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Ion pair interactions in noble metal complexes with halogen atoms

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Noble metals (NMs) are usually found in low abundance in only a few places on earth, and they belong to the "critical minerals" class [1]. The increased use of NMs in Hi-Tech goods, typically characterized by short lifetimes, has given rise to a large accumulation of NMs-rich waste, which is currently becoming a potential source of NMs. Recovering methods of NMs are often energy-intensive and/or based on harmful reagents and an intense research effort is dedicated to developing environmentally sustainable methods [2]. In this study, the Au and Pd dissolution capabilities of organic triiodide salts ($OrgI_3$, Org^+= phenylamino-1,2-dithiolylium $(PhHN)_2DTL^+$, morpholino-1,2-dithiolylium Mo_2DTL^+, TBA^+, $Ph4P^+$) were investigated in order to test their applicability in palladium and gold recovery from Hi-Tech wastes. The presence of an organic cation in the triiodide salt dramatically improved its Pd-leaching properties with respect to those of the KI_3 salt [3]. This was ascribed to the ionic-couple-driven production of $Org_2[Pd_2I_6]$ complexes which prevented the formation of the passivating PdI_2. Consistently, the X-ray molecular structures of the $Org_2[Pd_2I_6]$ and $Org[AuI_2]$ systems showed the occurrence of several secondary interactions between the Org^+ cation and the $[Pd_2I_6]^{2-}$ and $[AuI_2]^-$ anions. A given crystal packing usually corresponds to one of the most stable arrangements, hence with the strongest interactions between molecular components, hence the analysis of the ion-pair interactions in the solid state provided useful hints to predict the presence of similar interactions in solution. Among the investigated organic salts, $(PhHN)_2DTLI_3$ was capable of yielding strongly interacting ionic couples sustained by halogen bond formation between the iodine atoms of the complex anions and the $(PhHN)_2DTL^+$ cation. DFT computational studies gave information (electrostatic potential and Fukui functions) with respect to the preferred site of interactions between complementary fragments of the anions and cations. The strongly interacting ionic couple in $[(PhHN)_2DTL]_2[Pd_2I_6]$ was consistent with the highest reactivity of $(PhHN)_2DTLI_3$ towards palladium, making $(PhHN)_2DTLI_3$ a promising reagent for NMs recovery.

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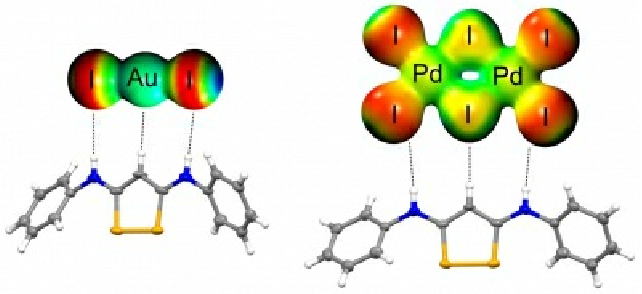

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