

Supporting Information

Oxidant/Complexing Properties of the Methimazole (MeImHS)/Iodine System Towards Palladium and Gold Metals. Crystal structure of the complex cation $[\text{Pd}^{\text{II}}(\text{MeImHS})_4]^{2+}$ balanced by a tetraiodide/iodide mixture.

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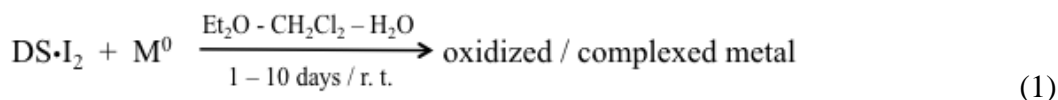
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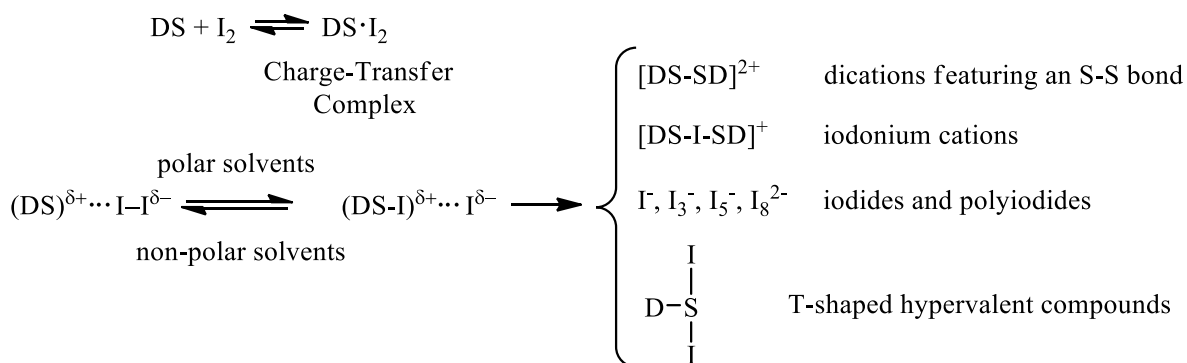
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Factors that influence the course of the reaction (1):



- The thioamido DS unit should be stable enough to prevent its oxidation by iodine with formation of disulphides and (poly)-iodides derivatives (Scheme S1). Under these circumstances, the oxidation/complexation of metals is not observed. If the charge-transfer complex DS-I₂ is in equilibrium with DS and I₂ (Scheme S1), due to a low value of the equilibrium constant, the latter species can react with the oxidized/complexed metal, with the result that the outcome of reaction (1) becomes unpredictable.
- Even if the oxidation of metals often occurs under the experimental conditions outlined in reaction (1), with formation of “hard” ions [R. G. Pearson: *“Hard and Soft Acids and Bases”*. *J. Am. Chem. Soc.*, **1963** *85*(22), 3533–3539], the corresponding complexes with the thioamido DS are difficult to isolate since the “soft” S-donor atom is intrinsically a poor coordinating agent towards these ions, and the formation of dense oils is commonly observed.
- Reaction conditions (solvent, temperature, reaction time, mode of stirring) and the DS/I₂ to M⁰ molar ratio influence the outcome of the reaction and need to be optimised to favour both a high metal oxidation yield, and the formation of purer compounds.



Scheme S1 Top: in non-polar solvents, compounds containing S-donor Lewis base (DS) generally form only 1 : 1 charge-transfer complexes with I₂. The formation constant of the 1 : 1 complex (K_f) depends on the equilibrium molar concentrations according to the equation $K_f = [\text{DS}\cdot\text{I}_2]/[\text{DS}][\text{I}_2]$.¹ Bottom: the interaction between DS and I₂ to give 1 : 1 adducts containing an almost linear S–I–I fragment can be seen as a charge-transfer process $n \rightarrow \sigma^*$ (i.e. MO combination of a lone pair from the donor with the empty σ^* orbital of I₂). Depending on the charge density transferred by the DS donor molecule to I₂ and the nature of the solvent, this can result in lengthening of the I–I bond and finally the breaking of this bond and formation of new species.²

¹ M. C. Aragoni, M. Arca, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis and G. Verani, *Coord. Chem. Rev.*, 1999, 184, 271–290; and references therein. ² W. T. Pennington, T. W. Hanks and H. D. Arman, in *Halogen Bonding with Dihalogens and Interhalogens: Fundamentals and Applications*, ed. P. Metrangolo and G. Resnati, Springer-Verlag, Berlin, 2008, pp. 65–104, and references therein.

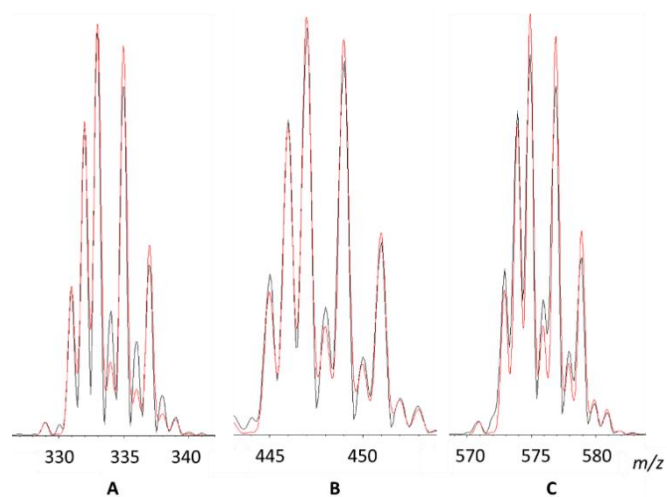


Fig. S1 Fitting of the isotopic pattern for $[\text{Pd}(\text{L-H})\text{L}]^+$ (333 m/z), $[\text{Pd}(\text{L-H})\text{L}_2]^+$ (447 m/z) and $[\text{PdL}_3\text{I}]^+$ (575 m/z), red line calculated pattern, black line experimental pattern. L = MeImHS.

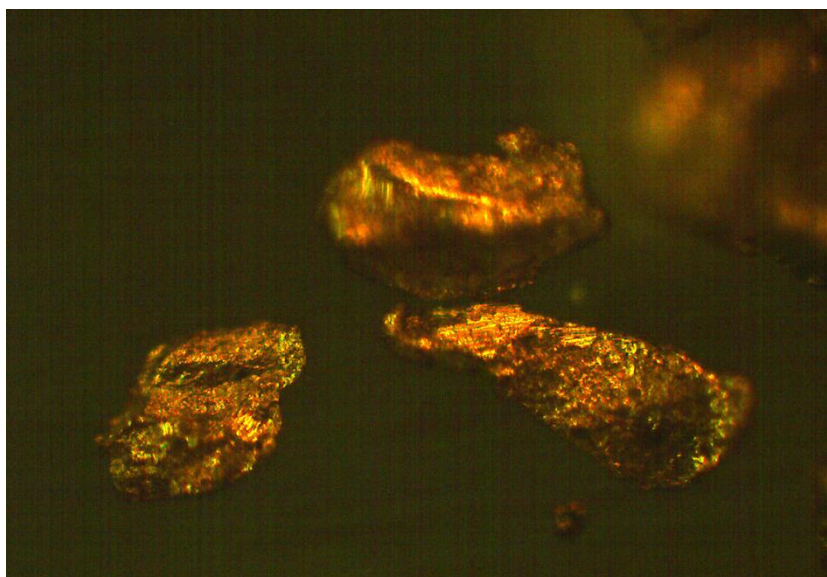


Fig. S2 Palladium deposited on magnesium powder, image captured with a MOTIC BA210E, Epi-LED S Fluorescence attachment – Exciter 480SP Dichroic 505LP Barrier 520LP.

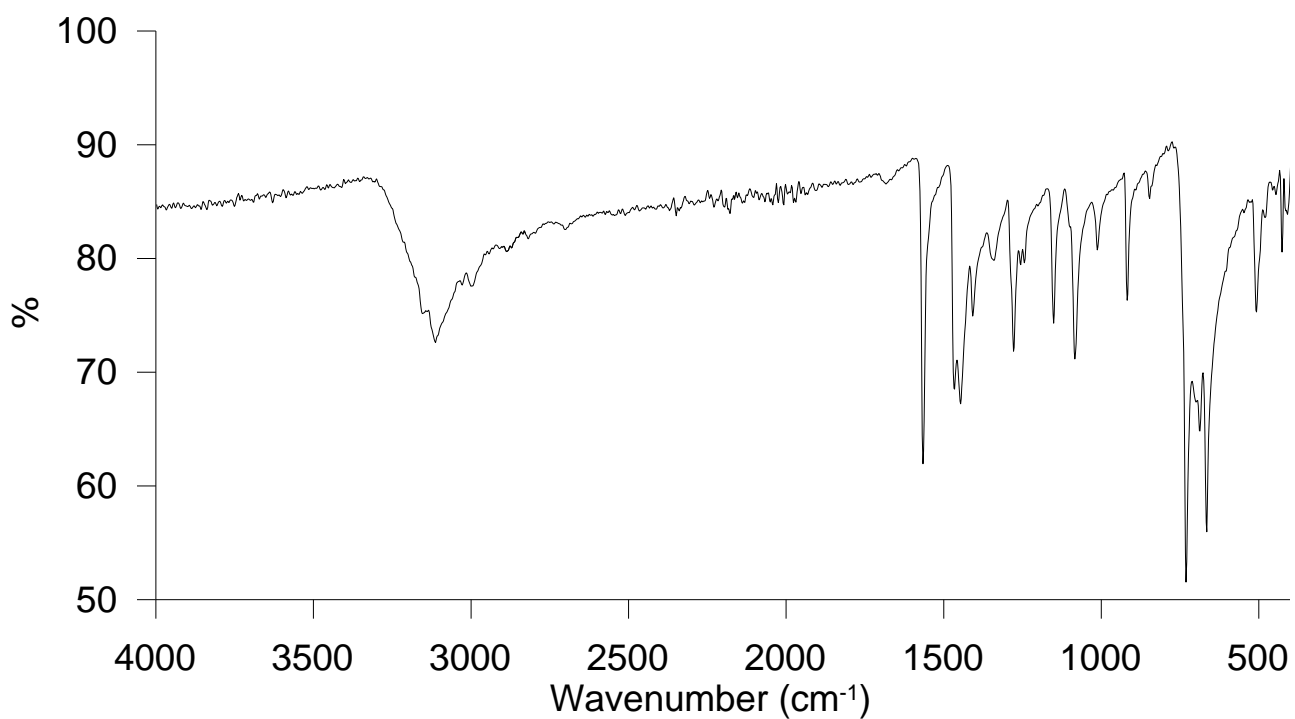


Fig. S3 Infrared spectrum of complex $[\text{Pd}(\text{MeImHS})_4](\text{I}_4)_{0.73}(\text{I})_{0.27}$

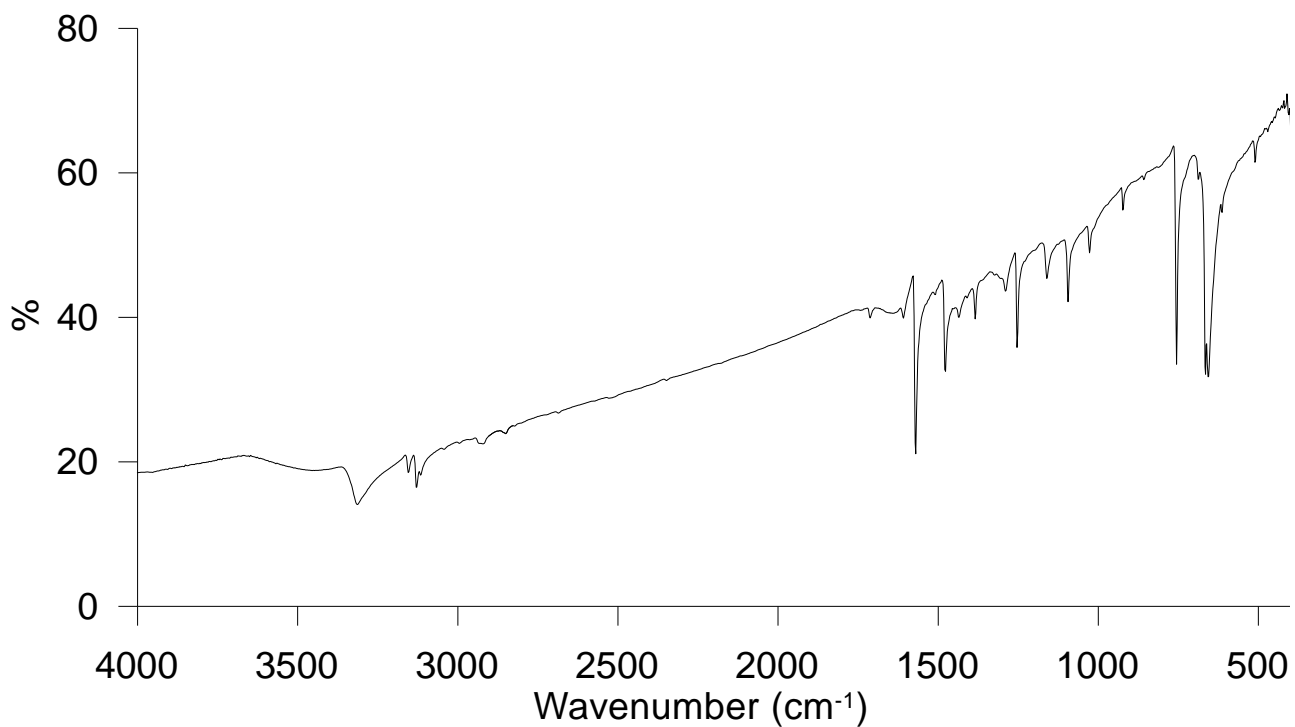


Fig. S4 Infrared spectrum of complex $[\text{Au}(\text{MeImHS})_2]\text{I}_3$.