were synthesized by reacting M^{2+} ions with $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ under conditions very similar to that used for the synthesis of **1**, we were not able to synthesize $[\text{Co}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-SiW}_9\text{O}_{34}\text{H})_2]^{10-}$ (SiCo_2W_9) starting from $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ under the same conditions. Interestingly, the reaction starting from $[\beta\text{-SiW}_9\text{O}_{34}\text{H}]^{9-}$ resulted in $[\text{B-}\alpha\text{-SiW}_9\text{O}_{34}\text{H}]^{9-}$ anions in compound **1**, which meant that the mechanism of the metal insertion reaction must be accompanied by isomerization ($[\beta\text{-SiW}_9\text{O}_{34}]^{10-} \rightarrow [\text{B-}\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$). In our attempts to perform the reaction starting from $\text{Na}_{10}[\alpha\text{-SiW}_9\text{O}_{34}]$ [6], strangely, the crystals of the same compound could not be obtained. We speculated the $\text{Na}_{10}[\alpha\text{-SiW}_9\text{O}_{34}]$ synthesized according to Tézé's method was a mixture of $[\text{A-}\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$ and $[\text{B-}\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$, and thus caused the desired compound hard to be crystallized. Also deserving attention, despite the synthesis distinction between compound **1** and the three compounds (SiMn_2W_9 , SiCu_2W_9 , and SiZn_2W_9), they display the same anion $[\text{B-}\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$, which indicates that formation of the $(\text{B-}\alpha\text{-SiW}_9\text{O}_{34})$ fragment in a heated aqueous acidic medium is strongly favored.

Variable-temperature (2–300 K) magnetic susceptibility data at a magnetic field strength of 2 kg were collected for compound **1**. The χ_M and μ_{eff} vs. T plots are shown in Fig. 3. The μ_{eff} at room temperature, 10.36 B.M., is larger than the spin-only value of 7.74 B.M. for the magnetically isolated high-spin octahedral Co_4 species

due to the splitting of the 4T_1 term through spin–orbit coupling and local distortion of the octahedral sites. When the temperature is lowered, the value of μ_{eff} decreases smoothly, reaching a minimum at ca. 30 K ($\mu_{eff} = 9.43$ B.M.). Below 30 K, the μ_{eff} increases smoothly upon cooling further and reaches a maximum with 9.81 B.M. at 9 K. After this maximum, the μ_{eff} value decreases quickly, with 8.52 B.M. at 2 K. All the data measured from 2 to 300 K can be roughly fitted to a Curie–Weiss law with $C = 13.62 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -4.86$ K. Interestingly, here the plot of μ_{eff} vs. T looks like that found in some irregular spin state complexes [10]. To the best of our knowledge, the case has not been previously reported in other sandwich-type TMSPs. However, the magnetic mechanism of **1** is completely distinct from that of those irregular spin state compounds.

In order to explain the observed magnetic property of the title compound, the following exchange scheme has been used:



The interactions between the metal ions of the Co_4O_{16} unit can be described by two exchange coupling constants J and J' , where J represents the interactions along the sides of the rhombus while J' represents interactions along the short diagonal of the rhombus. As far as the existence of strong spin–orbit coupling for cobalt(II) ions was concerned, the magnetic data were analyzed by the following equations:

$$\chi_{\text{tet}} = \frac{Ng^2\beta^2}{3kT} \frac{\sum_i S_i(S_i + 1)(2S_i + 1) \exp(-E_i/KT)}{\sum_i (2S_i + 1) \exp(-E_i/KT)}$$

$$\chi_{\text{Lig}} = \frac{N\beta^2}{3kT} \frac{3[3.15x+3.18+(2.84x+2.13) \exp(-3.75x)+(4.7x-6.05) \exp(-6x)]}{x[3+2 \exp(-3.75x)+\exp(-6x)]}$$

$$(x = \lambda/kT)$$

$$\chi_M = \chi_{\text{tet}} + 4\chi_{\text{Lig}} - \frac{Ng^2\beta^2}{3kT} \left[4 \times \frac{3}{2} \left(\frac{3}{2} + 1 \right) \right]$$

Best fitting for the experimental data leads to $J = -0.77 \text{ cm}^{-1}$, $J' = 3.12 \text{ cm}^{-1}$, $g = 2.34$, $\lambda = -129 \text{ cm}^{-1}$, with the agreement factor $R = \sum (\chi_{\text{obsd}} - \chi_{\text{calcld}})^2 / \sum \chi_{\text{obsd}}^2 = 2.73 \times 10^{-4}$. The results reveal that magnetic interaction between Co1 and

Co1 is ferromagnetic while the Co1 and Co2 interaction is antiferromagnetic. The exchange interactions in the compound are slightly different from that found in the silicon-containing analogues $[\{\text{SiM}_2\text{W}_9\text{O}_{34}(\text{H}_2\text{O})\}_2]^{12}$ ($\text{M} = \text{Mn}^{2+}, \text{Cu}^{2+}$) [1c], in which the central Mn_4 unit exhibits antiferromagnetic ($J = -1.77(5) \text{ cm}^{-1}$) as well as weak ferromagnetic ($J' = 0.08(2) \text{ cm}^{-1}$) Mn–Mn exchange interactions and the Cu–Cu exchange interactions are antiferromagnetic ($J = -0.10(2) \text{ cm}^{-1}$, $J' = -0.29(2) \text{ cm}^{-1}$). It is believed that the major structural factors affecting exchange coupling in these compounds are the polyoxometalate matrixes since the polyoxometalate matrix may be considered a diamagnetic host encapsulating and thereby isolating magnetic clusters of transition metals.

In summary, we have synthesized a sandwich tetracobalt(II) substituted tungstosilicate which displays interesting isomerization ($[\beta\text{-SiW}_9\text{O}_{34}]^{10-} \rightarrow [\text{B-}\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$). The magnetism has been studied based on an isotropic Heisenberg model supplemented by a zero-field splitting term. It must be noted that it is an approximate method and usually insufficient for cobalt(II) exchange system due to the existence of spin anisotropy, and it is still a great challenge to well-understand the cobalt magnetism.

Acknowledgements

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Appendix A. Supplementary material

X-ray crystallographic file in CIF format, complementary drawings, and complementary equations. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.08.025.

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- [7] IR: 987,951,904,876,850,757,723,532,512, and 486 cm^{-1} . Anal. Calcd (Found): K 7.1 (7.2), Co 4.3 (4.4), W 60.2 (59.7), Si 1.0 (1.1).
- [8] *Crystal data for the compound:* $\text{Co}_4\text{H}_{48}\text{K}_{10}\text{O}_{91}\text{Si}_2\text{W}_{18}$, $M_r = 5496.58$, monoclinic, $P2(1)/n$, $a = 12.296(3) \text{ \AA}$, $b = 21.285(6) \text{ \AA}$, $c = 15.792(4) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 92.208(5)^\circ$, $\gamma = 90^\circ$, $V = 4130(2) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 4.420 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 26.39^\circ$ ($-12 \leq h \leq 15$, $-26 \leq k \leq 23$, $-19 \leq l \leq 19$), $T = 294(2) \text{ K}$, $F(000) = 4868$, $\text{GOF} = 0.975$, $R_1 = 0.0576$, $wR_2 = 0.1492$. CSD 416730.
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List of Figures

- Fig. 1. Ball and stick (left) and polyhedral (right) representations of **1**. The color code is as follows: cobalt (purple), tungsten (black), silicon (blue), and oxygen (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
- Fig. 2. ORTEP drawing of the central Co₄O₁₆ fragment of **1**; thermal ellipsoids are drawn at the 30% probability level.
- Fig. 3. χ_M (Δ) vs. T and $\mu_{eff}(\text{O})$ vs. T plots for the compound **1**; the solid lines represent the theoretical values based on the equations.

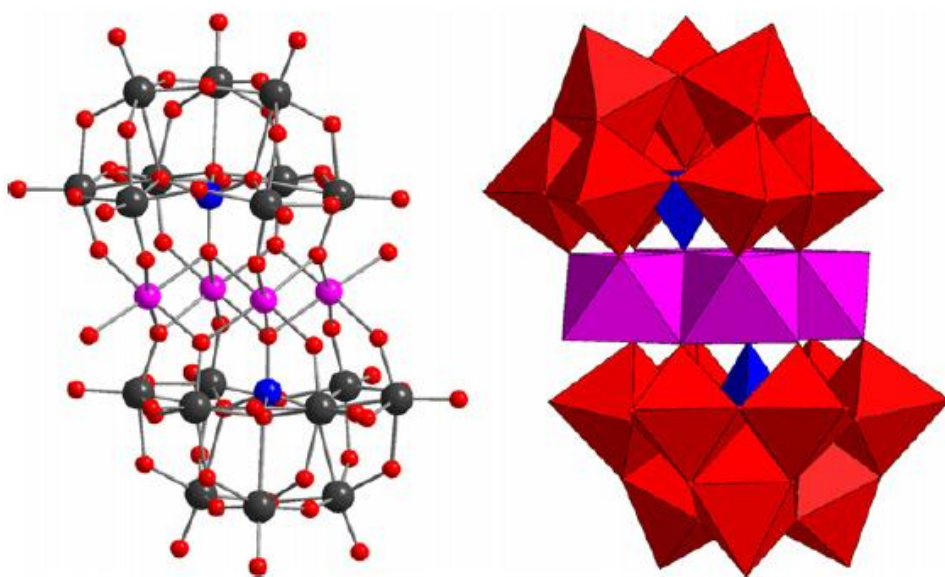


Fig. 1

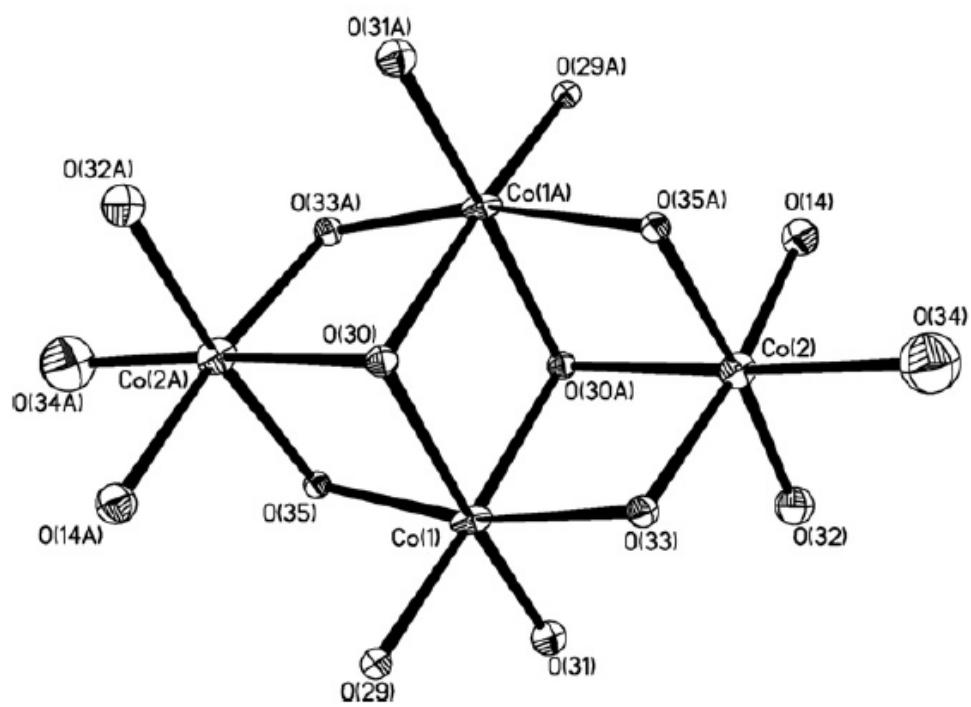


Fig. 2

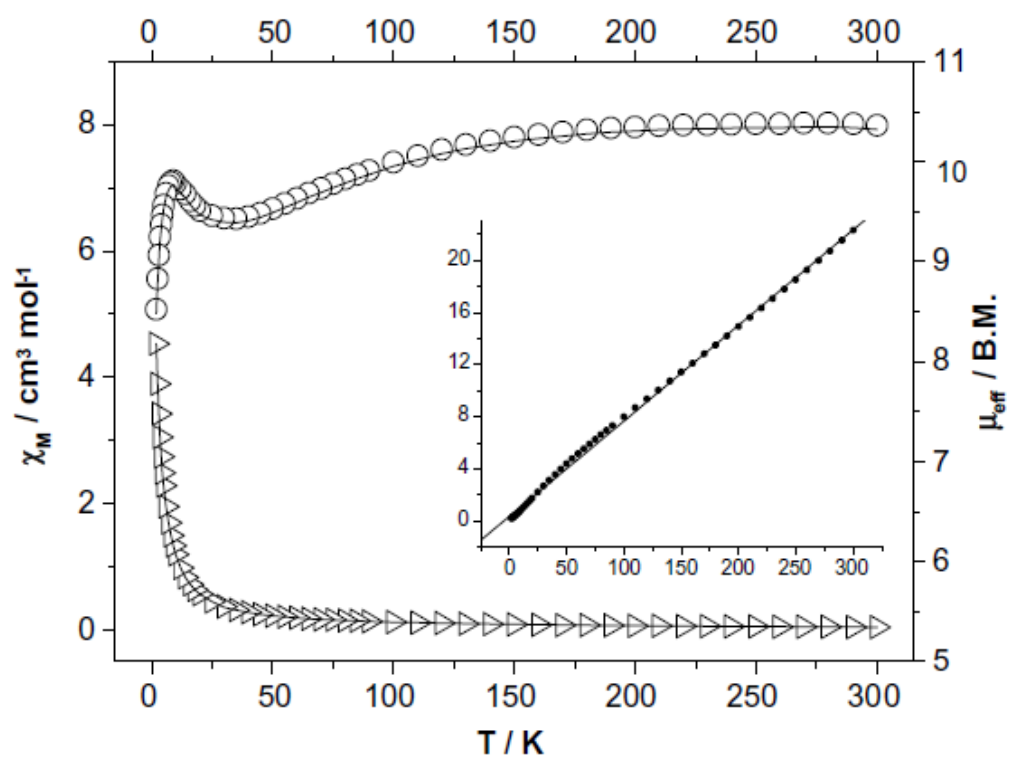


Fig. 3