Direct Synthesis, Crystal Structures, High-Field EPR and Magnetic Studies of Heterometallic Polymers Containing Mn(II) Carboxylates Interconnected by [Cu(en)]$_2$$^{2+}$

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Introduction

A novel synthetic strategy has been developed to directly obtain heterometallic polymeric coordination complexes in a ‘one-pot’ reaction. In this work the magnetic properties and High-Field EPR spectra of the compound [Cu(en)$_2$][Mn$_2$(succ)$_2$Cl$_2$] containing chains of dimeric [Mn$_2$(succ)$_2$Cl$_2$]$_2$-anions linked by [Cu(en)$_2$]$^{2+}$ cations, (en = ethylene diamine), were studied.

Experimental

High-frequency EPR spectra up to 413 GHz were recorded on the transmission spectrometer at the EMR facility of the NHMFL. Magnetic susceptibility data of a powdered sample were measured with a SQUID magnetometer (Quantum Design MPMSXL-5) over the temperature range 1.8–300 K at the magnetic induction of 0.5 T.

Results and Discussion

The dominant feature of the low-temperature high-field EPR spectra was an axially-symmetric spin-triplet (S=1) signal characterized by isotropic g factor equal to 2 and the zero-field splitting parameter D of -3.046 cm$^{-1}$. A $D_{Mn}$ value for separate Mn(II) ions (S=5/2) of +0.38 cm$^{-1}$ was deducted from these data and satisfactorily reproduced by using a Density Functional Theory calculation that resulted in $D_{Mn}$ = +0.32 cm$^{-1}$. Additional signals seen in EPR spectra as well as magnetic susceptibility data allowed to conclude that the ‘one-pot’ synthetic method produced 92% of the intended complex [Cu(en)$_2$][Mn$_2$(succ)$_2$Cl$_2$], while in the remaining 8% the Mn(II) and Cu(II) ions were ‘swapped’ to form a [Mn(en)$_2$][MnCu(succ)$_2$Cl$_2$] system. The magnetic susceptibilities of the main complex ($\chi$) and that of the ‘swapped’ system ($\chi^{sw}$) were expressed as

$$\chi = \frac{N g_{Cu}^2 \beta^2}{3kT} \sum_{S=1}^{S=1} (2S+1)(S+1)S \exp(-J_{Cu-Mn}(S+1)/2kT) + \frac{N g_{Mn}^2 \beta^2}{3kT} \sum_{S=0}^{S=2} (2S+1) \exp(-J_{Mn-Mn}(S+1)/2kT)$$

and the exchange integral $J_{Mn-Mn}$ magnitude of 32 cm$^{-1}$ was found from fitting procedures. The DFT calculation (‘broken-symmetry’ approach) resulted in $J_{Mn-Mn}$ = 44 cm$^{-1}$, in a reasonable agreement with experiment.

Conclusions

Magnetic susceptibility measurements and high-frequency EPR studies proved the absence of exchange interactions between [Cu(en)$_2$]$^{2+}$ units and Mn$^{II}$-carboxylate anions, while the manganese ions in the dimeric anion were found to be exchange-coupled. The single-ion $D_{Mn}$ was satisfactorily reproduced by a DFT calculation using the ORCA software package, as was the exchange integral magnitude $J_{Mn-Mn}$. The magnetic and EPR results indicate that the ‘one-pot’ synthesis was highly, but not perfectly efficient in putting manganese and copper ions in desired locations.

Acknowledgements

This work was supported in part by INTAS (project YS 05-109-4488) and by the NHMFL. The NHMFL is funded by the NSF through the Cooperative Agreement No. DMR-0084173 and the State of Florida.

References

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