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Coordination Chemistry Reviews 252 (2008) 1200–1212
COORDINATION CHEMISTRY REVIEWS
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Review

Charge transfer complexes of dithioxamides with dihalogens as powerful reagents in the dissolution of noble metals

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Received 11 July 2007; received in revised form 23 January 2008; accepted 23 January 2008
Available online 2 February 2008

In memory of Francesco Bigoli

Contents

Abstract

Commonly involved in the recovery/refining processes of noble metals (NMs), coordination chemistry is now required by new legislation to face requirements in the selection of ligands that must combine effectiveness with low environmental impact, in order to balance sustainability with economic development for conventional applications and for the recovery of NMs from secondary sources thus helping to convert *Trash in Resource*. In this paper, we review the properties of dihalogen/cyclic-dithioxamide adducts as a case-study to show how suitable complexes can provide innovation in the recovery processes of NMs from secondary sources and in the gold etching process in improving the reliability of microelectronic devices. These adducts, which do not show cytotoxicity, are capable of dissolving metal palladium and even gold in a one-step reaction and under mild conditions. In particular, $Me_2dazdt\cdot 2I_2$ ($Me_2dazdt = N,N'$-dimethyl-perhydrodiazepine-2,3-dithione) has proved to be the most effective in practical applications. It has been used in the palladium recovery from model spent three way catalysts (TWC). It selectively dissolved palladium, almost quantitatively, under mild conditions, even in a complex system such as an exhaust catalytic converter, a ceramic material that has undergone severe thermal and chemical stresses. Quite satisfactory results have also been obtained in gold recovery from selected WEEE (waste from electrical and electronic equipments) scrap and from deprocessing procedures for the failure analysis of microelectronic devices.

Keywords: Halogens; Adducts; S-donors; Dithioxamides; Noble-metals recovery; Gold; Palladium

1. Background

1.1. Introduction

Coordination chemistry is commonly involved in the recovery/refining processes of noble metals (NMs), providing a wide

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doi:10.1016/j.ccr.2008.01.024

choice of ligands that allow the formation of metal complexes, whose physico-chemical properties and relative stability may be properly tuned with the ligand and/or the metal. Currently, new legislation requires coordination chemistry to combine effectiveness with low environmental impact in its selection of ligands, in order to balance economic development with sustainability. For this reason, research and development has been searching for new safer reagents with the right strength and selectivity: (i) to replace the more aggressive and/or polluting reagents used in conventional NMs dissolution methods; (ii) to respond to the increasing demand of methods of NMs recovery from secondary sources so as to meet health, safety and waste disposal concerns.

The environmental, economic and strategic interest in the recovery of NMs from secondary sources is even more significant because of their extensive use in conventional and novel technologies (electronics, catalysts, including automotive, as well as the emerging area of fuel-cells etc.). In particular gold is recovering its key role as a reserve asset and its demand for jewellery is on the increase in emergent countries (China, India). This leads to the following: (i) higher prices; (ii) unbalanced supply/demand ratio; (iii) depletion of limited natural sources; (iv) economical and political dependence on suppliers [1]. In order to comply with economic and environmental requirements, in recent years most countries have promoted new strategies on waste management. In particular, the European Union's (EU) general strategy on waste management [2] states that member states should take appropriate measures to encourage the prevention of waste production (*precautionary principle*) and the recovery of waste by recycling, reuse or reclamation in the extraction of raw materials. Due to the recent large accumulation of scrap materials, EU Directives on *end-of-life* vehicles [3] and waste from electrical and electronic equipments (WEEE) [4] have established the producer's responsibility (*responsibility principle*) in the disposal of the scrap materials from their production, meeting targets for recycling, reuse and recovery without endangering human health and without using processes or methods that could harm the environment, aimed at preventing rather than treating pollution. NMs are traditionally dissolved through oxidation processes that often involve energy intensive and/or unattractive agents both for the environment and for operators as in the case of the pyrometallurgical chlorination that requires energy intensive and toxic reagents (Cl_2, $COCl_2$, etc.) [5], while methods based on the use of selective complexing reagents require pre-treatment with strong oxidizing acids [6]. Aqua-regia dissolves gold via the formation of the chloraurate ion, and cyanides in air or pure oxygen gas are capable of converting gold into water-soluble aurocyanide ions [7–9]. The cyanide process is very simple to apply and is commonly used in gold extraction, but presents environmental hazards due to the fact that cyanides are highly toxic, as experienced in the year 2000 when a dam at a goldmine reprocessing facility in Romania released wastewater contaminated with cyanide into the river Danube causing a major environmental disaster.

The search for environmentally friendly processes, the development of take-back legislation, the accumulation of WEEE due to increased production together with a reduced lifetime of goods, the search for NMs recovery from secondary sources, pose challenging targets to coordination chemistry to provide reagents for NMs dissolution that should meet the requirements of both economic development and environment safeguard.

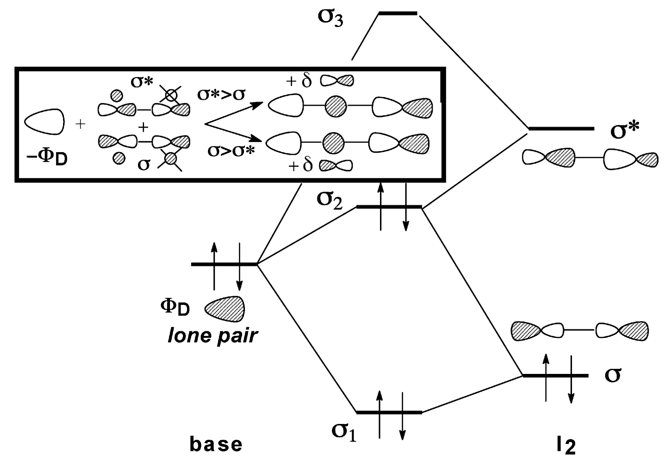
In this paper, we review the properties and applications of a unique class of non-cytotoxic reagents, dihalogen/cyclic-dithioxamide adducts: (i) for palladium recovery from model spent three way catalysts (TWC); (ii) for gold recovery from WEEE; and (iii) for gold removal from electronic devices in the failure analysis.

1.2. σ-Donor/dihalogen adducts

σ-Donor/dihalogen adducts belong to the well-known class of complexes formed by the interaction between a σ-donor with a relatively high-lying HOMO and a dihalogen that works as an acceptor through the relatively low-energy LUMO (σ*). Among the dihalogens, diiodine adducts are the most widely investigated [10] giving rise to a large number of structurally and spectroscopically characterized $D{\cdot}I_2$ adducts that has led to a systematic study of their nature and properties and their classification into three main types of complexes: $D\cdots I–I$ (1); D–I–I (2); $D–I^+\cdots I^-$ (3), (the notations $\cdots$ and – refer, respectively, to intermolecular and intramolecular distances), based on the type of the interaction contained in these systems [11].

In particular, Raman spectroscopy has a highly diagnostic value in distinguishing the different types of adducts. We can summarize the spectral expectations for these compounds as follows: the $\nu_{I–I}$ vibration for type 1 adducts is observed in the region 140–180 cm^{-1} of the Raman spectrum. The frequency is lower than that of I_2 itself (180 cm^{-1} in the solid) due to the I–I elongation caused by the weak $D\cdots I_2$ interaction. In types 2 adducts of, the D–I and I–I distances are comparable and Raman spectra show two peaks ascribable to the antisymmetrical and symmetrical stretching of the extended D–I–I system. In type 3 adducts, where short D–I intra- and long $I\cdots I$ distances are found, only one peak ascribable to the D–I vibration is observed in the Raman [11].

These spectral differences indicate that the simplest MO model where the σ lone pair of the donor (often the HOMO) donates part of its electron density to the relatively low lying σ* level, fits well the type 1 adducts (weaker donors), and explains the interiodine elongation proportional to the donor–acceptor interaction as a consequence of the population of the I_2 σ* orbital. Also, the electronic transition from the adduct-bonding orbital (still primarily associated with the donor) to the adduct-antibonding orbital (primarily associated with I_2 σ*) gives rise to a new band in the near ultraviolet region. The widely used expression charge transfer (CT) complexes for these adducts reflects the CT character (from the donor to the acceptor) of this band. Moreover, the destabilization of the I_2 σ* orbital shifts the typical visible absorption of diiodine to a higher frequency ($\pi^* \rightarrow \sigma^*$ transition). The study of spectrophotometric data of these systems is useful to calculate the equilibrium constants by computer analysis [12].

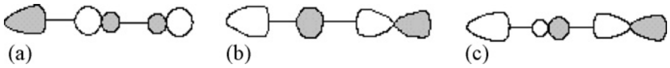


Scheme 1. Frontier MOs diagram of a $D\cdot I_2$ CT-complex. Reprinted with permission from [15] Copyright 1999 American Chemical Society.

As the interatomic D–I and I–I distances vary in type 2 and 3 adducts, so does the overall MO picture. Accordingly, the system must be described by a model that changes dynamically with limiting forms. Recently, Hoffman et al. [13] have illustrated the electronic effects for I_3^- and for the anions of the type X–I–I$^-$ (X = halogen) by applying the concepts of perturbation theory to three-centre systems. Essentially the original three-centre/four-electron model for the bonding proposed by Pimentel and Rundle is confirmed [14]. Thus one overall σ-bonding and one non-bonding MO (mostly centred at the terminal positions) are populated, while only the extended antibonding MO is empty. The perturbative effects of the heteroatoms on central or terminal positions have been highlighted in Refs. [13,15]. A similar approach has been applied to thione-diiodine systems, in particular to $ptc\cdot I_2$ and $ttb\cdot I_2$ (the diiodine adducts of 1,3-dithiacyclohexane-2-thione and 4,5-ethylenedithio-1,3-dithiole-2-thione, respectively), which are examples of type 1 CT-complexes compared to $R_3P\cdot I_2$ and $R_3N\cdot I_2$, examples of type 2 and type 3 respectively, in order to describe appropriately by a MO diagram the different nature of the bonding when varying the donor atom.

Scheme 1 reproduces the interaction among three FMOs (fragment molecular orbitals), which involves mainly the lone pair of the donor (left side) Φ_D and both the filled and empty σ and σ* combinations of I_2. The latter are made prevalently of the iodine *p* axial orbitals with some s orbital contribution. The perturbation of the donor (left side) induces substantial mixing between σ and σ* with major consequences to the nature of the central MO σ_2 in the adduct.

As shown in the box for σ_2, the central s orbital sums up from both I_2 components, while the p orbital contribution is cut off though it disappears only in the case of I_3^- (as imposed by symmetry) or when Φ_D is at an intermediate energy with respect to the σ and σ* FMOs of the acceptor, as in the case of type 2 adducts (see Scheme 2b). In type 1 adducts, where a low-lying σ-donor orbital occurs, a σ_2-MO of type a (Scheme 2) can be found. Due to their simplicity as models and thanks to the amount of available structural data, the adducts $R_3N\cdot I_2$ and $R_3P\cdot I_2$ define the two limiting situations a and c represented in Scheme 2. The strength of thionic sulfur donors, which may be affected by the vicinal groups, has been evaluated to be more comparable to the amine than to the phosphine ligands in the cases of ptc and ttb donors.

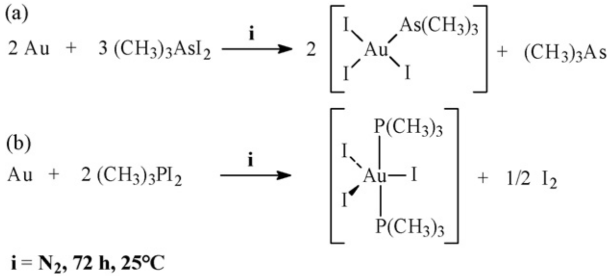


Scheme 2. σ_2-MO for: (a) $R_3N\cdot I_2$ or very weak type 1 adducts; (b) I_3^- or medium strength type 2 adducts; (c) $R_3P\cdot I_2$ or type 3 adducts.

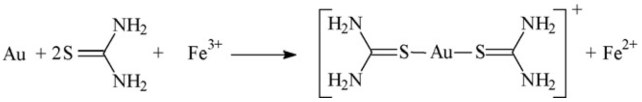
Structural data on a large number of triaryl, mixed arylalkyl or trialkyl phosphine diiodine adducts have shown that a four-coordinated tetrahedral structure $R_3P–I\cdots I$ with a high interiodine separation predominates [D(I–I) > 3.0 Å] [16], in agreement with the limiting situation c shown in Scheme 2. An extensive investigation on tertiary phosphines (and arsines)-dihalogen adducts has been performed by the McAuliffe group, who has disclosed their peculiar reactivity towards crude inactivated metal powders to form metal complexes of metals in high oxidation states [17]. CT complexes, which play an important role in many red–ox reactions [18], may be described as “intermediates” sufficiently stable to be isolated, and attempts to correlate structural changes with the dynamic of reacting chemical species have been performed for a long time [19], but no systematic kinetic study addressed to find a general reaction mechanism for these reactions is available. It has been found remarkably that $R_3D\cdot I_2$ (R = Alkyl; D = As, P) are capable of oxidizing even a noble metal such as gold in a one-step reaction, as summarized in Scheme 3 [20].

The innovative aspect of this reaction is related to the possibility of dissolving elemental metals through a one-step reaction in relatively mild conditions by using reagents that combine complexing and oxidizing properties in the same molecule. Moreover the system seems easily tunable potentially, because by changing the donor and/or the halogen, metals can be discriminated and thus separated. However, these reactions seem unsuitable for practical applications, since they require strictly anaerobic and anhydrous conditions [21], and also because these reagents are toxic [22,25].

Sulfur-donor/dihalogen adducts seem particularly suitable to provide the proper soft-donor capable of coordinating noble soft-metals, as shown by the numerous examples of soft-metal complexes with this kind of ligands, also applied to NMs leaching [9,23,24]. In particular thiourea leaching in the presence of



Scheme 3. Oxidation reactions of Au-metal by $R_3D\cdot I_2$ (R = Alkyl; D = As, P) CT-complexes.



Scheme 4. Oxidation reactions of Au-metal by thiourea leaching.

H_2O_2 or O_3 or Fe^{3+} (Scheme 4) [9,25,26] in the gold dissolution process has been widely investigated.

In addition since donors that bear two thionic donors in vicinal position are suitable to work as chelating ligands, they may favour further the dissolution of soft NMs stabilizing d^8 metal ions such as Au(III), Pd(II) and Pt(II) in their preferred square–planar geometry thanks to the compatible softness of the donor atoms and the metal centre, and the chelation properties of the ligands.

Based on the above, since dithioxamides bear two vicinal thioamide groups, they have been selected as suitable bidentate S,S-donors to prepare CT-adducts with dihalogens/interhalogens to be checked as dissolution reagents towards NMs.

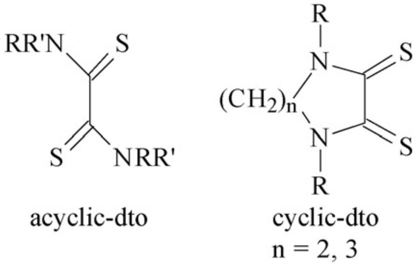
2. Oxidation reagents based on dithioxamide/dihalogen complexes

Scheme 5 shows the different classes of dithioxamide ligands that have been selected to use as donors to react with dihalogens in preparing the donor–acceptor adducts.

The reaction of these ligands with halogen/interhalogen gives the products listed in Scheme 6.

In Table 1 the reagents based on the dto/dihalogen precursors that have proved to be effective in NMs dissolution, are reported.

Among these reagents, R_2dto and R_2dazdt ligands with I_2 and/or IBr produce the expected 1:2 CT-complexes [27,12c,28], while in the cases of R_2pipdt ligands, hexa-atomic cyclic-dithioxamides, unexpected results show: (i) that the addition of the IBr solution produces unidentified decomposition products; and (ii) that the reactions with I_2 did not produce the 1:2 adduct but a triiodide salt of the protonated form of the donor [29,30]. Further experimental and theoretical studies are required to elucidate these aspects. In any case also this reagent possesses useful coordinating-oxidation properties in dissolving NMs. The proton source as well as the different reactivity of R_2pipdt have not been investigated yet.



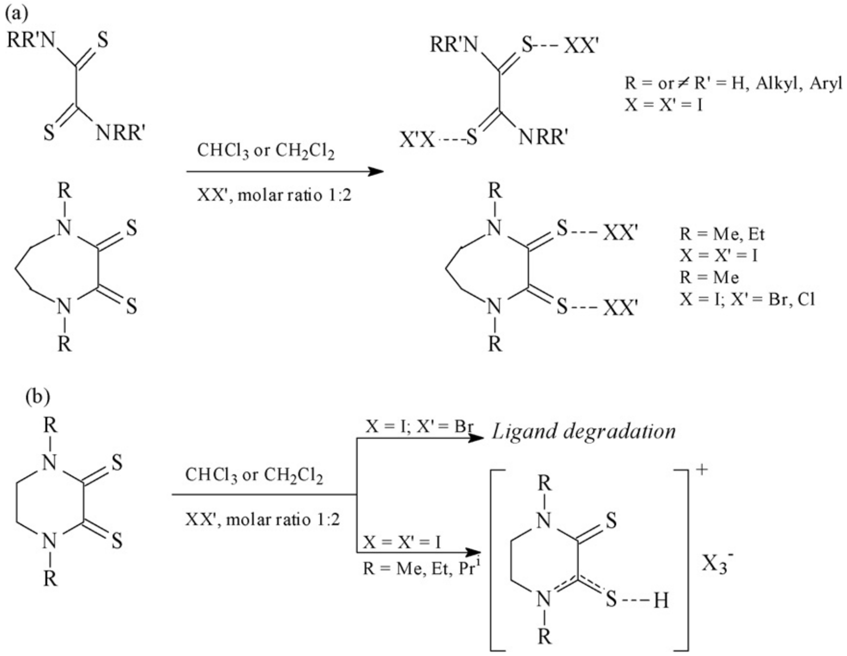
Scheme 5. Dithioxamide ligands.

The main features of the reagents are summarized in Table 2.

The UV–vis as well as Raman spectra of $[R_2pipdtH]I_3$ are dominated by the typical features of the triiodide anion.

Thanks to the evaluation of cytotoxic activity at the MNTD50 (maximal non-toxic dose that reduced cell multiplication less than 50% in DMSO) of these reagents and of their precursors, it was possible to determine that these compounds do not show cytotoxicity [30]. This feature adds value to these reagents as regards practical applications.

Based on the above described features, the ability of these compounds to dissolve NMs has been tested as described in Section 3.



Scheme 6. Synthesis of oxidation reagents based on dto/dihalogen precursors.

Table 1
dto/dihalogen complexes tested as NMs dissolution reagents

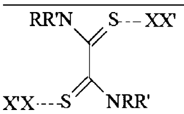
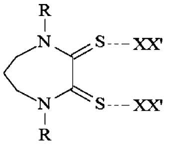
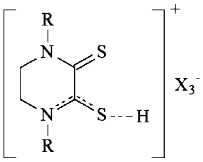
Compound	Halogen	Substituents	Acronym
	I_2	R = R' = Me; [bis(*N*, *N*-dimethyl)-dithioxamide]-bis(diiodine)] R = R' = Et; [bis(*N*,*N*-diethyl)-dithioxamide]-bis(diiodine)] NRR' = Mo; bis(morpholinothicarbonyl)-bis(diiodine)]	$Me_4dto \cdot 2I_2$ $Et_4dto \cdot 2I_2$ $Mo_2dto \cdot 2I_2$
	I_2	R = Me, *N*,*N*'-dimethyl-perhydrodiazepine-2-3-dithione-bis(diiodine)	$Me_2dazdt \cdot 2I_2$
	IBr I_2	R = Me, *N*,*N*'-dimethyl-perhydrodiazepine-2-3-dithione-bis(bromideiodine) R = Me; triiodide salt of the protonated *N*,*N*'-dimethyl-piperazine-2,3-dithione	$Me_2dazdt \cdot 2IBr$ $[Me_2pipdtH]I_3$

Table 2
Summary of selected structural and spectroscopic data of the adducts

Compound	X-ray data		Electronic spectroscopy			Raman spectroscopy	Ref.
	$d(S \cdots I_1)$ (Å)	$d(I_1 \cdots X_2)$ (Å)	CT-band (nm)	$\pi^* \to \sigma^*$ dihalogen band (nm)	Log K_1 (15 °C)	$\nu(I–I)$ (cm^{-1}) *intensity*	
I_2	–	2.715(1)	–	515[a]	–	180 vs	[11]
$Mo_2dto \cdot 2I_2$	2.851(6)	2.770(3)	310[b]	∼430[b,c]	2.227(9)	170 s	[11]
$Me_2dazdt \cdot 2I_2$	2.786(2)	2.818(2)	332[b]	420[b]	2.04(2)	150 ms	[31a]
IBr	–	2.521(4)	–	479[d]	–	216 vs	[28b]
$Me_2dazdt \cdot 2IBr$	2.673(2)	2.6702(14)	257[b]	320[b]	n. a.[e]	172 vs	[28b]

vs, very strong; s, strong; ms, medium strong.
[a] THF.
[b] $CHCl_3$.
[c] Shoulder.
[d] CH_2Cl_2.
[e] The solutions were not suitable for the evaluation of the equilibrium constants showing time dependance.

3. Reactivity towards NMs

The capability, effectiveness and selectivity of the reagents in NMs dissolution have been preliminarily checked on pure samples of Au, Pd and Pt in the form of powder, foil or wire.

The reactions of $Me_2dazdt \cdot 2I_2$ [28a,31], $Me_2dazdt \cdot 2IBr$ [28b] and $[Me_2pipdtH]I_3$ [29] with metals and the experimental conditions are brought together in Scheme 7. These complexes are insoluble in water but they show satisfactory solubility in organic solvents such as MEK (methyl ethyl ketone), CH_3CN. The solubility of metal complexes, obtained by reaction with the reagent selected for the applications ($Me_2dazdt \cdot I_2$) falls in the range 1.0×10^{-3} to 1.0×10^{-4} mol L^{-1} for the solvents cited above. The obtained metal complexes, which are stable both in solution and in the solid state, have been fully characterised, and the X-ray crystal structure for each compound has been solved.

The reactivity of diiodine adducts with some acyclic dithioxamides $R_2dto \cdot 2I_2$ (see Table 1) has also been checked. While the products have yet not been characterised, $R_2dto \cdot 2I_2$ can dissolve gold and palladium, quantitatively, and in a short time under the same mild conditions used for $Me_2dazdt \cdot 2I_2$ and $Me_2dazdt \cdot 2IBr$ [32]. $R_2dto \cdot 2I_2$ is not active towards platinum. Instead $[Me_2pipdtH]I_3$ [29] can even dissolve metal platinum.

Kinetic experiments performed by means of spectrophotometric measurements following the formation of the complexes using adducts based on cyclic-dto and crude metals have shown the following:

- The dissolution of the palladium powder follows a first order kinetics and the fastest process is achieved with $Me_2dazdt \cdot 2I_2$ (Fig. 1).
- The dissolution process of calibrated gold wires using $Me_2dazdt \cdot 2I_2$ and $Me_2dazdt \cdot 2IBr$ THF- solutions (Fig. 2),[1]

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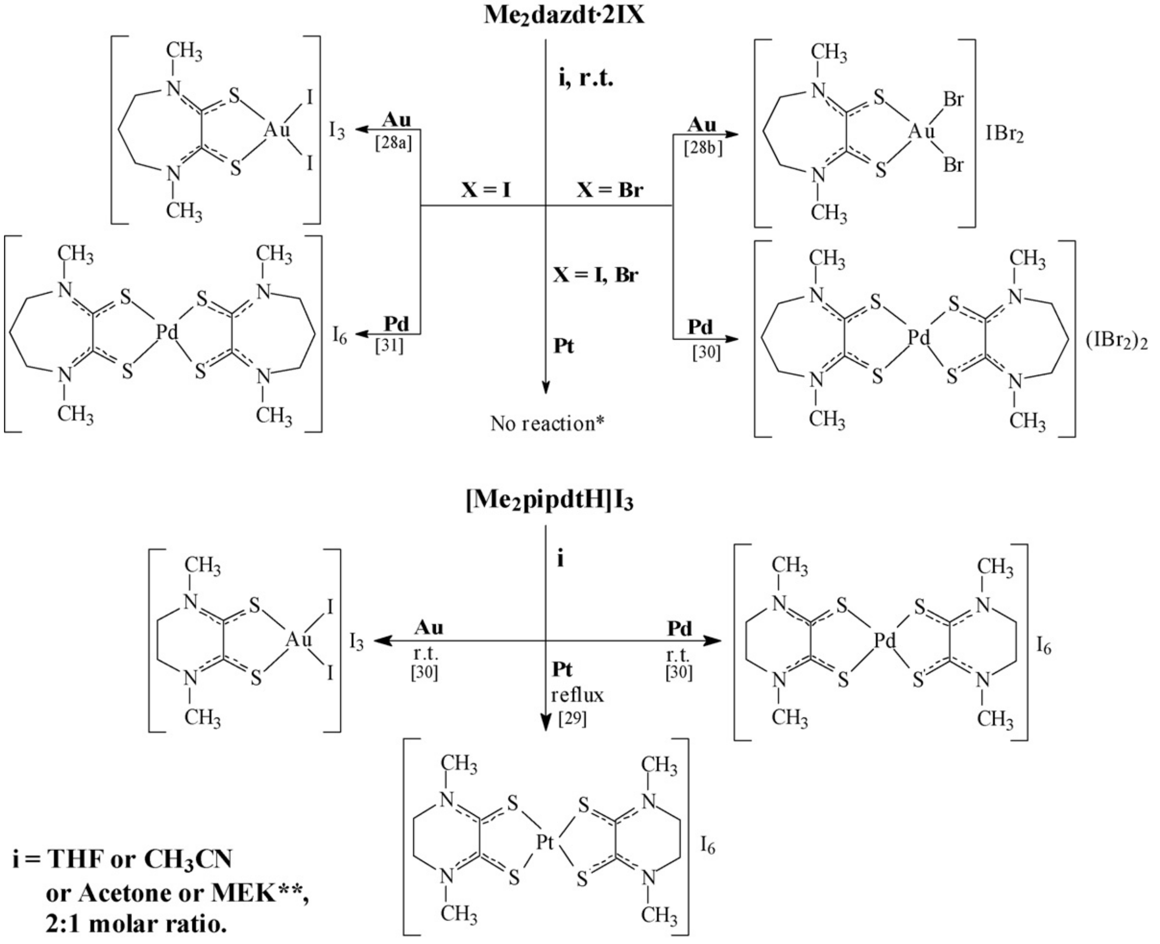
[1] $[Me_2pipdtH]I_3$ was not used since it does not show the desired selectivity for the applications described in section 4, because it can dissolve both gold and platinum.



Scheme 7. Reactivity of cyclic-dithioxamide/halogen complexes with NMs. (*) The reaction does not occur even in refluxing CH_3CN; (**) methyl ethyl ketone.

showed that the I_2-adduct works faster for gold etching compared to the IBr-adduct, and also compared to the I^-/I_2 (H_2O) solution which is currently used as a reagent for example in microelectronic applications.

In conclusion, on the basis of the experimental results on crude metals, $Me_2dazdt{\cdot}2I_2$ seems to be most suitable towards palladium and gold and has been selected to be checked for practical applications.

4. Applications

4.1. Pd-recovery from spent catalytic converters

Notably, Pd-only technology has been introduced in catalytic converters in the last years. Due to their limited lifetime, a significant amount of these converters should be discharged soon. It is estimated that the car industry alone, which puts about 40 million new cars on the market every year, represents an annual resource

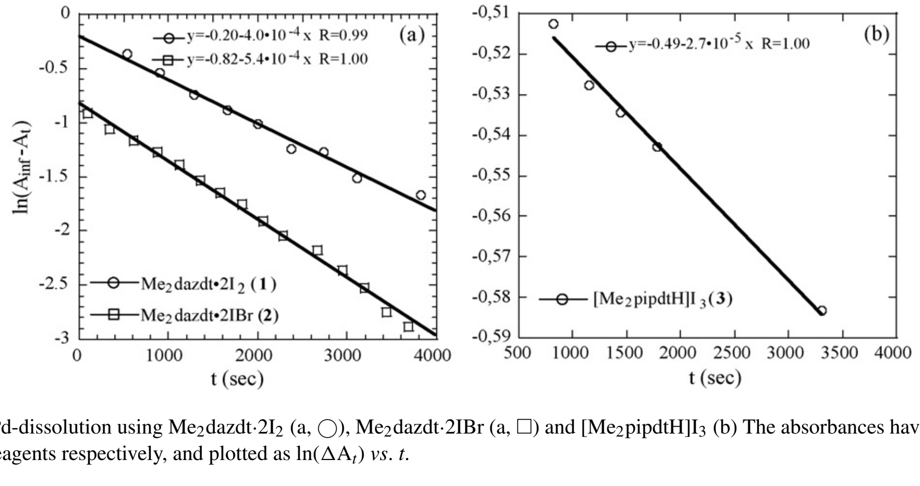


Fig. 1. Kinetic studies on Pd-dissolution using $Me_2dazdt{\cdot}2I_2$ (a, ◯), $Me_2dazdt{\cdot}2IBr$ (a, □) and $[Me_2pipdtH]I_3$ (b) The absorbances have been recorded at 292, 405 and 453 nm, for the three reagents respectively, and plotted as $\ln(\Delta A_t)$ *vs. t*.

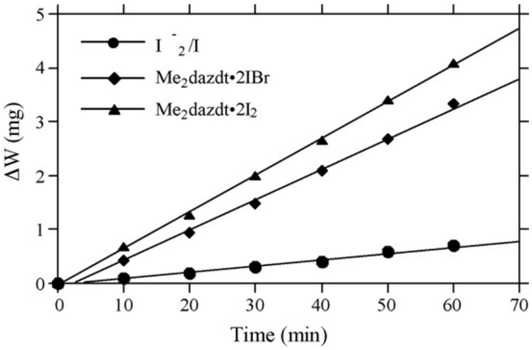


Fig. 2. Dissolution process of calibrated Au wires ($l = 2$ cm, Ø = 0.25 mm) using Me_2dazdt·$2I_2$ (THF, ▲), Me_2dazdt·2IBr (THF, ♦) and I^-/I_2 (H_2O, ●).

of $1 billion of Pd recovery. Currently significant but still low (∼20%) NMs recycling from spent car converters [1] is done by non-selective unattractive methods involving pyrometallurgical chlorination [5] or dissolution with strong oxidizing acids [6] in the crucial metal-dissolution step. Based on the promising results obtained with crude metal palladium, the effectiveness of Me_2dazdt·$2I_2$ has been checked on model three-way catalysts (TWC), in order to evaluate its potential in Pd recovery from spent car converters. The model samples have been prepared taking into account the chemical composition of the commercial wash-coats in use since the 1980s. Samples containing Pd in the 0.5–3.0 wt% range (typical loading in commercial wash-coats), supported both on Al_2O_3 and CeO_2–ZrO_2/Al_2O_3 [33] have been used: Al_2O_3 represents the typical support used in the 80’s and in early 90’s, CeO_2–ZrO_2/Al_2O_3 is the most advanced support in current technologies [34]. In order to simulate the deactivation of the TWC, an accelerated ageing protocol (1050 °C/200 h) has been used. The subsequent characterization indicates that the nature of the aged model catalysts mimics real systems [35]. By stirring a MEK (methyl ethyl ketone) solution of the reagent with the model aged catalysts at the boiling temperature of the solvent (80 °C) for a week, an almost quantitative extraction yield was obtained in mild conditions and using a friendly reagent and solvent. Moreover, Me_2dazdt·$2I_2$ is inactive towards metallic Pt and Rh, which are also present in several car catalysts. For this reason, unlike in current methodologies, the present Pd recovery method shows an intrinsic selectivity. Therefore, despite the fact that the whole recovery process takes long times, it still offers the advantage of avoiding a laborious multi-step procedure for metal dissolution, complexation and separation, since it is based on a one-step oxidizing/complexing reaction. These peculiar results are particularly remarkable when one takes into account: (i) the low Pd-content of the samples; (ii) the Pd-metal dispersion on the wash-coat where the metal strongly interacts with CeO_2–ZrO_2; (iii) the strong sintering of the catalyst; and (iv) the presence of PdO crystallites.

For comparison, Pd recovery with an I^-/I_2 mixture, the well-known “tincture of iodine”, previously proposed to dissolve NMs (Ag, Au, Pd) [36], provided a significantly lower extraction yield (11%). Also, Me_2dazdt·$2I_2$ represents a significant improvement over other dihalogen or interhalogen adducts earlier proposed by the McAuliffe group [20], which are unsuitable for practical applications, and also over other methods [6], which are based on selective complexing reagents that require time-consuming pre-treatment procedures with strong oxidizing acids.

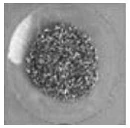
Pd-metal can easily be recovered from the complex through conventional thermal treatment (Pd, $T < 600$ °C for a few minutes).

4.2. Gold dissolution and recovery from WEEE

Gold is extensively used in electronics due to its good conductivity, ductility and resistance to corrosion. It is present in different amounts in every electronic board, smart and SIM cards, printer cartridges, etc., and often combined with a larger amount of copper, especially as a thin layer coating electrical connector for exposed connections. Increased production combined with a reduction in the average life-time of these goods has led to the accumulation of e-waste. It has been estimated that 20 kg/person of WEEE is produced yearly in Europe, and that the average content of gold in PC scraps is approximately 16 g Au/ton, four to eight times higher than the content of an Italian gold mine (in the 2–4 g Au/ton range). While the content of gold depends on the e-waste and is generally small, the scarcity of natural sources combined with an increase in its use and the need for recycling has led to considerable interest in safe industrial processes.

Preliminary experiments have been made to characterize selected typologies of electronic scrap materials of increasing complexity: ink-jet printer cartridges, SIM cards and a milled sample of different kinds of WEEE. In the latter case conventional pre-treatment procedures have been set-up to eliminate metallic and/or non-metallic interferences (glass, plastics, aluminium and magnetic metals) and to allow NMs to be exposed to the action of the reagents. In the ink-jet printer cartridges, gold is contained as an outer metallization of a three-layer Au–Cu–Au system supported by a plastic strip that ensures an electric contact with the printer. The content of gold is relatively low, but taking into account the large number of exhausted cartridges already collected for recycling purposes and considering that the strip is easily removed from scrap, the recovery of gold, and of copper, becomes advisable. The best conditions to recover both metals are summarized in Table 3. Accordingly, the strip is milled, washed with acetone and water. The copper is selectively removed through a dissolution reaction with ammonia in the presence of H_2O_2 and $(NH_4)_2SO_4$, forming the deep blue tetraamminecopper(II) complex, which is collected through filtration and treated with zinc to be reduced to copper metal. The solid collected from filtration is treated with a Me_2dazdt·$2I_2$ acetone solution to give a brown solution of the gold complex. The solution is treated with magnesium, which reduces the gold complex to the desired gold-metal and gives rise to a partial decomposition (∼40%) of the ligand. The remaining ligand (60%) is recovered from the solution to be reused. The final wastes are submitted to conventional special-waste treatment, after solvent recovery. Both copper and gold are recovered in high yields. The morphology of these recovered metals, obtained

Table 3
Summary of the experimental results in NMs recovery from WEEE [32]

WEEE	Metals	Preliminary	Metal dissolution		
			HCl dil, Δ, Ar	$NH_3/(NH_4)_2SO_4/H_2O_2$ (yield, %)	$Me_2dazdt \cdot 2I_2$ (yield, %)
	Cu (125 mg), Au (5 mg)	(1) Selection of the strip with metals; (2) milling; (3) washing by acetone and water.	–	Cu (∼100%), 1 h[a]	Au (∼100%), 6 h[a]
	Ni (4 mg), Cu (40 mg), Au (0.4 mg)	(1) Milling; (2) Washing by acetone and water.	Ni, 10 h[a]	Cu (∼100%), 30′[a]	Au (75–100%), 4 h[a]
	Ni[b] (50 mg), Sn (1.0 g), Pb (0.70 g), Zn (0.20 g), Al, Cr, Mn, Fe, Co,Cd (0.14 g), Cu (7.9 g), Ag (6 mg), Au (1 mg)	–	Pb, Sn, Zn, Ni, Fe, 24 h[a]	Cu (95%), Ag, 2 h[a], Solution A	Au (96%), 8 h[a], Solution B

Solution A: Cu(s) recovery by reduction with Zn(s) or, alternatively, CuO(s) precipitation by slow evaporation of NH_3. Solution B: Au(s) recovery by reduction with Mg(s).

[a] The dissolution time can be reduced increasing the temperature and/or using a milled sample with smaller grain size.

[b] On 10 g of milled sample.

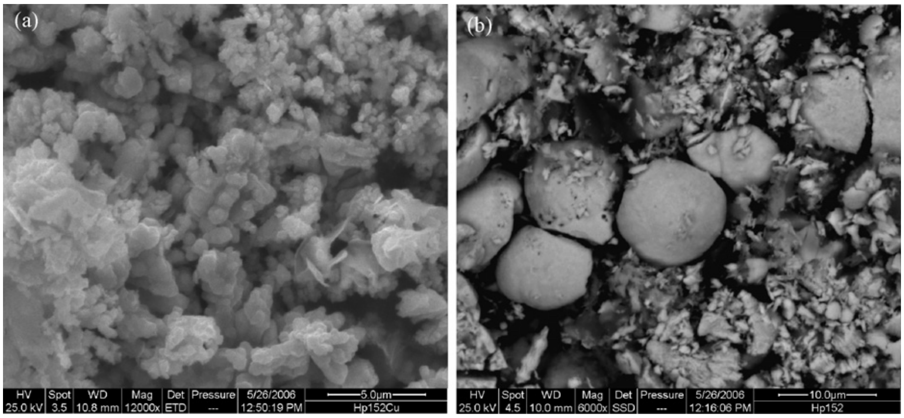


Fig. 3. (a) SEM micrographs of Cu(s) obtained by reduction with Zn(s) (particles average radius: ~500 nm) (b) Au(s) obtained by reduction with Mg(s) (particles Ø in the range 0.5–10 μm) the microanalysis shows the presence of respectively Zn and Mg impurity which can easily be removed for washing with HCl.

with Scanning Electron Microscopy (SEM) is shown in Fig. 3(a) (Cu) and (b) (Au).

SIM-cards show a more complex multi-layer Au–Cu–Ni–Au system, thus an additional step with HCl under argon to dissolve the nickel is required. The content of gold is very low and its recovery may be significant only in the presence of integrated recycling processes which treat a large amount of e-scrap. The content of NMs, as well as the composition of a milled sample of different kinds of WEEE in Table 3 must be taken as largely approximate, since it strongly depends on the nature of the milled e-waste. A satisfactory gold recovery is obtained through a three-step treatment similar to the one applied to SIM-cards, but in this case the step with HCl will dissolve other non-noble metals besides nickel, while the step with ammonia will dissolve silver together with copper. Details on the experimental procedures are available in the patent recently deposited by Sardegna Ricerche (research centre of the Sardinian regional government) [32]. The obtained lab-scale results have stimulated the interest of the recycling industries, which are creating a business cluster with the aim of transferring the proposed method to an industrial scale.

4.3. Gold removal from microdevices for failure analysis

Failure analysis studies are performed on an *end-of-life* microelectronic device with the view of finding defects that could be the cause of its degradation. The failures can be due to surface or internal defects that are responsible for the life time of the device [37].

In this context, Au removal is a crucial step in the deprocessing procedures performed for microdevice failure analysis. As a matter of fact, Au is widely used in the packages, where

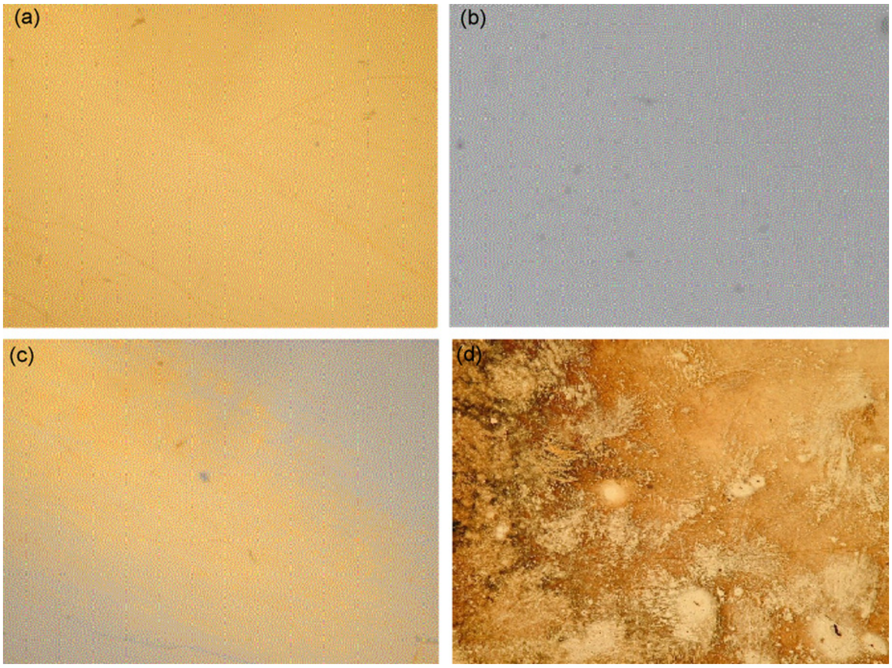
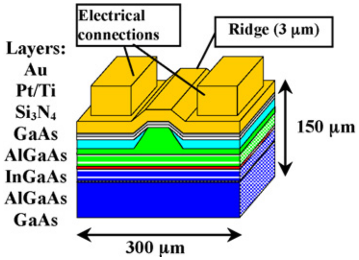
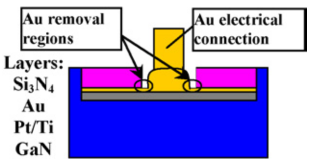
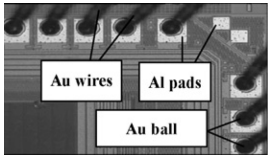
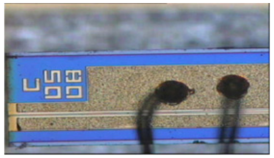
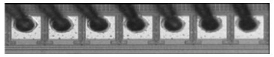
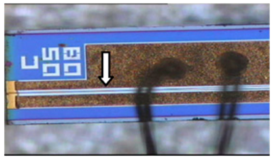
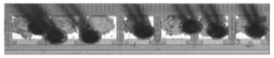


Fig. 4. Si/SiO$_2$/Ti/Au thin layers before (a) and after 5′ of etch by Me$_2$dazdt·2I$_2$ (b) and Me$_2$dazdt·2IBr (c) THF solutions, and I$^-$/I$_2$ water solution (d) $c = 5.0 \times 10^{-3}$ mol L^{-1}.

Table 4
Summary of the experimental results obtained on real *end-of-life* microelectronic devices

	GaAs-based laser diodes[a]	GaN-based LEDs	Al–Silicon ICs
Microdevice			
Before Etching			
Experimental conditions	$Me_2dazdt{\cdot}2I_2$ 4.3 × 10^{-3} M, acetone, r.t., 3′.[39]	$Me_2dazdt{\cdot}2I_2$ 5.0 × 10^{-3} M, Acetone, r. t., 10′.[30]	$Me_2dazdt{\cdot}2I_2$ 8.6 × 10^{-3} M, THF, r. t., 11′.[41]
After etching			

These compounds have shown to be effective in mild conditions also as powerful etching reagents for microelectronic device failure analysis. In particular $Me_2dazdt{\cdot}2I_2$ has proved to be the most useful reagent to replace the current I^-/I_2 chemical etch.

[a] Reprinted with permission from [39] Copyright 1999 Elsevier Science Ltd.

it is in intimate contact with active regions as an upper metallization of a complex multilayer system, typically Ti/Pt/Au in GaAs-based devices, (Ti and/or Pt)/Au in GaN-based LEDs (Light Emitting Diodes), or simply in massive bonding (pads and wires) on Al-metallized Silicon ICs (integrated circuits). Au thus plays the role of a first huge barrier to the examination of devices, i.e. after life tests, or during the setting up of new processing steps; both uniform layers and Au wires hide the view of inspection instruments (mainly SEM or EBIC [38] – *Electron Beam Induced Current* – techniques) and prevent the examination of bulk phenomena that are very useful as a diagnostic tool for failure analysis. In particular, EBIC resolution is greatly affected by the presence of thick Au metallization over the areas to be investigated [39]. The high electron absorption of gold, indeed, not only reduces the total amount of primary electrons that reach the semiconductor (because of absorption) and requires high electron energy, but it introduces large scattering in the residual beam. Au removal should then be advisable, provided no damage is caused to the device, and defects are preserved for failure analysis. In the case of Al–Silicon ICs, failure analysis is performed for the optimization of probing and bonding parameters during packaging development and assembly.

A commonly used method to identify microcracks under a wire-bonded pad is using an etch to remove the ball bond, thus allowing visual access to the layers under the pad. Under the best conditions, etches will provide access to the entire pad area for all the pads on a device in a short time (minutes to hours). However, many etches do not work well on devices with very strong intermetallic formations, or on devices aged by time and/or temperature. In addition, shrinking geometries and changing material sets need etches that are not as aggressive towards Al and underlying materials. Thus, it is desirable to develop an etch that can remove a ball bond from an Al pad while retaining the impression of the probe mark for site-directed FIB (*Focused Ion Beam*) inspection for microcracks.

Also in this case cyclic dithioxamide/dihalogen CT complexes have been shown to be the right solution to these technological problems.

Selection of $Me_2dazdt{\cdot}2I_2$ as the more effective reagent has been confirmed by comparing the gold selective dissolution capability of $Me_2dazdt{\cdot}2I_2$ and $Me_2dazdt{\cdot}2IBr$ on $Si/SiO_2/Ti/Au$ thin layers (thickness 300 μm/0.5 μm/15 nm/200 nm) [28b]. The test specimen was prepared to mimic those used in microelectronics for photonic devices such as laser diodes.

Fig. 4 shows the optical micrographs of the thin layers before and after etching using $Me_2dazdt{\cdot}2I_2$ and $Me_2dazdt{\cdot}2IBr$ and, for comparison, the conventional I^-/I_2 aqueous mixture.

The overall effect is a fast (only 4 min to remove a 200 nm thick gold layer for the diiodine-adduct), effective, selective (the Ti layer was completely preserved) and homogeneous gold dissolution, and in agreement with the previously reported results on Au wires (see Section 3) it shows that the adducts work better than the I^-/I_2 aqueous solution and the diiodine adduct is the most powerful. Further experiments on analogous samples carried out with tuned experimental conditions (solvent, temperature) showed that while THF is the most effective solvent in terms of time, acetone and MEK give a more homogeneous gold removal. Experiments on similar thin films using thiols such as 4-pyridinethiol in EtOH solution recently reported by Repo et al. [40], obtain gold dissolution in a time range of 1 h to several months.

Table 4 summarizes the results obtained using $Me_2dazdt{\cdot}2I_2$ on real *end-of-life* microelectronic devices.

5. Conclusions

Dithioxamide/dihalogen compounds have been shown to be an important class of powerful oxidation reagents towards crude NMs. In particular these reagents possess appealing features, such as effectiveness combined with low environmental impact, for use in practical applications to replace energy intensive and environmentally unattractive methods or less effective reagents.

Among these $Me_2dazdt{\cdot}2I_2$ has proved to be the most effective to dissolve NMs: (i) in palladium recovery from model spent TWC; (ii) in gold recovery from WEEE.

Methods based on this reagent have been optimized for the different cases. The reagent can dissolve metal palladium selectively and under mild conditions even when contained in a complex system such as a car catalyst, a ceramic material that has undergone severe thermal and chemical stress.

Satisfactorily results have been described for gold dissolution, the most noble metal, in applications in the field of gold recovery from WEEE.

In both cases, the methods allow a mild one-step metal oxidizing-complexing reaction. By combining effectiveness with low environmental impact, the proposed methods seem to comply with the requirements on waste management, besides making the recovery of palladium and gold from the secondary sources cited above appealing.

Moreover, this reagent has shown optimal properties as an etching reagent for gold removal from electronic devices in the failure analysis of microelectronic-devices. As a matter of fact this reagent is more effective than the conventionally used etching reagents, is easy to handle, works under mild conditions without protection from the air and/or moisture, and does not produce toxic fumes. All very desirable features, especially when the reagent is employed by non-specialists in chemistry as may happen in this application.

Acknowledgements

This research was carried out as part of the projects: (a) “Nuovi reagenti per l’attacco dell’oro (NRAAU)” supported in 2000–2001 by Regione Autonoma della Sardegna–Consorzio 21; (b) “Chemical Methods for Characterization and Deprocessing of Photonic Devices” supported by MIUR-PRIN 2002 09815_003 and Università di Cagliari; (c) “Recupero dell’oro da Rifiuti Elettrici ed Elettronici” supported in 2005–2006 by PROMEA-Sardegna Ricerche, Regione Autonoma della Sardegna.

The collaboration with L. Marchiò (University of Parma, Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica), M. Graziani and P. Fornasiero (University of Trieste, Dipartimento di Scienze Chimiche and Centre of Excellence on Nanostructured Materials) and M. Vanzi (Univerity of Cagliari, DIEE—Dipartimento di Ingegneria Elettrica ed Elettronica) has been crucial to achieve the reported results.

References

[1] (a) T. Kendall, Platinum 2007, Johnson Matthey, London, 2007;
(b) World Gold Council web site http://www.gold.org.

[2] (a) EC Council Directive 91/156/EC;
(b) EC Council Resolution 97/C 76/01.

[3] EC Council Directive 2000/53/EC.

[4] EC Council Directive 2003/96/EC.

[5] M.W. Ojeda, M. Del, C. Ruiz, M.E. Godoy, J.B. Rivarola, Trans. Instn. Min. Metall. C: Miner. Process. Extr. Metall. 108 (1999) C33 (and references therein).

[6] (a) J.-P. Cuif, Patent US 6,455,018 (2002);
(b) P. Yong, N.A. Rowson, J.P.G. Farr, I.R. Harris, L.E. Macaskie, Environ. Technol. 24 (3) (2003) 289;
(c) K. Katsuya, B. Yoshinari, Patent No. JP2000126504 (2000);
(d) B. Yoshinari, M. Iwakuma, Patent No. JP2003119032 (2003).

[7] P.J. Sadler, in: H. Schmidbaur (Ed.), Gold-Progress in Chemistry, Biochemistry and Technology, John Wiley & Sons, Chichester, 1999.

[8] (a) J.S. MacArthur, W. Forrest, British Patent No. 14,174, Britain (1888);
(b) G. Deschenes, R. Lastra, J.R. Brown, S. Jin, O. May, E. Ghali, Miner. Eng. 13 (2000) 1236;
(c) Y. Zhang, Z.H. Fang, M. Muhammed, Hydrometallurgy 46 (1997) 251;
(d) M.I. Jeffrey, P.L. Breuer, Miner. Eng. 13 (2000) 1097.

[9] P.A. Tasker, L.C. Plieger, in: J.A. McCleverty, T.J. Meyr (Eds.), West Compr. Coord. Chem. II, vol.9, Elsevier, 2004, pp. 759–807, and references therein.

[10] (a) F.H. Herbstein, W. Schwotzer, J. Am. Chem. Soc. 106 (1978) 2367, and references therein;
(b) M.C. Aragoni, M. Arca, F. Demartin, F.A. Devillanova, A. Garau, F. Isaia, V. Lippolis, G. Verani, Trends Inorg. Chem. 6 (1999) 1.

[11] P. Deplano, J.R. Ferraro, M.L. Mercuri, E.F. Trogu, Coord. Chem. Rev. 188 (1999) 71, and references therein.

[12] (a) F. Bigoli, P. Deplano, M.L. Mercuri, M.A. Pellinghelli, A. Sabatini, E.F. Trogu, A. Vacca, J. Chem. Soc., Dalton Trans. (1996) 3538;
(b) F. Bigoli, P. Deplano, M.L. Mercuri, M.A. Pellinghelli, A. Sabatini, E.F. Trogu, A. Vacca, Can. J. Chem. 73 (1995) 380;
(c) D. Atzei, F. Bigoli, P. Deplano, M.A. Pellinghelli, E.F. Trogu, A. Vacca, Can. J. Chem. 66 (1988) 1483.

[13] M.L. Munzarová, R. Hoffmann, J. Am. Chem. Soc. 124 (2002) 4787, and references therein.

[14] (a) G.C. Pimentel, J. Chem. Phys. 19 (1951) 446;
(b) R.J. Hack, R.E. Rundle, J. Am. Chem. Soc. 73 (1951) 4321.

[15] F. Bigoli, P. Deplano, A. Ienco, C. Mealli, M.L. Mercuri, M.A. Pellinghelli, G. Pintus, G. Saba, E.F. Trogu, Inorg. Chem. 38 (1999) 4626.

[16] a) W. W. Du Mont, M. Batcher, S. Pohl and W. Saak, Angew. Chem., Int. Ed. Engl., 26 (1987) 912. b) G. J. Leigh and N. Winterton eds., “Modern Coordination Chemistry” The Royal Society of Chemistry (2002), S.M. Godfrey, C.A. McAuliffe section C, p. 79.

[17] (a) S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, J. Chem. Soc., Dalton Trans. (1993) 371;
(b) S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, J. Chem. Soc. Dalton Trans. (1993) 2875;
(c) N. Bricklebank, S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, J. Chem. Soc. Chem. Commun. (1992) 944;
(d) N. Bricklebank, S.M. Godfrey, C.A. McAuliffe, A.G. Mackie, R.G. Pritchard, J. Chem. Soc. Chem. Commun. (1994) 695;
(e) N. Bricklebank, S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, J. Chem. Soc. Dalton Trans. (1996) 157;
(f) S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, J. Chem. Soc. Chem. Commun. (1994) 45;
(g) S.M. Godfrey, D.G. Kelli, C.A. McAuliffe, R.G. Pritchard, J. Chem. Soc. Dalton Trans. (1993) 2053;
(h) S.M. Godfrey, C.A. McAuliffe, A.G. Mackie, R.G. Pritchard, Angew. Chem. Int. Ed. Engl. 31 (1992) 919.

[18] G.J. Corban, S.K. Hadjikakou, N. Hadjiliadis, M. Kubicki, E.R.T. Tiekink, I.S. Butler, E. Drougas, A.M. Kosmas, Inorg. Chem. 44 (2005) 8617.

[19] (a) H.B. Bürgi, J.D. Dunitz, Accounts Chem. Res. 16 (1983) 153, and refences therein;
(b) H.A. Bent, Chem. Rev. 68 (1968) 587.

[20] S.M. Godfrey, N. Ho, C.A. McAuliffe, R.G. Pritchard, Angew. Chem. Int. Edit. English 35 (1996) 2344.

[21] (a) F. Ruthe, P.G. Jones, W.-W. Du Mont, P. Deplano, M.L. Mercuri, Z. Anorg. Allg. Chem. 626 (2000) 1;
(b) P. Deplano, S.M. Godfrey, F. Isaia, C.A. McAuliffe, M.L. Mercuri, E.F. Trogu, Chem. Ber. 130 (1997) 299.

[22] G.M. Kosolapoff, L. Maier (Eds.), Organic Phosphorus Compounds, vol. 1, John Wiley & Sons, 1972, p. 89.

[23] (a) M.G. Alymore, D.M. Muir, Miner. Eng. 14 (2001) 135;
(b) C. Abbruzzese, P. Fornari, R. Massidda, F. Veglio, Hydrometallurgy 39 (1995) 265;
(c) J.C. Bailar, in: A.F. Trotman-Dickinson (Ed.), Comprehensive Inorganic Chemistry, vol. 5, Pergamon Press, Elmsford, NY, 1973.

[24] (a) P.L. Breuer, M.I. Jeffrey, Miner. Eng. 16 (2003) 21;
P.L. Breuer, M.I. Jeffrey, Miner. Eng. 13 (2000) 1071;
(b) C.K. Chu, P.L. Breuer, M.I. Jeffrey, Miner. Eng. 16 (2003) 265;
(c) E. Molleman, D. Dreisinger, Hydrometallurgy 66 (2002) 1.

[25] R. Schulze, Ger. Offen. DE. 3401961 Cl. C22B3/00 (1984).

[26] (a) T. Groenewald, Hydrometallurgy 1 (1976) 277;
(b) S. Ubaldini, P. Fornari, R. Massidda, C. Abbruzzese, Hydrometallurgy 48 (1998) 113, and references there in;
(c) P. Lacoste-Bouchet, G. Deschenes, E. Ghali, Hydrometallurgy 47 (1998) 189.

[27] P. Deplano, F.A. Devillanova, J.R. Ferraro, F. Isaia, V. Lippolis, M.L. Mercuri, Appl. Spectrosc. 46 (11) (1992) 1625.

[28] (a) F. Bigoli, P. Deplano, M.L. Mercuri, M.A. Pellinghelli, G. Pintus, A. Serpe, E.F. Trogu, Chem. Commun. 2351 (1998);
(b) L. Cau, P. Deplano, L. Marchiò, M.L. Mercuri, L. Pilia, A. Serpe, E.F. Trogu, J. Chem. Soc. Dalton Trans. 1969 (2003).

[29] F. Bigoli, P. Deplano, M.L. Mercuri, M.A. Pellinghelli, G. Pintus, A. Serpe, E.F. Trogu, J. Am. Chem. Soc. 123 (2001) 1788.

[30] A. Serpe, Ph.D. Thesis University of Cagliari (2000–2003).

[31] (a) A. Serpe, F. Bigoli, M.C. Cabras, P. Deplano, P. Fornasiero, M. Graziani, M.L. Mercuri, T. Montini, L. Pilia, E.F. Trogu, Chem. Commun. (2005) 1040;
(b) P. Deplano, P. Fornasiero, M. Graziani, M.L. Mercuri, A. Serpe, E.F. Trogu, European and US Patent No. PCT/EP2005/051607 (2005).

[32] P. Deplano, M.L. Mercuri, L. Pilia, A. Serpe, M. Vanzi, Italian Patent No. RM2007A000073 (2007).

[33] R. Di Monte, P. Fornasiero, J. Kaspar, P. Rumori, G. Gubitosa, M. Graziani, Appl. Catal. B: Environ. 24 (2000) 157.

[34] (a) J. Kaspar, P. Fornasiero, N. Hickey, Catal. Today 77 (2003) 419;
(b) S. Bernal, G. Blanco, J.J. Calvino, J.M. Gatica, J.A. Pérez Omil, J.M. Pintado, Top. Catal. 28 (2004) 31.

[35] (a) R. Di Monte, P. Fornasiero, J. Kaspar, M. Graziani, J.M. Gatica, S. Bernal, A. Gómez-Herrero, Chem. Commun. (2000) 2167;
(b) J.R. Anderson, K.C. Pratt, Introduction to Characterization and Testing of Catalysts, Academic Press, New York, 1985 (Chapter 2);
(c) J. Kašpar, M. Graziani, P. Fornasiero, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 29, Elsevier Science B.V, Amsterdam, 2000, pp. 159–267 (Chapter 184).

[36] (a) Y. Nakao, J. Chem. Soc. Chem. Commun. (1992) 426;
(b) Y. Nakao, Chem. Commun. (1997) 1765, and references therein.

[37] (a) M. Vanzi, A. Bonfiglio, F. Magistrali, G. Salmini, Micron 31 (2000) 259;
(b) M. Vanzi, Proc. ISTFA95 (1995) 249.

[38] F. Magistrali, G. Salmini, G. Martines, M. Vanzi, Proc. ISTFA96 (1996) 233.

[39] M. Vanzi, A. Bonfiglio, P. Salaris, P. Deplano, E.F. Trogu, A. Serpe, G. Salmini, R. De Palo, Microelectron. Reliab. 39 (1999) 1043.

[40] M.T. Räisänen, M. Kemell, M. Leskelä, T. Repo, Inorg. Chem. 46 (2007) 3251.

[41] M. Vanzi, A. Serpe, E.F. Trogu, P. Deplano, C. Hartfield, W. Subido, Proc. ISTFA/2000 (2000) 235.