Development of Molecule-Based 2D Magnets

Natalie Jen, Miguel Gakiya-Teruya, Michael Shatruk

Department of Chemistry & Biochemistry, Florida State University, Tallahassee, Florida 32306

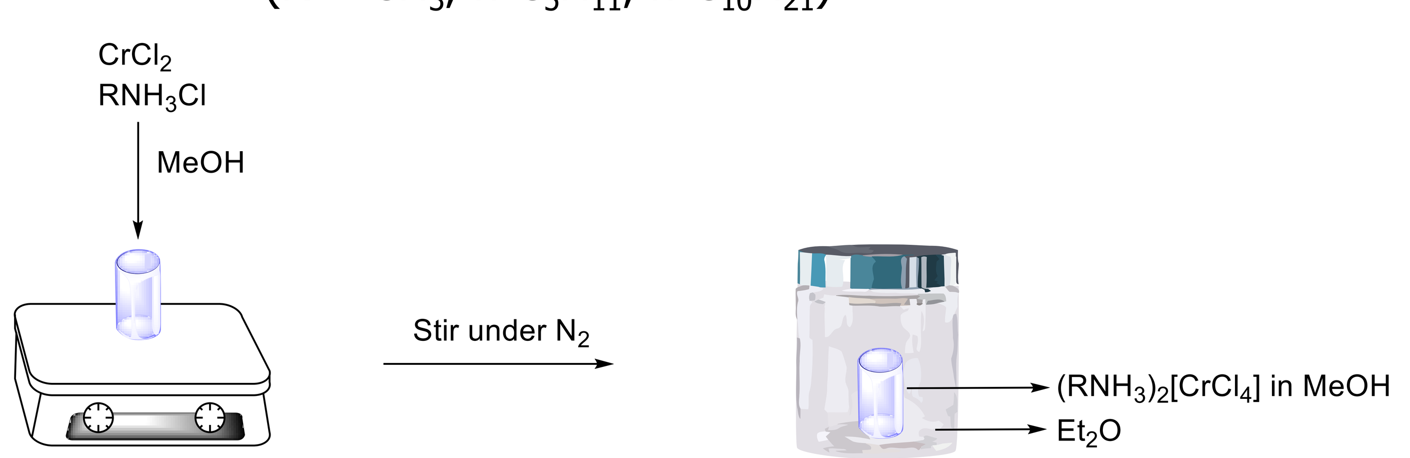
Background

Two-dimensional (2D) molecular materials represent an emerging class of ultrathin structures that can offer novel properties in comparison to parent bulk materials. 2D materials are intrinsically compatible with the architecture of modern electronic devices, which makes them suitable for future practical implementations. The majority of 2D materials reported to date have been derived from extended inorganic solids. Nevertheless, several recent reports have demonstrated the viability of creating 2D materials from molecule-based solids. In this contribution, we report the synthesis and magnetic properties of layered transition metal halides that serve as precursors to such 2D materials. Complexes $(RNH_3)_2[CrCl_4]$ (R = 1-aminodecane, amylamine, or methylamine) exhibit magnetic ordering at low temperatures, due to exchange interactions between the Cr^{2+} ions mediated by chloride bridges. We discuss possible pathways to creating 2D heterostructures with such magnetic layers and increasing the magnetic ordering temperature.

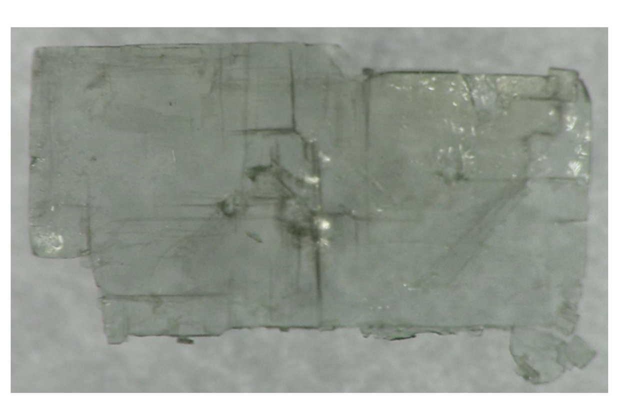
Synthesis

$$2RNH_3Cl + CrCl_2 \longrightarrow \mathbf{(RNH_3)_2[CrCl_4]}$$

(R = CH_3, *n*-C_5H_{11}, *n*-$C_{10}H_{21}$)



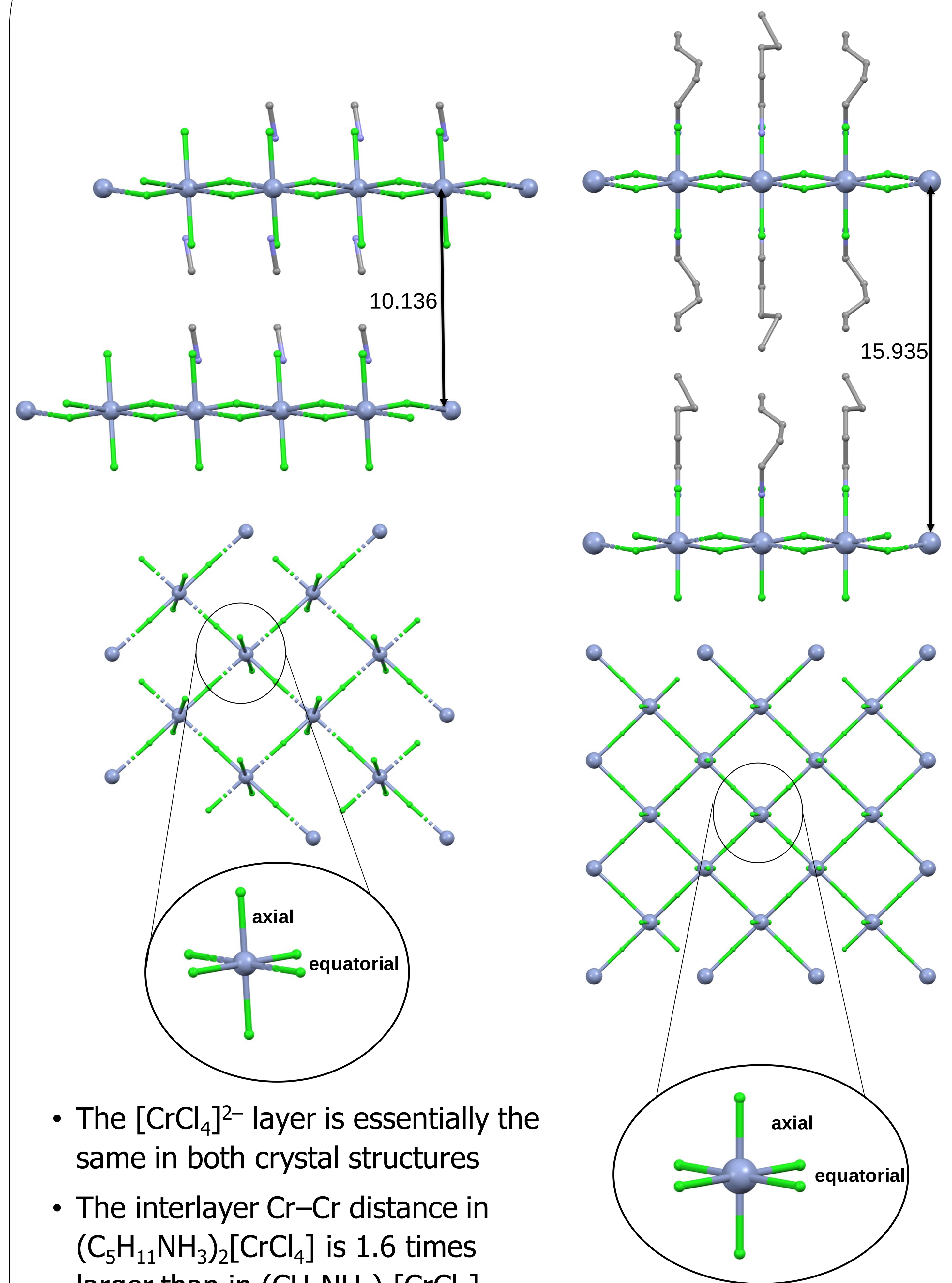
- Air-free synthesis followed by crystallization via vapor diffusion
- Air-sensitive and hydroscopic crystalline product obtained



$(CH_3NH_3)_2[CrCl_4]$

Crystal Structures

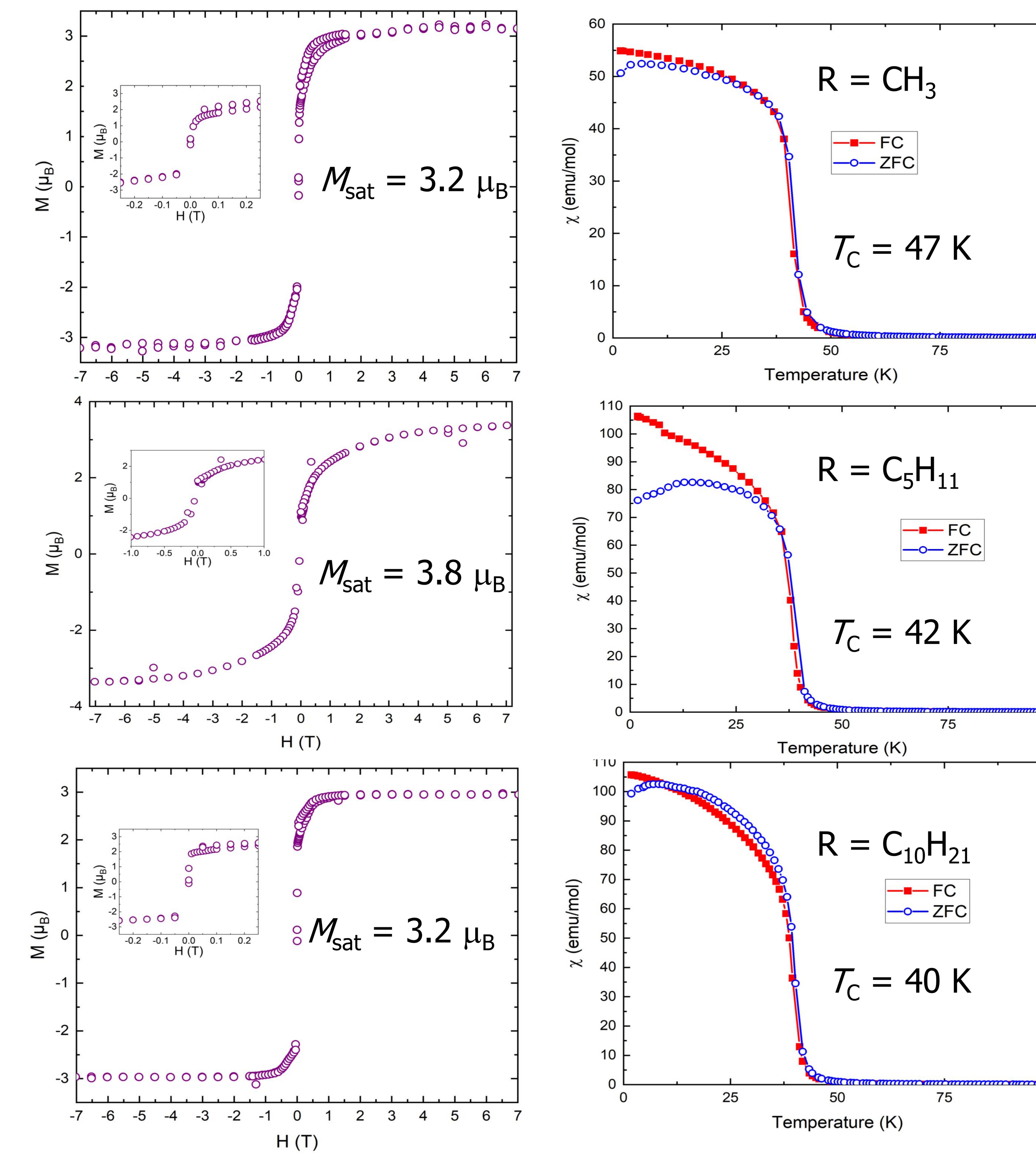
$(CH_3NH_3)_2[CrCl_4]$ **$(C_5H_{11}NH_3)_2[CrCl_4]$**



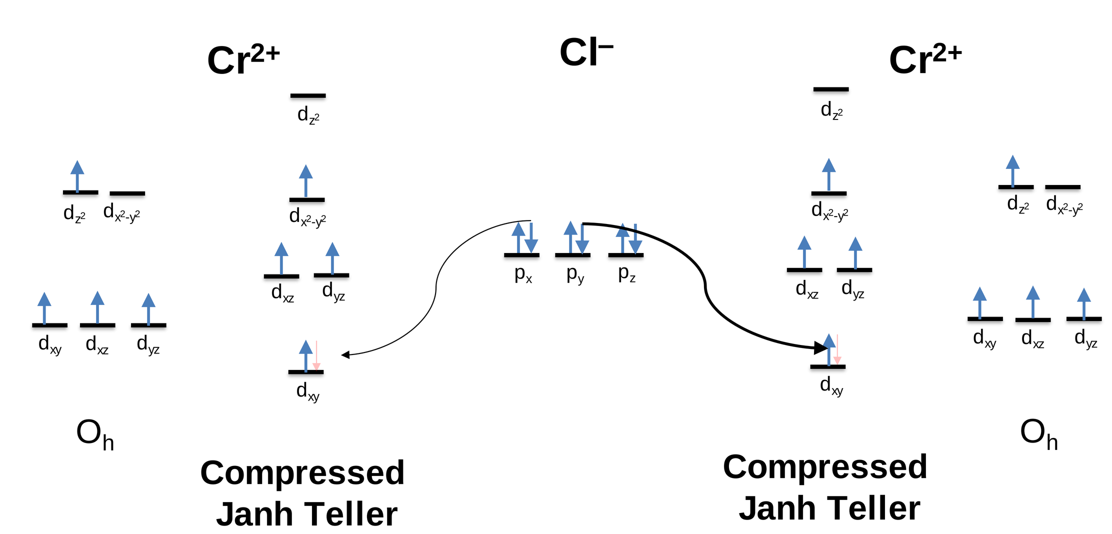
- The $[CrCl_4]^{2-}$ layer is essentially the same in both crystal structures
- The interlayer Cr–Cr distance in $(C_5H_{11}NH_3)_2[CrCl_4]$ is 1.6 times larger than in $(CH_3NH_3)_2[CrCl_4]$
- The structure of $(C_{10}H_{21}NH_3)_2[CrCl_4]$ is yet to be determined

Complex	d(Cr-Cl), Å axial	d(Cr-Cl), Å equatorial	Ref
$(CH_3NH_3)_2[CrCl_4]$	2.414	2.807	This Work
$(C_5H_{11}NH_3)_2[CrCl_4]$	2.411	2.666	This work
$CrCl_2$	2.488	2.713	4
$CrCl_3$	2.347	2.341	5

Magnetic Properties



- All materials behave as a soft ferromagnets with the ordering temperature around 40 K



References

1. Zhong, W. W.; Di, Y. Y.; Kony, Y. X.; Lu, D. F.; Dou, J. M. *J. Chem. Thermodynamics* **2014**, *72*, 100-107.
2. Polyakov, A. O.; Arkenbout, A. H.; Baas, J.; Palstra, T. T. M.; et al. *Chem. Mater.* **2012**, *24*, 133-139.
3. Gakiya-Teruya, M.; Jiang, X.; Le, D.; Rahman, T. S.; Hebard, A.; Shatruk, M.; et al. *J. Am. Chem. Soc.* **2021**, *143*, 14563-14572.
4. Morosin, B.; Narath, A. *J. Chem. Phys.* **1964**, *40*, 1958-1967,
5. Hagiwara, M.; Katsumata, K. *J. Magn. Magn. Mater.* **1995**, *140*, 1665-1666.

Conclusions & Future Work

- The SCXRD show that this complex present a layer structure making it likely that this material could be exfoliable to prepare thin films.
- These Cr complex show a ferromagnetic ordering around 41K
- In the future I will work with other transition metals such as Cu, Mn or Fe.
- Prepare thin films by mechanical exfoliation technique and study their magnetic properties in comparison to their bulk material