Structure and Properties of Safe and Powerful Noble-Metals Oxidation Reagents

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Molecular CT-complexes obtained by reacting acceptors such as diiodine with S-donor molecules, have been extensively studied mainly due to their intrinsic structural, spectroscopic, chemical and physical properties and, recently, to their applicability as conducting materials or as oxidation reagents towards transition metals. With the view to synthesize complexing-oxidizing agents capable to dissolve noble-metals (NMs) in mild conditions, we have chosen exa- and epta-atomic cyclic dithioxamides as bidentate S,S-donors. By reacting the N,N'-dialkyl-perhydrodiazepine-2,3-dithione (R_2dazdt, R=Me **(a)**, Et **(b)**) class of ligands with I_2 the expected 1:2 CT-complexes, R_2dazdt·$2I_2$ **(1)**, have been obtained as proved by structural and spectroscopic characterization.[1] Instead, by using the N,N'-dialkyl-piperazine-2,3-dithione (R_2pipdt, R=Me, Et, Pr^i **(c)**) class, which shows an exa-atomic ring in spite of the hepta-atomic one in R_2dazdt, the unexpected triiodide salt of the protonated donors, $[R_2\text{pipdtH}]I_3$ **(2)**, have been isolated. The different nature and structure of the two class of reagents is reflected on a different reactivity towards NMs: while class **1** adducts are capable to oxidize Pd and Au metal but are inactive towards Pt, class **2** reagents are capable to dissolve Pt metal too. Further studies are in progress in order to clarify the different behaviour of the two class of ligands and the source of H^+ in the reaction.

[1] Serpe A., et al., *Chem. Commun.*, 2005, 1040, *and refs therein*.

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