Redox-active complexes formed during the interaction between glutathione and mercury and/or copper ions

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Prompted by the recently reported capacity of the physiologically occurring Cu(I)-[glutathione]2 complex (Cu(I)-[GSH]]2) to reduce oxygen, the effect of various GSH-binding metals (Co2+, Cd2+, Zn2+, Pb2+, Al3+, Hg2+ and Ni2+) on the superoxide-generating capacity of such complex was investigated. Amongst all tested metals, only Hg2+ was able to substantially affect the capacity of Cu(I)-[GSH]2 to generate superoxide. When Hg2+ and Cu(I)-[GSH]2 were mixed equimolarly, the superoxide formation, assessed through the cytochrome c reduction and dihydroethidium oxidation, was increased by over 50%. Such effect was totally inhibitable by SOD. Based on the reportedly higher affinity of Hg2+ for GSH and the observed ability of Hg2+ to lower the concentration of Cu(I)-[GSH]2 (spectroscopically assessed), we suggest that Hg2+ displaces Cu(I) from Cu(I)-[GSH]2, to release Cu(I) ions and form a Hg(II)-[GSH]2 complex. The latter species would account for the Hg2+-induced exacerbation of the superoxi