



Quasi-1D Ni(II) chains based on NiX_2L_2 or NiX_2L_4 ($\text{X} = \text{halide}$; $\text{L} = 3,5\text{-dichloropyridine}$)

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Introduction

We have recently synthesized two new quasi-1D magnetic chains composed of six-coordinate Ni(II) cations combined with Cl^- or Br^- and 3,5-dichloropyridine. In NiCl_2L_2 (**1**), the Ni(II) coordination sphere consists of two axial L s and four Cl 's that affords bi-bridged linear chains (Fig. 1). The second compound, NiBr_2L_4 (**2**), contains molecular entities wherein close contacts of Ni-Br Br-Ni leads to a quasi-1D motif akin to $\text{NiBr}_2(3,5\text{-lutidine})_4$ [1]. According to high-field magnetization data, the resulting architectures leads to strikingly different magnetic behavior, ferromagnetic (FM) coupling in **1** and a Haldane gap in **2** [2].

Experimental

Pulsed-field magnetization measurements of powdered **1** and **2** were performed using the short-pulse 65 T magnet at NHMFL Los Alamos. The samples were cooled and measurements made at a variety of temperatures in the range $0.6 < T < 15$ K using a ^3He cryostat.

Results and Discussion

Fig. 2 shows the $T = 0.6$ K pulsed-field magnetization for **1** and **2** [2]. For **1**, the rapid rise in $M(H)$ and hysteresis are indicative of a FM component. A broad approach to saturation suggests the presence of a large- D . The apparent FM behavior is due to the intrachain Ni- Cl_2 -Ni interaction. In the case of **2**, a nearly flat change in $M(H)$ up to $\mu_0 H_{c1} = 1.8$ T is likely due to a singlet ground-state of the Ni(II) ion. Beyond $\mu_0 H_{c1}$, the magnetization rises in a nearly linear fashion up to a saturation field, $\mu_0 H_{c2}$, of 19.2 T. The overall $M(H)$ curve for **2** is reminiscent to that of a Haldane chain wherein the gap closes at 2.2 T. For an $S = 1$ ion, the energy scale of the intrachain interaction (J) and Haldane gap energy (Δ) can be estimated from the simple relations, $g\mu_B H_{c1} = k_B \Delta$ and $g\mu_B H_{c2} = 4k_B J$, to give $J = 7.1$ K, $\Delta = 2.7$ K and $\Delta/J = 0.38$. The magnetic behavior of **2** strongly contrasts that of $\text{NiBr}_2(3,5\text{-lutidine})_4$ which presents only weak intrachain coupling between molecular units ($J \approx 1$ K) with no evidence of a gap [1].

Conclusions

The Ni(II) compounds **1** and **2** show different crystal structures and magnetic properties owing to the presence of either Cl or Br anions. High-field $M(H)$ data reveal the FM and Haldane ground states observed in **1** and **2**, respectively.

Acknowledgments

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References

- [1] Blackmore, W.J.A., *et al.*, manuscript in preparation (2018).
- [2] Manson, J.L., *et al.* work in progress.

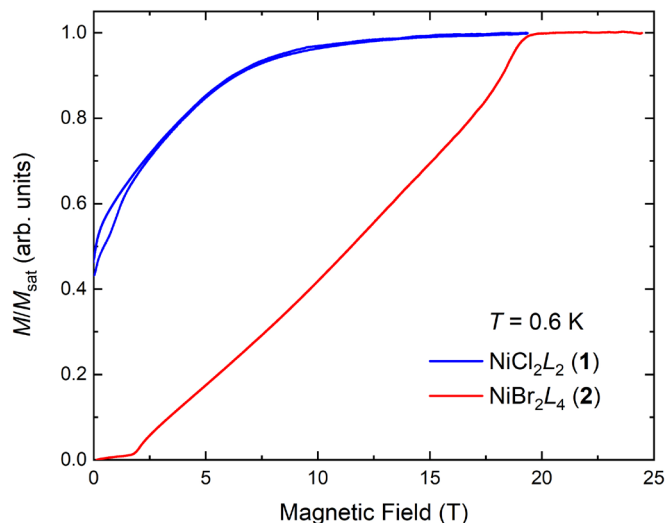
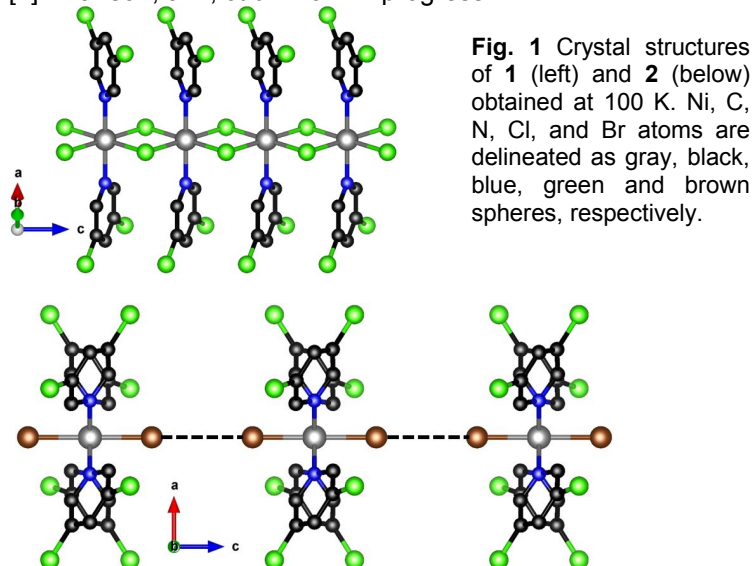


Fig. 2 Pulsed-field $M(H)$ data for **1** and **2** at $T = 0.6$ K.