# Crystal structure of *trans*-dichloro(dimethylsulfoxide)(diphenylsulfimide)-platinum(II) toluene hemisolvate, $PtCl_2(C_2H_6SO)(C_{12}H_{10}SNH) \cdot \frac{1}{2}C_7H_8$

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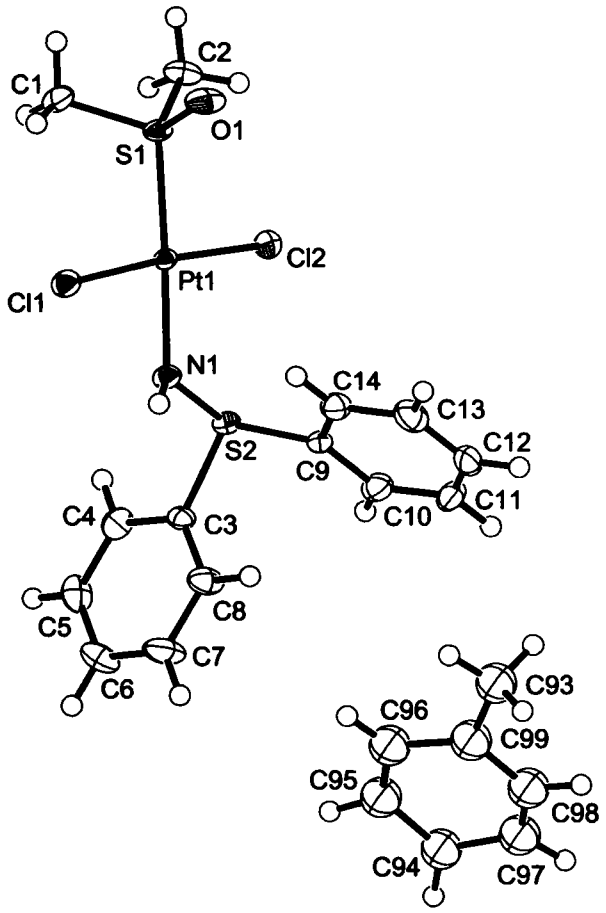


**Abstract**

$C_{17.5}H_{21}Cl_2NOPtS_2$, monoclinic, $P12_1/n1$ (no. 14), $a$ = 13.0955(6) Å, $b$ = 8.5320(6) Å, $c$ = 17.934(1) Å, $\beta$ = 92.776(4)°, $V$ = 2001.4 Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.023, $wR_{ref}(F^2)$ = 0.054, $T$ = 100 K.

**Source of material**

A solution of $Me_2SO$ (12 mg, 0.15 mmol) in water (1 mL) was added dropwise to a solution of $K_2[PtCl_4]$ (59 mg, 0.14 mmol) in water (2 mL) at 20-25 °C. The mixture was stirred for 4-5 h at room temperature until the color of the solution turned from reddish-orange to yellow. Then a solution of $Ph_2S{=}NH$ (31 mg, 0.14 mmol) in $Me_2CO$ (1 mL) was added. The formation of brownish-yellow precipitate was observed, whereupon the reaction mixture was stirred overnight at room temperature. Then the precipitate was separated by filtration and dried at room temperature (yield 62 mg, 77 % based on the starting $K_2[PtCl_4]$). Suitable crystals of the title compound for X-ray study were obtained by slow evaporation of a toluene-dichloromethane solution at room temperature.

**Experimental details**

The toluene solvent is disordered over two sites with equal occupancy of 0.5. There is half a molecule of toluene in the asymmetric unit. Due to the disorder the toluene carbons were refined only isotropically with equal $U_{iso}$. The NH hydrogen was located from the Fourier difference map and refined isotropically. Other hydrogens were positioned geometrically and allowed to ride on their parent atoms, with $d$(C—H) = 0.95 Å – 0.98 Å, and $U_{iso}$ = (1.2 – 1.5) $U_{eq}$ (parent atom).

**Discussion**

*S,S*-Diphenylsulfimide, $Ph_2S{=}NH$, has proved to act as an effective *N*-donor ligand to a range of metals, such as $Cu^{II}$ [1-4], $Ni^{II}$ [5], $Co^{II}$ [6,7], $Fe^{II}$ [7], $Pd^{II}$ [8], and $Pt^{II}$ [9-12]. The only example of a sulfimide unit bound through the sulfur atom as opposed to the nitrogen was found in the case of $Pt^{II}$ when $[PtCl_2(MeCN)_2]$ was employed as a starting material which results in a metal assisted addition of the sulfimide to the acetonitrile [10,11]. Complexes containing $Ph_2S{=}NH$ currently attract significant attention, due to their ability to exhibit such important features as strong hydrogen bonding between the sulfimide NH groups and the counter-ions [6], unexpected ability to crystallize in either square-planar or pseudo-tetrahedral environments [4], and unique cell formation [2]. Furthermore, $Ph_2S{=}NH$ was proved to be a very useful co-ligand in the preparation of MOF systems [1].

The title complex belongs to the class of square-planar platinum(II) species bearing two $Cl^-$ ligands in *trans*-position. The remaining coordination sites are occupied by *S,S*-diphenylsulfimide and dimethyl sulfoxide. *trans*-Arrangement of the complex is the result of a significant *trans*-effect of sulfoxides compared to chloride ligands facilitating the formation of kinetically controlled *trans*-isomers. The Pt—Cl bond distances ($d$(Pt1—Cl1) = 2.307 Å, $d$(Pt1—Cl2) = 2.300 Å) agree well with those in the previously characterized platinum(II) chloride compounds [13,14]. The Pt—S bond distance is 2.216 Å, which corresponds to the mean value of the Pt—S bond for S-bound sulfoxides [15,16]. In the coordinated *S,S*-diphenylsulfimide the value of the S=N bond length ($d$(S2—N2) = 1.620 Å) is in a good agreement with the previously reported distances for the S=N double bond in the metal-bound $Ph_2S{=}NH$ [3,5,12].

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**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | pale yellow block, size 0.04 × 0.06 × 0.24 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 74.92 $cm^{-1}$ |
| Diffractometer, scan mode: | Nonius KappaCCD, $\varphi/\omega$, $\kappa$ offset |
| $2\theta_{max}$: | 50° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 16804, 3518 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 3283 |
| $N(param)_{refined}$: | 218 |
| Programs: | SIR97 [17], SHELXL-97 [18] |

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | Occ. | x | y | z | $U_{iso}$ |
|---|---|---|---|---|---|---|
| H(1A) | 4e | | 0.2981 | 0.2210 | 0.6323 | 0.037 |
| H(1B) | 4e | | 0.3299 | 0.0940 | 0.6949 | 0.037 |
| H(1C) | 4e | | 0.3487 | 0.2765 | 0.7109 | 0.037 |
| H(2A) | 4e | | 0.2619 | 0.2681 | 0.8352 | 0.036 |
| H(2B) | 4e | | 0.2442 | 0.0835 | 0.8258 | 0.036 |
| H(2C) | 4e | | 0.1515 | 0.1944 | 0.8470 | 0.036 |
| H(4) | 4e | | −0.0062 | −0.5100 | 0.6426 | 0.026 |
| H(5) | 4e | | −0.0275 | −0.7171 | 0.5581 | 0.029 |
| H(6) | 4e | | −0.1629 | −0.7149 | 0.4689 | 0.033 |
| H(7) | 4e | | −0.2777 | −0.5065 | 0.4639 | 0.038 |
| H(8) | 4e | | −0.2573 | −0.2970 | 0.5479 | 0.029 |
| H(10) | 4e | | −0.3039 | −0.2957 | 0.7085 | 0.027 |
| H(11) | 4e | | −0.4527 | −0.1451 | 0.7161 | 0.036 |
| H(12) | 4e | | −0.4548 | 0.1155 | 0.6772 | 0.036 |
| H(13) | 4e | | −0.3089 | 0.2290 | 0.6312 | 0.034 |
| H(14) | 4e | | −0.1597 | 0.0804 | 0.6223 | 0.025 |
| H(01) | 4e | | −0.035(4) | −0.115(7) | 0.580(3) | 0.02(1) |
| C(94) | 4e | 0.5 | 0.4677(8) | −0.215(2) | 0.5106(7) | 0.039(1) |
| H(94) | 4e | 0.5 | 0.4446 | −0.3245 | 0.5056 | 0.046 |
| C(95) | 4e | 0.5 | 0.5626(9) | −0.138(2) | 0.4840(7) | 0.039 |
| H(95) | 4e | 0.5 | 0.6067 | −0.2239 | 0.4701 | 0.046 |
| C(96) | 4e | 0.5 | 0.5835(9) | 0.018(1) | 0.4721(7) | 0.039 |
| H(96) | 4e | 0.5 | 0.6457 | 0.0551 | 0.4533 | 0.046 |
| C(97) | 4e | 0.5 | 0.3939(9) | −0.097(2) | 0.5297(7) | 0.039 |
| H(97) | 4e | 0.5 | 0.3320 | −0.1270 | 0.5512 | 0.046 |
| C(98) | 4e | 0.5 | 0.4117(9) | 0.049(2) | 0.5178(7) | 0.039 |
| H(98) | 4e | 0.5 | 0.3576 | 0.1183 | 0.5282 | 0.046 |
| C(99) | 4e | 0.5 | 0.5004(8) | 0.120(2) | 0.4914(7) | 0.039 |
| C(93) | 4e | 0.5 | 0.5099(9) | 0.293(2) | 0.4903(7) | 0.039 |
| H(93A) | 4e | 0.5 | 0.5758 | 0.3217 | 0.4705 | 0.058 |
| H(93B) | 4e | 0.5 | 0.5060 | 0.3335 | 0.5411 | 0.058 |
| H(93C) | 4e | 0.5 | 0.4543 | 0.3372 | 0.4584 | 0.058 |

**Table 3.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | x | y | z | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| C(1) | 4e | 0.3029(3) | 0.1999(6) | 0.6861(3) | 0.016(2) | 0.024(3) | 0.034(3) | −0.006(2) | 0.001(2) | −0.004(2) |
| C(2) | 4e | 0.2131(4) | 0.1871(6) | 0.8183(3) | 0.030(3) | 0.023(3) | 0.019(2) | −0.005(2) | −0.007(2) | −0.003(2) |
| C(3) | 4e | −0.1298(3) | −0.3857(5) | 0.6021(2) | 0.018(2) | 0.012(2) | 0.017(2) | −0.003(2) | 0.001(2) | −0.001(2) |
| C(4) | 4e | −0.0612(4) | −0.5094(6) | 0.6061(3) | 0.019(2) | 0.023(3) | 0.023(2) | 0.000(2) | −0.000(2) | 0.005(2) |
| C(5) | 4e | −0.0741(4) | −0.6317(6) | 0.5561(3) | 0.030(3) | 0.012(2) | 0.032(3) | 0.004(2) | 0.009(2) | 0.005(2) |
| C(6) | 4e | −0.1544(4) | −0.6305(6) | 0.5032(3) | 0.042(3) | 0.016(3) | 0.025(3) | −0.002(2) | 0.000(2) | −0.005(2) |
| C(7) | 4e | −0.2224(4) | −0.5066(6) | 0.5003(3) | 0.036(3) | 0.027(3) | 0.030(3) | −0.001(2) | −0.014(2) | −0.009(2) |
| C(8) | 4e | −0.2107(4) | −0.3824(6) | 0.5499(3) | 0.027(3) | 0.016(2) | 0.028(3) | 0.002(2) | −0.008(2) | −0.002(2) |
| C(9) | 4e | −0.2189(3) | −0.1195(5) | 0.6640(2) | 0.013(2) | 0.019(2) | 0.015(2) | −0.001(2) | −0.002(2) | −0.004(2) |
| C(10) | 4e | −0.3053(3) | −0.1895(6) | 0.6926(3) | 0.020(2) | 0.028(3) | 0.019(2) | −0.005(2) | 0.002(2) | −0.001(2) |
| C(11) | 4e | −0.3930(4) | −0.1000(7) | 0.6971(3) | 0.015(2) | 0.048(4) | 0.026(3) | −0.006(2) | 0.004(2) | −0.010(2) |
| C(12) | 4e | −0.3942(4) | 0.0551(7) | 0.6740(3) | 0.020(2) | 0.042(3) | 0.027(3) | 0.007(2) | −0.004(2) | −0.017(2) |
| C(13) | 4e | −0.3077(4) | 0.1224(6) | 0.6465(3) | 0.030(3) | 0.024(3) | 0.031(3) | 0.008(2) | −0.006(2) | −0.007(2) |
| C(14) | 4e | −0.2193(4) | 0.0347(6) | 0.6413(3) | 0.021(2) | 0.020(2) | 0.022(2) | −0.003(2) | 0.001(2) | −0.002(2) |
| N(1) | 4e | −0.0155(3) | −0.1309(5) | 0.6237(2) | 0.016(2) | 0.020(2) | 0.015(2) | −0.005(2) | 0.001(2) | 0.001(2) |
| O(1) | 4e | 0.1441(3) | 0.3770(4) | 0.7128(2) | 0.027(2) | 0.010(2) | 0.044(2) | 0.002(1) | −0.014(2) | −0.003(2) |
| S(1) | 4e | 0.18008(8) | 0.2144(1) | 0.72231(6) | 0.0147(5) | 0.0098(5) | 0.0220(6) | −0.0006(4) | −0.0044(4) | −0.0007(4) |
| Cl(1) | 4e | 0.14185(8) | 0.0575(1) | 0.55794(6) | 0.0179(5) | 0.0223(6) | 0.0186(5) | −0.0039(4) | 0.0020(4) | 0.0001(4) |
| Cl(2) | 4e | −0.00152(8) | −0.0009(1) | 0.78565(6) | 0.0184(5) | 0.0235(6) | 0.0186(5) | −0.0009(4) | 0.0023(4) | −0.0027(4) |
| S(2) | 4e | −0.10167(8) | −0.2288(1) | 0.66587(6) | 0.0148(5) | 0.0142(5) | 0.0156(5) | −0.0030(4) | −0.0011(4) | 0.0008(4) |
| Pt(1) | 4e | 0.07614(1) | 0.03161(2) | 0.674356(9) | 0.01016(9) | 0.0097(1) | 0.0171(1) | −0.00006(6) | −0.00123(6) | −0.00095(6) |

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