

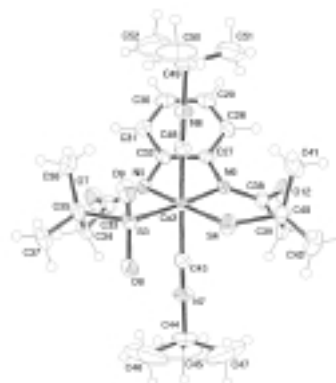
Selective synthesis of disulfinate, disulfonate and mixed thiolate / sulfinate pseudopeptidic species: biological relevance

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Oxidation of diamidato / dithiolato complexes results in the formation of disulfinate or disulfonate species, whether the metal cation is Fe^{III},^[1] Co^{III},^[2] or Zn^{II}.^[3] In this later case the disulfonate formation is associated to disruption of the Zn-S bonds and subsequent zinc release, as observed during the irreversible oxidation of Zinc-finger motifs. Finally, following this two-step reaction (complexation and oxidation) only symmetrically oxygenated thiolates are obtained. A new route is proposed to selectively prepare mixed thiolate / sulfinate derivatives: the one-step metallation of a cyclic pseudopeptidic thiosulfinate after cleavage of the S(O)-S bond under alkaline conditions. Such a reaction might be biologically relevant. Thiosulfonates derived from glutathion have been reported to be generated under oxidative stress conditions and to react with free or zinc-bonded thiolates.^[4] We suggest i) that they might also result from a post-translational oxidation of

cysteines containing proteins and ii) that they could be trapped by metallic cations as shown herein using this chemical approach.



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