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# Synthesis and Crystal Structure of $(Bu_4N)_2Hg(i\text{-}mnt)_2$

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**Abstract:** The synthesis and the crystal structure of the title compound $(Bu_4N)_2Hg(S_2C{=}C(CN)_2)_2$ **1** is reported herein. The crystal is attributed to triclinic system and space group $P\bar{1}$, *fw*=965.88. The crystal lattice parameters are *a*=9.450(1), *b*=15.827(2), *c*=17.619(2)Å, $\alpha$=108.12(2), $\beta$=99.54(2), $\gamma$=97.60(2)°, *V*=2421.9(8)Å$^3$, $\mu$ ($MoK_\alpha$)=3.390mm$^{-1}$, *Z*=2, $D_c$=1.324g.cm$^{-3}$, *F*(000)=996, *R*=0.054, *wR*=0.058.

**Keywords:** Synthesis, crystal structure, mercury(II) complex , isomaleonitrile dithiolate.

In recent years, the mixed-metal cluster were studies extensively. Hundreds of M-Mo(W)-S clusters have been synthesized[1]. But only two Hg-W-S clusters $[PPh_4]_2[HgWS_4L_2]\cdot 0.5$ MeCHO (L= CH=CH$_2$ **2** or C≡CH **3**)[2] were reported. We tried to synthesize i-mnt-Hg-Mo(W)-S cluster by using isomaleonitrile dithiolate (i-mnt=1,1dicyano-2,2-ethylene-dithiolato), but obtained $(Bu_4N)_2Hg(i\text{-}mnt)_2$. The synthesis and structure of $[Hg(i\text{-}mnt)_2]^{2-}$ are reported in this paper, and compared to other M-i-mnt complexes (M=Zn(II)[3] **4**, Cd(II)[4] **5**, Ni(II)[5] **6**, Pd(II)[6] **7**, Pt(II)[7] **8**, Pb(II)[8] **9**), $[(AuPPh_3)_2(i\text{-}mnt)]$[9]**10**, mnt-Pd-W-S cluster $[(Bu_4N)_2(mnt)PdWS_4]$[10] **11**(mnt=1,2-dicyano-1,2-ethylenedithiolato) and Hg-W-S cluster **2**, **3** respectively.

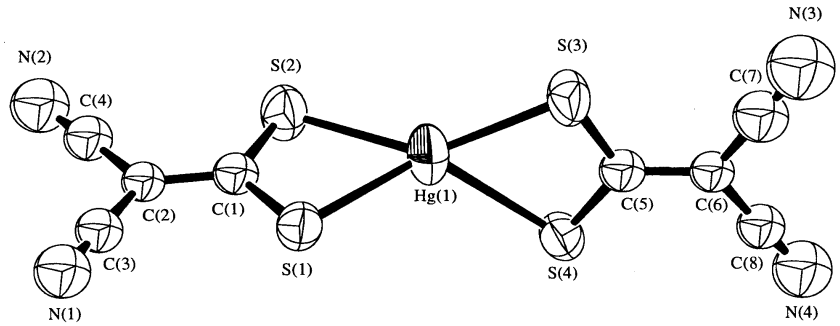
A well-ground mixture of HgI, $(Bu_4N)Br$, $Na_2(i\text{-}mnt)$, $(Et_4N)_2WS_4$ was heated at 90°C for 10 h under a nitrogen atmosphere. The raw product was extracted with $CH_2Cl_2$. Vapour diffusion of $CH_2Cl_2$ gave products as red block crystals. Cacld. for $HgS_4N_6C_{40}H_{72}$ : C, 49.74, H 7.51, N, 8.70 %. Found : 49.50, H, 7.31, N, 8.42 %.

In the title complex (**Fig.1**), $[Hg\ (i\text{-}mnt)_2]^{2-}$ has a symmetrical axis through the Hg atom, the Hg atom is at the center of the tetrahedron formed by the four sulfur atoms of two i-mnt anions.

The average Hg-S distance (2.566 Å) is shorter than the Hg-S bonds in **2 (**2.734 Å**), 3** (2.729 Å) and **9 (**Pb-S 2.88 Å), but longer than other metal-S distances in **4**-**8** and **10**, (Zn-S 2.347 Å, Cd-S 2.63 Å, Ni-S 2.205 Å, Pd-S 2.323 Å, Pt-S 2.315 Å, Au-S 2.313 Å).

The average S-Hg-S angles [70.31°] are bigger than the S-Cd-S angles in **5** (68.90 °) and significantly smaller than the S-M-S angles in **2** and **3** (S-Hg-S 82.9(2)°)**, 4** (S-Zn-S 77.91°), **6** (S-Ni-S 79.52°), **7** (S-Pd-S 75.21°), **8** (S-Pt-S 74.71°), **9** (S-Pb-S 72.23°), **11** (S-Pd-S 91.2°).

**Figure 1** The structure of $[Hg(i\text{-}mnt)_2]^{2-}$




The ligand i-mnt is a versatile and classic ligand in the synthesis of complexes and clusters. Due to the extensive ground-state π–electron delocalisation of i-mnt, one i-mnt-Pd-W-S cluster and many metal-i-mnt complexes have been produced. But no i-mnt-Hg-W-S was reported, and the title compound is the only Hg-i-mnt complex. The difficulty in producing Hg complex with i-mnt ligand may be due to the weak Hg-S bonds caused by the big van der Waals radium of Hg atom. We get Hg-i-mnt instead of i-mnt-Hg-W-S cluster, this is because of the specially big Hg atom and the strong coordination ability of i-mnt to Hg. The former makes the Hg-W distance (3.299(1) Å) in **2** and **3** longer than the Pd-W distance (2.917(1) Å) in **11,** and the latter makes all Hg atoms coordinate to i-mnt in **1**.

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