

ENDOR study of the heterometallic wheel [(CH₃)₂NH₂][Cr₇NiF₈(O₂CCCH₃)₁₆]

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The crystallographically characterised family of heterometallic wheels¹ [Cr₇MF₈(O₂CCCH₃)₁₆]⁻, where M = Ni(II), Co(II), Mn(II) or Fe(II), prepared directly from the homometallic [Cr₈F₈(O₂CCCH₃)₁₆], shows adjacent antiferromagnetically coupled metal ions bridged by one μ₂-F and two μ-1,3-pivalates (Fig. 1). A dialkylammonium cation in the centre of the metallocycle forms three N-H-F bonds. Paramagnetic ground spin states can be tuned by the choice of M(II). For example, Q-band EPR of {Cr₇Ni}, the title compound (1), at 5 K shows an axial *S* = 1 spectrum with *g*_z = 1.740 and *g*_{xy} = 1.781. An ENDOR investigation (Fig. 2) of {Cr₇Ni} at both X- and Q-band frequencies shows coupling to ¹H and ¹⁴N nuclei of the bridging ammonium cations in the cavity of the wheel. Most surprisingly no hyperfine coupling to ¹⁹F has been detected, despite extensive variation of experimental parameters. The electronic structure of 1, as revealed by ENDOR data, will be described.

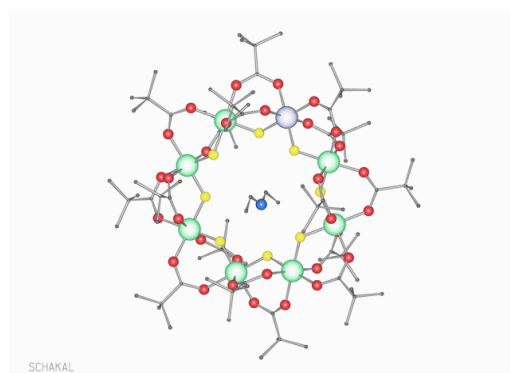


Fig. 1.

Molecular Structure of
[(CH₃)₂NH₂][Cr₇NiF₈(O₂CCCH₃)₁₆] (1)

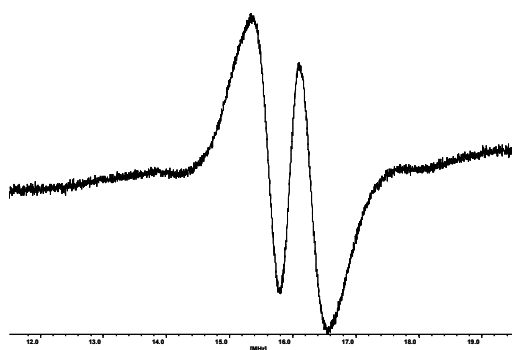


Fig. 2. X-band ¹H ENDOR spectrum at 3672.9 G of [(CH₃)₂NH₂][Cr₇NiF₈(O₂CCCH₃)₁₆] (1) in *d*₈-toluene at 4K

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