

# Poster Presentations

## [MS37-P02] *In situ* Co(II) oxidation upon coordination to the dithiocarbamate derivative

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Dithiocarbamate derivatives, besides other industrial applications, are used for many years now as powerful fungicides and pesticides.

[1] Complexes of Co(II) and Co(III) with our, previously reported, biologically active ligand, *N,N*-diacetato-*N*-dithiocarbamate (dadtc<sup>3-</sup>) (**1**) [2] were prepared and characterized by classical physico-chemical methods, with the aim of enhancing the already intriguing fungicidal activity of the ligand itself. Anionic Co(II) complex [Co<sub>2</sub>(H<sub>2</sub>dadtc)<sub>5</sub>]<sup>-</sup> (**2**), obtained by a simple addition of the acidic ligand solution to the aqueous solution of [Co(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>2</sub> at RT, undergoes, in presence of air, over several days, spontaneous Co(II) oxidation to the Co(III) state, followed by an overall chemical rearrangement, resulting in the formation of the molecular Co(III) complex **3**. Complex **2** reveals a binuclear structure where two hexacoordinated cobalt(II) centres (CoA and CoB) are presumably double-bridged by two sulfur atoms from two ligand molecules. Remaining two sulfurs of these ligand molecules both coordinate the CoB centre. Its octahedral coordination sphere is completed by two sulfurs from the CSS group of the third ligand molecule. CoA is also bound to four sulfurs from remaining two ligand molecules. Formation of the anionic species (**2**) was undoubtedly proven by MALDITOFF analysis. Magnetic measurements revealed a strong antiferromagnetic coupling of two neighbouring paramagnetic Co(II) centres,

suggesting the double bridged arrangement as described here and by others.[3] The elemental analysis is in a very good agreement with NH<sub>4</sub><sup>+</sup> as a counterion, giving a reliable proof that the cobalt ions are not oxidized to the Co(III) state at this point. The structure of the Co(III) complex (**3**) reveals a neutral mononuclear complex molecule with a hexacoordinated cobalt(III) centre of a molecular formula [Co(dadtc)<sub>3</sub>]. It crystallizes in orthorhombic space group *Pnna*, with four molecules per unit cell, *a* = 10.1024 (3) Å, *b* = 18.9591 (7) Å, *c* = 16.9287 (5) Å. Co(III) lies at the twofold rotation axis, and is in the centre of a significantly distorted octahedron formed by six sulfur atoms from three CSS groups belonging to three ligand molecules.

[1] Hogarth, G. Transition Metal Dithiocarbamates: 1978 – 2003, (2005) *Progress in Inorg. Chem.* **53**, pp. 72-561, and the references therein.

[2] Leka, Z.B., Leovac, V.M., Lukić, S., Sabo, T.J., Trifunović, S.R., Szecsenyi, K.M. (2006) *J. Therm. Anal. Cal.* **83**, 687-691.

[3] Hodgson, M.C., Brothers, P.J., Clark, J.R., Ware, D.C. (2008) *Journal of Inorganic Biochemistry*, **102**, 789-797.

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