N,N′-Dimethylpiperazinium-2,3-dithione Triiodide, [Me_2Pipdt]I_3, as a Powerful New Oxidation Agent toward Metallic Platinum. Synthesis and X-ray Structures of the Reagent and the Product [Pt(Me_2Pipdt)$_2$](I_3)$_2$

Francesco Bigoli,† Paola Deplano,* Maria Laura Mercuri,
Maria Angela Pellinghelli,† Gloria Pintus, Angela Serpe, and
Emanuele F. Trogu

Dipartimento di Chimica Inorganica ed Analitica
Università di Cagliari, Cittadella di Monserrato
I-09042 Monserrato, Cagliari, Italy

Received September 12, 2000

The oxidation of noble metals involves energy-intensive and environmentally unattractive agents, such as boiling aqua-regia and cyanide. Many efforts have been dedicated to finding both safer and selective reagents, since the separation of metals that are close to each another in the periodic table is one of the great challenges in the metal refining industry and in other important fields of application (selective gold etching on GaAs-based devices and extraction of noble metals in the mining industry and from exhausted catalysts).[1,2]

The phenomenon of metal powder activation, including gold, by dihalogen or interhalogen adducts such as $R_3PE_2{\cdot}X_2$ and $R_2E'{\cdot}X_2$ (R = alkyl, aryl; E = P, As, Sb; E′ = S, Se; $X_2 = I_2$, Br_2, IBr) has been pointed out by the extensive work of McAuliffe et al.[3] This finding has a great potential in opening new perspectives, but these reagents appear unsuitable in practice, because they require strictly anhydrous and anaerobic conditions and long reaction times, and because they use polluting materials.

Other dihalogen adducts in polar organic solvents, among them the well-known "tincture of iodine", have been successfully used to dissolve noble metals (Ag, Au, Pd). Noteworthy, Nakao et al.[4] have found that gold can be dissolved in the $I_2/I^-/CH_3CN$ system on heating, and deposited from the resulting solution on cooling. No reports on the Pt dissolution by these or similar one-step methods are found in the literature to the best of our knowledge.

With a view to adding favorable conditions to the spontaneity and selectivity of the oxidation reaction, we selected the diiodine adducts of cyclic dithio-oxamide donors. These polyfunctional *"soft"* donors can give chelation and favor the square-planar geometry preferred by the *"soft"* d^8 noble-transition metals (Pd(II), Pt(II), Au(III)).[5] Moreover these reagents are easy to handle and are not cytotoxic. The bis-diiodine adduct of *N,N′*-dimethylperhydrodiazepine-2,3-dithione (**D**) has been shown to be capable of oxidizing gold in very mild conditions (room temperature) to form the salt [AuDI_2]I_3, and to be suitable for use in practical applications. This reagent is now used in selectively removing the gold layer from InGaAs SL SQW laser diodes, without destroying the electrical contacts.[2] This is important in analyzing possible defects at the metal/semiconductor interface by means of EBIC (Electron Beam Induced Current) analysis, which should have a poor resolution for the location of the electrically active lattice fracture when the gold layer acts as an absorption and scattering layer for incoming primary electrons. This adduct is not active toward Pt either at room temperature or in refluxing THF or CH_3CN. The reaction of diiodine with *N,N′*-dimethylpiperazine-2,3-dithione (Me_2pipdt), another cyclic dithiooxamide with a hexatomic ring despite the heptatomic one in the previous cited reagent, produces a salt [Me_2pipdt]I_3 (**1**) where [Me_2pipdt]$^+$ is the monocation of the donor. **1** was characterized by X-ray structure determination (Figure 1).[6]

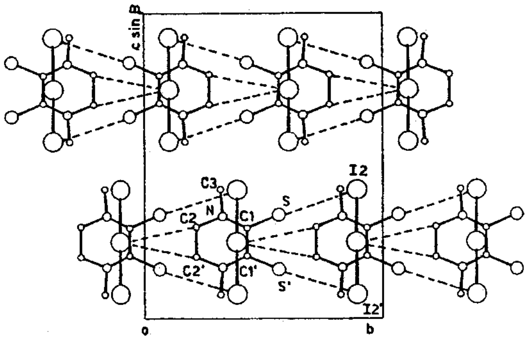
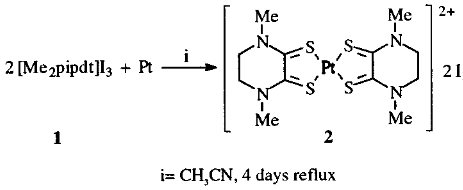


Figure 1. Projection of the structure of [Me_2pipdt]I_3 along *a*. Selected bond lengths (Å) and angles (deg): I(1)−I(2) 2.909(1); S−C(1) 1.684(7); N−C(1) 1.285(9); N−C(2) 1.447(10); N−C(3) 1.468(8); C(1)−C(1′) ($1 - x$, y, $^1/_2 - z$) 1.544(12); C(2)−C(2′) 1.438(14); I(2)−I(1)−I(2′) 179.11(3); S−C(1)−N 123.7(5); S−C(1)−C(1′) 118.1(2); C(1)−N−C(2) 122.2(5); C(1)−N−C(3) 121.9(7); C(2)−N−C(3) 115.2(6); N−C(1)−C(1′) 118.2(4); N−C(2)−C(2′) 114.0(5).

Scheme 1



A binary axis, crossing the midpoint of C(1)−C(1′), C(2)−C(2′), and I(1), passes through both the cation and the anion. Chains along *b* are formed through the contacts S···I(2) 3.932(3) Å, I(1)···S 3.993(3) Å, and I(1)···C(2) (x, $1 + y$, z). I···C contacts among the chains give rise to layers parallel to the plane (001). Interactions among the layers are due to C···C contacts.

By reacting **1** with metallic platinum (powder, <400 mesh) in the stoichiometric ratio, the complex [Pt(Me_2pipdt)$_2$](I_3)$_2$ (**2**) is obtained (yield 65%), as reported in Scheme 1. The X-ray characterization of a crystal of **2**[10] shows that the metal lies on a center of symmetry and has a square-planar coordination, while no planar fragments are found in the ligand. The chelation ring shows an "envelope" conformation, and the piperazine ring shows a half-chair conformation. The molecular structure of the [Pt(Me_2pipdt)$_2$]$^{2+}$ cation is shown in Figure 2.

---

† Present address: Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parco Area delle Scienze 17A, I-43100 Parma, Italy.

(1) Ubaldini, S.; Fornari, P.; Massidda, R.; Abruzzese, C. *Hydrometallurgy* **1998,** *48*, 113. Schulze, R. German Offen. DE. 3401961 (Cl. C22B3/00) Aug, 23, 1984.

(2) Vanzi, M.; Bonfiglio, A.; Salaris, P.; Deplano, P.; Trogu, E. F.; Serpe, A.; Salmini, G.; De Palo, R. *Microelectron. Reliab.* **1999**, *39*, 1043−1047.

(3) Godfrey, S. M.; Ho, N.; McAuliffe, C. A.; Pritchard, R. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *33*, 2344.

(4) Nakao, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 426. Nakao, Y.; Sone, K. *J. Chem. Soc., Chem. Commun.* **1996**, 897.

(5) Bigoli, F.; Deplano, P.; Mercuri, M. L.; Pellinghelli, M. A.; Pintus, G.; Serpe, A.; Trogu, E. F. *J. Chem. Soc., Chem. Commun.*, **1998**, 2351 and references therein.

(6) General X-ray structure data: Siemens AED diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å) with $\theta-2\theta$ scan technique, $T = 293(2)$ K, absorption correction following an empirical method,[6] structure solution by using direct method (Sir-92[7]), refinement against F^7 (SHELXL-97[8]). **1**: $C_6H_{10}I_3N_2S_2$, red-brown crystals, $M = 554.98$, crystal dimensions $0.10 \times 0.23 \times 0.55$ mm^3, monoclinic, *C*2/*c*, $a = 8.764(5)$ Å, $b = 11.259(5)$ Å, $c = 14.458(5)$ Å, $\beta = 93.13(2)°$, $V = 1424.5(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.588$ Mg m^{-3}, $\mu = 6.843$ mm^{-1}, transmission coefficients 1.0000 and 0.5870, 1622 data collected, 1565 unique data ($R_{int} = 0.0851$), 1565 data with $F > 4\sigma(F)$, 63 refined parameters, $R1 = 0.0447$, $WR2 = 0.1509$ (all data).

(7) Walker, N.; Stuart D. *Acta Crystallogr.* **1983**, *39A*, 158.

(8) Altomare A.; Cascarano G.; Giacovazzo C.; Guagliardi A.; Burla M. C.; Polidori G.; Camalli M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

10.1021/ja0056015 CCC: $20.00

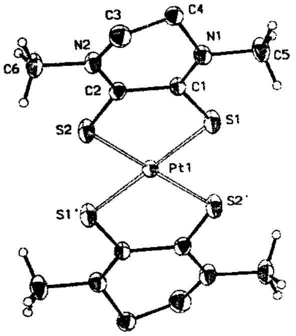


Figure 2. Molecular structure of $[Pt(Me_2pipdt)_2]^{2+}$ in $[Pt(Me_2pipdt)_2](I_3)_2$. Selected bond lengths (Å) and angles (deg): Pt−S(1) 2.274(4); Pt−S(2) 2.289(4); S(1)−C(1) 1.676(15); S(2)−C(2) 1.695(13); N(1)−C(1) 1.317(18); N(1)−C(4) 1.490(17); N(2)−C(2) 1.321(15); N(2)−C(3) 1.427(18); C(1)−C(2) 1.534(18); C(3)−C(4) 1.46(2); S(1)−Pt−S(2) 88.85(15); S(1)−Pt−S(2′) 91.15(15); C(1)−S(1)−Pt 105.7(5). Symmetry transformations used to generate equivalent atoms: $-x + 1$, $-y + 1$, $-z + 1$.

The triiodide counterions are slightly asymmetrical [I(1)−I(2) 2.899(2) Å and I(2)−I(3) 2.933(2) Å]. The FT-Raman spectrum shows two peaks at 139 (2.7) and 113 (10) cm^{-1} assigned to I−I−I antisymmetrical and symmetrical stretching, respectively. The Raman activity of the antisymmetrical stretching is due to the asymmetry of the system. As expected, the relative intensity of the peaks is reversed in the infrared spectrum.[11]

The $[Pt(Me_2pipdt)_2]^{2+}$ cation shows interesting properties; it undergoes multistep reversible monoelectronic reductions ascribed to the following processes:

$$[Pt(Me_2pipdt)_2]^{2+} \xrightleftharpoons{E_{1/2}^{1}} [Pt(Me_2pipdt)_2]^{+} \xrightleftharpoons{E_{1/2}^{2}} [Pt(Me_2pipdt)_2] \xrightleftharpoons{E_{1/2}^{3}} [Pt(Me_2pipdt)_2]^{-} \xrightleftharpoons{E_{1/2}^{4}} [Pt(Me_2pipdt)_2]^{2-}$$

The half-wave potentials, measured by cyclic voltammetry (Figure 3),[12] are respectively −0.13, −0.40, −0.91, and −1.19 V ($E_a - E_c$ in the 58−62 mV range).

This cation, as the BF_4^- salt, shows two strong absorptions in the visible region [489 sh and 516 nm (ϵ = 13300 mol^{-1} dm^3 cm^{-1})]. An approximate calculation of the frontier orbitals using the package CACAO[13] based on the extended Hückel method (EHMO) has been performed.[13c] The frontier orbitals are π orbitals, and while HOMO-1 and HOMO contain a significant contribution of d_{yz} and d_{xy} orbitals of the metal, respectively, the LUMO is a π^* orbital mainly related to the ligand. The cited absorptions are ascribed to these $\pi \rightarrow \pi^*$ transitions.

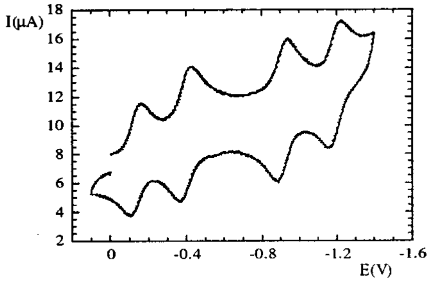


Figure 3. Cyclic Voltammetry of **2**.

Experiments in progress show that $[Me_2pipdt]I_3$, as well as $D \cdot 2I_2$, can be used to oxidize noble metals (Cu, Ag, Au, Pd) in very mild conditions (room temperature) with high yields and short reaction times.

In conclusion, apart from the interest in the new Pt complex, the relevance of the described reaction lies in the discovery of a new class of powerful oxidation reagents toward noble metals, which work in a one-step reaction, and are scarcely polluting and easy to handle. These reagents have a high potential in that they can offer industry the possibility of clean and safe technology for the extraction of noble metals.

Acknowledgment. This research was carried out as part of the project "Nuovi reagenti per l'attacco dell'oro" supported by the Consorzio 21 (Regione Autonoma della Sardegna) on UE funds.

Supporting Information Available: Table of crystal data, structure solution and refinement, atomic coordinates, bond lengths, angles, and anisotropic thermal parameters for **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0056015

---

(9) Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Determination; Universität Göttingen, Germany 1997.

(10) X-ray crystal data for **2**: $C_{12}H_{20}I_6N_4PtS_4$, dark shiny crystals, M = 1305.04, crystal dimensions 0.11 × 0.13 × 0.17 mm^3, monoclinic, $P2_1/n$, a = 9.072(6) Å, b = 13.303(5) Å, c = 12.611(5) Å, β = 107.99(2)°, V = 1447.5(12) $Å^3$, $Z = 2$, ρ_{calcd} = 2.994 Mg m^{-3}, μ = 11.542 mm^{-1}, transmission coefficients 1.0000 and 0.6526, 3281 data collected, 3150 unique data (R_{int} = 0.0618), 3150 data with $F > 4\sigma(F)$, 128 refined parameters, $R1$ = 0.0506, $WR2$ = 0.1393 (all data).

(11) Deplano, P.; Ferraro, J. R.; Mercuri, M. L.; Trogu, E. F. *Coord. Chem. Rev.* **1999**, *188*, 71−95.

(12) Pt electrodes; supporting electrolyte Bu_4NPF_6 0.1 mol dm^{-3}; scan rate 100 mV s^{-1}; reference electrode Ag/AgCl; solvent CH_3CN; T = 25 °C.

(13) (a) Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 399. (b) Mealli, C.; Ienco, A.; Proserpio, D. M. *Book of Abstracts of the XXXIII ICCC* **1998**, 510. (c) Deplano, P.; Ienco, A.; Mealli, C.; Pintus, G. Unpublished results.