SHORT COMMUNICATION

On the Use of the Bis(diiodine) Adduct of 1,4-Dimethylperhydro-1,4-diazepine-2,3-dithione (Me_2dazdt) to Recover Liquid Mercury Producing [Hg(Me_2dazdt)I_2] in a One-Step Reaction

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Diiodine adducts with cyclic dithio-oxamides, where complexing and oxidising properties coexist in the same molecule, have been shown to be powerful oxidising reagents towards selected metals. Here we describe the reaction of Me_2dazdt·2I_2 [Me_2dazdt = 1,4-dimethylperhydro-1,4-diazepine-2,3-dithione (**1**)] with highly toxic liquid mercury which gives the complex [Hg(Me_2dazdt)I_2] (**2**) in a one-step reaction. X-rays analysis of **2** shows that the Hg^{II} centre is coordinated by two sulfur atoms of the chelating ligand and by two iodine atoms in a distorted tetrahedral geometry. The molecule is asymmetric and crystallizes in the chiral space group $P2_12_12_1$. In the unit cell only the M enantiomer is present [τ (S1–C1–C2–S2) = –61.1(5)°].

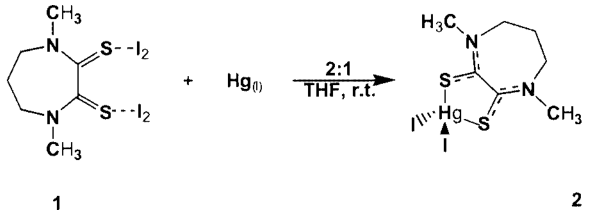
Introduction

Many efforts are currently devoted to find safe, nonpolluting reagents which are effective for the dissolution of noble and heavy metals. The recovery of these metals has both environmental and economic relevance because of waste accumulation and simultaneous decrease of raw materials due to their extensive usage in novel technologies.[1] Diiodine adducts with appropriate donors, where complexing and oxidizing properties coexist in the same molecule, have a high potential to dissolve the above-cited metals under mild conditions.[2–4] Successful results have been obtained by our group using the bis(diiodine) adduct of 1,4-dimethylperhydro-1,4-diazepine-2,3-dithione [Me_2dazdt·2I_2 = (**1**)] to dissolve elemental gold in a one-step reaction, under mild conditions and in a short time.[5] Moreover, it is inert towards air and moisture and does not exhibit cytotoxicity.[6] These properties make this reagent an optimal candidate for such applications.[7] We are now employing this dissolution method towards highly toxic and heavy metals, with the view to remove them from waste from electronic equipment before disposal in order to prevent the metal dispersion into the soil. In this paper we show the reactivity of **1** towards liquid mercury which exhibits extremely high toxicity,[8] as well as great affinity for sulfur-donors.

Results and Discussion

[Hg(Me_2dazdt)I_2]

Me_2dazdt·2I_2 (**1**)[5] has been reacted with liquid mercury according to Scheme 1. Liquid mercury (24 mg) was consumed under the experimental conditions shown in Scheme 1 (2:1 adduct excess, room temperature, THF solvent) in approximately two hours. By Et_2O diffusion into the THF solution, well-formed, shiny, pale-yellow crystals precipitated in an almost quantitative yield.



Scheme 1

These crystals have been isolated and characterised as [Hg(Me_2dazdt)I_2] (**2**). The use of Me_2dazdt·2I_2 has allowed the oxidation and complexation of liquid mercury producing **2** in a very easy and convenient route, under mild conditions and through a one-step reaction. An X-ray dif-

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fractometric study on **2** has been performed. The molecular structure and the atomic-labelling scheme for **2** are shown in Figure 1. Bond lengths and angles are reported in Table 1.

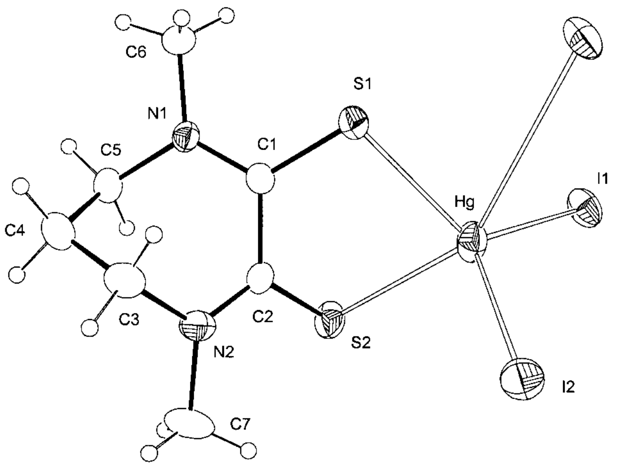

Figure 1. Perspective view of $[Hg(Me_2dazdt)I_2]$; thermal ellipsoids are drawn at the 30 % probability level

Table 1. Bond lengths [Å] and angles [deg] for $[HgI_2(Me_2dazdt)]$ (**2**)

Hg−I1	2.6931(4)	N1−C6	1.456(6)
Hg−I2	2.7091(5)	N1−C5	1.468(6)
Hg−S1	2.554(1)	N2−C2	1.326(6)
Hg−S2	2.776(1)	N2−C7	1.471(6)
Hg−I1[a]	3.8188(5)	N2−C3	1.474(6)
S1−C1	1.692(5)	C1−C2	1.507(6)
S2−C2C2	1.674(5)	C3−C4	1.507(8)
N1−C1	1.323(6)	C4−C5	1.508(7)
I1−Hg−I2	116.55(2)	C2−N2−C7	120.7(5)
I1−Hg−S1	119.89(4)	C3−N2−C7	118.0(4)
I1−Hg−S2	108.81(3)	N1−C1−C2	117.1(4)
I2−Hg−S1	119.18(4)	N1−C1−S1	121.8(4)
I2−Hg−S2	99.74(4)	C2−C1−S1	121.1(3)
S1−Hg−S2	82.37(4)	N2−C2−C1	116.8(4)
C1−S1−Hg	100.3(2)	N2−C2−S2	124.4(4)
C2−S2−Hg	89.4(2)	C1−C2−S2	118.7(4)
C1−N1−C5	120.8(4)	N2−C3−C4	111.4(5)
C1−N1−C6	121.1(4)	C3−C4−C5	111.6(4)
C5−N1−C6	118.0(4)	N1−C5−C4	110.7(4)
C2−N2−C3	121.1(4)		

[a] Symmetry = $-x + 1, y - 1/2, -z + 1/2$.

The mercury atom is in a severely distorted tetrahedral environment, coordinated by two iodine and two sulfur atoms of the chelating ligand. However, the Hg−S interatomic distances are significantly different [Hg−S1 = 2.554(1), Hg−S2 = 2.776(1) Å] as a consequence of a long contact between the metal and an iodine atom of an adjacent molecule [Hg−I1′ = 3.8188(5) Å] that renders the overall coordination geometry nearly trigonal bipyramidal with the equatorial positions occupied by the S1, I1 and I2 atoms. The lengthening of the Hg−S2 bond length is in accordance with the apical position occupied by S2 and by the *trans* influence of the iodine atom I1′. The I1′−Hg−S2 angle is significantly bent [150.07(3)°] and the S1−Hg−S2 angle is forced to be 82.37(4)° due to ligand chelation. The metal lies out of the S1−I1−I2 plane by 0.322(1) Å and is directed toward the S2 atom (cf. 0 Å for trigonal bipyramidal geometry and ca. 0.9 Å for tetrahedral coordination with average Hg−X bond lengths of ca. 2.7 Å). These main structural features are similar to those found in the complex $[Hg(bzimtH_2)_2I_2]$ ($bzimtH_2$ = benzo-1,3-imidazole-2-thione) where the mercury atom is similarly coordinated but the two sulfur atoms belong to two monothionic donors.[9] In other similarly coordinated complexes with heterocyclic thiones, shorter Hg−S interatomic distances and longer Hg−I interatomic distances were found and explained by considering the existence of different intermolecular interactions.[10,11] In the case of complex $[Hg(bzimtH_2)_2I_2]$, the long Hg−S interatomic distances were ascribed to the presence of NH···S interactions which were absent in complexes with shorter Hg−S interatomic distances.

In complex **2**, the C−S and the C−N interatomic distances of the two NCS fragments (Table 1) are in agreement with a strong electron delocalisation inside the thioamidic moieties as has been reported for similar systems.[12−15] Furthermore, no extension of the electron delocalization between the two planar thioamide groups is observed [C1−C2 1.507(6) Å]. The molecule is asymmetric and is therefore chiral. The S1−C1−C2−S2 torsion angle [−61.1(5)°] can be used to define the chirality of the molecular entity.[16]

The IR and Raman bands that are most significant in investigating the coordination mode of the Me_2dazdt ligand are ν(CN) and ν(C=S). In fact, sulfur donation should be accompanied by a shift to lower frequencies of ν(C=S) and simultaneously to higher frequencies of ν(CN).[17] Conflicting literature assignments of ν(C=S)[18−20] reflect difficulty in identifying this vibration, which may be extensively coupled with other vibrations and in several cases, this peak is not very sensitive to coordination.[21] Instead, the assignment of the ν(CN) is well established and can give useful information on the coordination of the ligand. Accordingly, the strong peak at $\tilde{\nu} = 1532\ cm^{-1}$ in **2** ($\tilde{\nu} = 1530\ cm^{-1}$ in **1**, $1493\ cm^{-1}$ in the free ligand) is assigned to the ν(CN) vibration. A medium weak band ($\tilde{\nu} = 826\ cm^{-1}$) in **2** ($\tilde{\nu} = 824\ cm^{-1}$ in **1**, $836\ cm^{-1}$ in the free ligand) is tentatively assigned to ν(C=S). Thus, in accordance with X-ray results, vibrational spectroscopy shows that mesomeric forms involving CN double bonds contribute more than in the free ligand to the description of the structure of Me_2dazdt both in the adduct [ν(CN) = $1532\ cm^{-1}$] and in **2**. Therefore, when the sulfur atoms function as donors, the polar form of Me_2dazdt is favoured. Also, this contribution is very similar in the adduct and in the complex. Vibrational spectra of **2** in the Far-IR region are shown in Figure 2.

In **2**, a broad, very strong band centred ($\tilde{\nu} = 139\ cm^{-1}$) with shoulders (ca. $\tilde{\nu} = 150$ and $125\ cm^{-1}$) appears in the Raman spectrum and in the IR spectrum ($\tilde{\nu} = 150$ with a shoulder at $139\ cm^{-1}$). These overlapping bands are assigned to Hg−I vibrations ($\nu_{as} = 150$ and $139\ cm^{-1}$ and

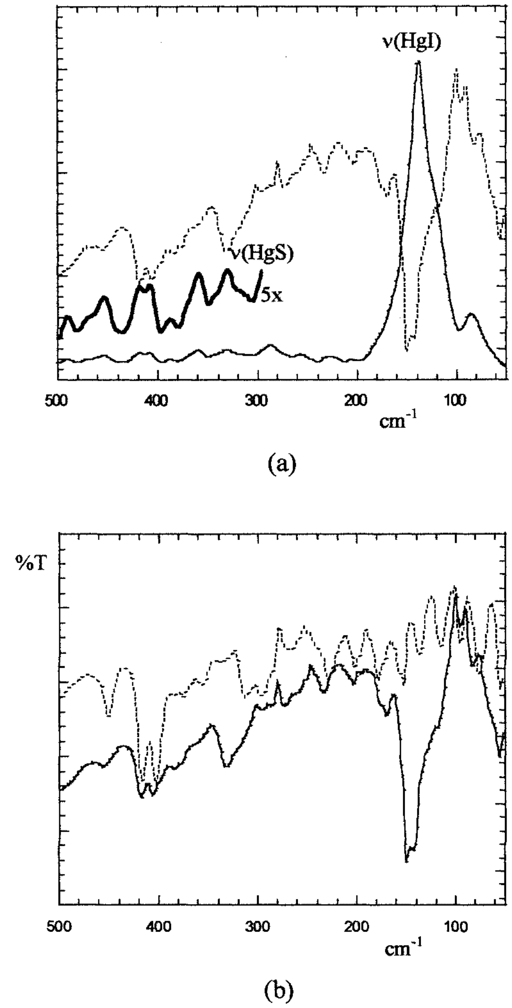

Figure 2. (a) Superimposed FT-Raman (continuous line), 5 times amplified FT-Raman (thick line) and FT-IR spectra (dotted line) of [Hg(Me$_2$dazdt)I$_2$]; (b) Far-IR spectra of polyethylene pellets of Me$_2$dazdt (dotted line) and [Hg(Me$_2$dazdt)I$_2$] (continuous line); transmittance is reported in arbitrary units

$\nu_s = 125$ cm^{-1}; Figure 2, a).[22] The two weak Raman peaks ($\tilde{\nu} = 333$ and 318 cm^{-1}; the spectrum is dominated by very strong Hg−I vibrations) which appear in the Far-IR spectrum as a broad peak ($\tilde{\nu} = 332$ cm^{-1} with a shoulder at 318 cm^{-1}) and are not present in the free ligand's spectrum, (Figure 2, b) are tentatively assigned to Hg−S vibrations.

Conclusion

Me$_2$dazdt·2I$_2$, [the bis(diiodine) adduct of 1,4-dimethylperhydro-1,4-diazepine-2,3-dithione] was shown to be a valuable reagent towards liquid mercury, capable of dissolving the highly polluting metal in a one-step reaction to form the complex [Hg(Me$_2$dazdt)I$_2$] under mild conditions and has been fully characterised. The effectiveness and ease of the reaction coupled with the low environmental impact of the reagent and the extremely high toxicity of the metal make the reported dissolution technique relevance to Hg-recovery.

Experimental Section

General: Reagents and solvents of reagent grade quality were used as furnished by Aldrich. The adduct Me$_2$dazdt·2I$_2$ (**1**) and the ligand Me$_2$dazdt were prepared according to literature procedures.[23,4]

Synthesis of [Hg(Me$_2$dazdt)I$_2$]: A Me$_2$dazdt·2I$_2$ solution (0.170 g, 0.24 mmol in 100 mL of THF) and liquid mercury (0.024 g, 0.12 mmol; 2:1 molar ratio) were mixed in a heterogeneous phase and allowed to react while stirring at room temperature for 2 h. The red-brown solution of the adduct developed into a clear orange-yellow solution. Shiny yellow crystals of [Hg(Me$_2$dazdt)I$_2$], suitable for X-ray analysis, were obtained by slow crystallization from THF/Et$_2$O, with quantitative yield referred to Hg. C$_7$H$_{12}$HgI$_2$N$_2$S$_2$ (642.7): calcd. C 13.08, H 1.88, N 4.36, S 9.98; found C 13.42, H 1.62, N 4.40, S 9.86. Mid-IR (KBr pellets, cm^{-1}): $\tilde{\nu}$ = 2955 vw, 2923 w, 2852 vw, 1532 vs, 1458 ms, 1440 w, 1398 s, 1358 w, 1331 w, 1287 ms, 1278 s, 1255 m, 1212 vw, 1184 w, 1118 s, 1074 w, 1028 w, 967 w, 826 w, 751 w, 695 vw, 613 mw, 591 w, 538 vw, 417 vw. Far-IR (Polyethylene pellets, cm^{-1}): $\tilde{\nu}$ = 418 ms, 406 ms, 383 mw, 377 mw, 332 ms, 296 w, 273 w, 234 w, 203 w, 170 m, 150 vs, 142 vs, 96 vw, 83 w, 56 m. Raman (cm^{-1}): $\tilde{\nu}$ = 2983 w, 2926 mw, 1526 mw, 1458 w, 1439 vw, 1400 mw, 1358 w, 1287 w, 1256 w, 1213 vw, 1184 vw, 1108 vw, 887 vw, 696 vw, 614 vw, 540 mw, 419 w, 334 w, 283 w, 164 sh, 150 sh, 139 vs, 127 sh, 121 sh, 86 m, 75 mw. UV-Vis (ε = L·mol^{-1}·cm^{-1}): λ = 290 sh (ca. 600) nm, 340 sh (ca. 500).

Measurements: Microanalyses were performed on a Carlo−Erba CHNS elemental analyser model EA1108. IR spectra (4000−50 cm^{-1}) were recorded as KBr (Mid-IR) and polyethylene (Far-IR) pellets with a spectrometer Bruker Equinox-55 (resolution 4 cm^{-1}). FT-Raman spectra were recorded on a Bruker RFS100/S FT-spectrometer, fitted with an InGaAs detector (room temperature) and operating with an excitation frequency of 1064 nm (Nd:YAG laser). The power level of the laser source was 100 mW. The solid samples were introduced into a capillary tube and then fitted into the compartment designed for a 180° scattering geometry (resolution 4 cm^{-1}). No sample decomposition was observed during data collection. Electronic spectra (1500−300 nm) were recorded on a Cary 5 spectrophotometer by using CH$_3$CN solvent. Polarimetric measurements were performed on a Polax-D instrument using a 10 cm cell.

X-ray Crystallographic Study: A summary of data collection and structure refinement for **2** are reported in Table 2. Single-crystal data were collected with a Bruker AXS Smart 1000 area detector diffractometer (Mo-K_α, λ = 0.71073 Å). Cell parameters were refined from the observed setting angles and detector positions of selected strong reflections. Intensities were integrated from several series of exposure frames covering a hemisphere of reciprocal space.[24] No crystal decay was observed. Absorption correction using the program SADABS[25] was applied and resulted in transmission factors ranging from 0.408−1.000. The space group ($P2_12_12_1$) was chosen on the basis of the systematic extinction and intensity statistics, the absolute configuration has been confirmed at the 3σ level of the Flack parameter [−0.012(4)].[26] The structure was solved by direct methods (SIR97)[27] and refined with full-matrix least-squares (SHELXL-97),[28] using the Wingx software package.[29] Non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed at their calculated positions. The maximum and minimum peaks on the final difference Fourier maps corresponded to 0.806 and −1.040 e·Å^{-3}. The programs Parst [30,31] and ORTEP3 for Windows[32] were also used. CCDC-199303 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystallographic data of compound [$HgI_2(Me_2dazdt)$] (**2**)

Empirical Formula	$C_7H_{12}HgI_2N_2S_2$
M_r [g·mol^{-1}]	642.70
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (No.19)
a [Å]	9.047(1)
b [Å]	9.216(1)
c [Å]	18.139(1)
V [Å^3]	1512.4(2)
Z	4
D [Mg·m^{-3}]	2.823
Wavelength [Mo-K_α]	$\lambda = 0.71073$ Å
T [K]	293
μ [mm^{-1}]	14.507
R_f collected/unique	16959/3485
R_{int}	0.0435
No. of parameters refined	130
GooF	1.017
R_1[a], wR_2[b]	0.0231, 0.417
R_1, wR_2 (all data)	0.0291, 0.427

[a] $R_1 = ||F_o| - |F_c||/|F_o|$. [b] $wR_2 = [w(F_o^2 - F_c^2)^2/wF_o^4]^{1/2}$.

Acknowledgments

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