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Using pressure to enhance the magnetic exchange interactions within Cr(III) dimers

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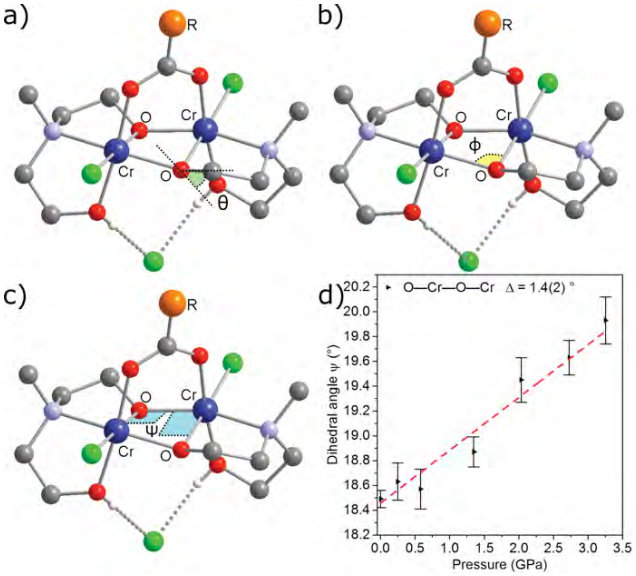
We have investigated a large series of Cr(III) dimer complexes with general formula $[Cr_2(Me\text{-}deaH)_2(O_2CR)Cl_2]_2$. In these materials, magnetic properties are determined by highly deformable intermolecular interactions. The carboxylate above the Cr2 moiety distorts the planarity of the $[Cr_2O_2]$ unit, promoting a net ferromagnetic exchange between the metals.

Through substitution of R with eight organic groups, and DFT calculations the key structural contributions to the net exchange, which has both anti- and ferromagnetic contributions, have been identified. The key contributions are the out of plane angle, θ, the Cr—O—Cr angle, φ, and the distortion of the planarity of the $[Cr_2O_2]$ unit, ψ (Figure 1a, b, c respectively). [1]

We now use pressure to drive these structural transformations in three dimers where R = Me (acetate), tBu (pivalate) and Ph (benzoate); a method which has previously successfully been used to enhance the magnetic exchange in Re(IV) molecular magnets. [2] Through applications of pressures up to 4.6 GPa, we have increased θ by up to 5.1(6) ° and ψ by up to 1.4(2) °, (Figure 1d) which was predicted to increase the ferromagnetic contribution and decreased φ by up to 2.0(4) ° which was predicted to increase the *antiferromagnetic* contribution.

Considering both the pressure-induced structural deformations, and the ambient pressure DFT we have predicted the optimum pressures to enhance the ferromagnetic exchange in these dimers, and compared the predictions against high-pressure magnetic susceptibility measurements.



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[1] Fraser, H. W. L. et al. (2018). In preparation
[2] Woodall, C. H. et al. (2016). Nat. Commun, 7, doi:10.1038/ncomms13870

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