Poster

Experimental demonstration of a second polymorph of Osmium acetylacetonate(III) by magnetometric technique.

A. Raza,[1] L. Chelazzi,[2] S. Ciattini,[2] L. Sorace[1], M. Perfetti[1]

[1]Department of Chemistry "Ugo Schiff"—DICUS and INSTM Research Unit, University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (Fi), Italy, [2] Centro di Servizi di Cristallografia Strutturale, CRIST, Via della Lastruccia, 13 - 50019 Sesto Fiorentino (FI), Italy

arsen.raza@unifi.it

The magnetic properties of heavy transition metal complexes are poorly explored, even though they possess huge potential for different applications, including quantum information technology. We decided to study a simple but versatile system: Osmium(III) acetylacetonate, ([Os(acac)$_3$]). This complex has been reported in 1955[1] but its structure has only been solved in 1998[2]. We isolated crystals of two different shapes, which turned out to correspond to two polymorphs (Fig. 1**a**). X-ray single crystal diffraction at extremely low temperature (15 K) confirmed that the prisms correspond to the sole [Os(acac)$_3$] reported structure (α polymorph, monoclinic P2$_1$/c), but failed in determining the space group of the rectangular blocks.

A full magnetic and spectroscopic characterization allowed to determine the space group of the second type of crystals (β polymorph, orthorhombic Pbca), overcoming the limits imposed by X-ray characterization. The EPR study (Fig. 1**b**) has allowed to identify hyperfine coupling and g values in a 2% solid solution of [Os(acac)$_3$] in [(Ga(acac)$_3$)] ($g_\perp$=0.915, $g_{//}$=2.271 $A_\perp$= 1150 MHz). This is the first evidence of hyperfine coupling on an Osmium complex. Cantilever Torque Magnetometry reveals an easy axis anisotropy pointing along the pseudo-C$_3$ symmetry axis of the molecule (Fig. 1**c**). Slow relaxation of the magnetization was detected and modelled according to a combination of relaxation pathways (Fig. 1**d**).

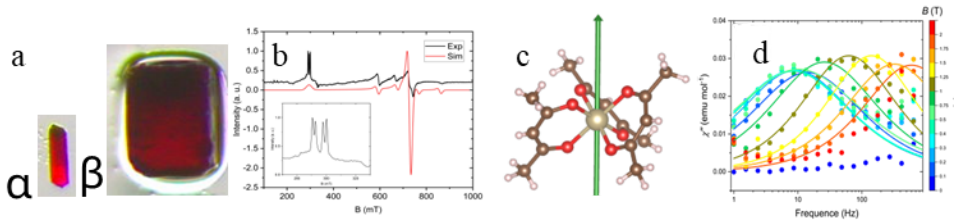

Figure 1. a α and β, **b** EPR of 2% [Os(acac)$_3$], **c** easy axis in [Os(acac)$_3$], **d** ac of 2% [Os(acac)$_3$].

.

[1] Dwyer, F. P., Sargeson, A., *J. Am. Chem. Soc.*, *(*1955), ***77***, 1285.

[2] Dallmann, K., Preetz, W., *Zeit. Naturforsch. B*, (1998), ***53*** (2), 232.

Funded by the European Union (ERC, ELECTRA, 101039890) and by the MUR - Dipartimenti di Eccellenza 2023-2027 (DICUS 2.0) (ref. no. B96C1700020008).