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***N*<sup>1</sup>,*N*<sup>1</sup>-Dimethyl-3-oxopiperazinium(1+)  
Trichloro(dimethyl sulfoxide-*S*)-  
platinate(1-), (C<sub>6</sub>H<sub>13</sub>N<sub>2</sub>O)[PtCl<sub>3</sub>(C<sub>2</sub>H<sub>6</sub>OS)]**

NORA VELDMAN AND ANTHONY L. SPEK

*Bijvoet Center for Biomolecular Research,  
Department of Crystal and Structural Chemistry,  
Utrecht University, Padualaan 8, 3584 CH Utrecht,  
The Netherlands*

MARIEKE J. BLOEMINK, JACO P. DORENBOS,  
ROB J. HEETEBRIJ AND JAN REEDIJK

*Leiden Institute of Chemistry, Gorlaeus Laboratories,  
Leiden University, PO Box 9502, 2300 RA Leiden,  
The Netherlands*

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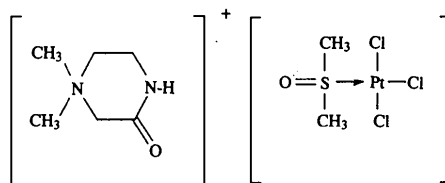
**Abstract**

The title compound, *N*<sup>1</sup>,*N*<sup>1</sup>-dimethyl-3-oxopiperazinium trichloro(dimethyl sulfoxide-*S*)platinate(II), (C<sub>6</sub>H<sub>13</sub>N<sub>2</sub>O)[PtCl<sub>3</sub>(C<sub>2</sub>H<sub>6</sub>OS)], was obtained from the reaction of PtCl<sub>2</sub>(dms<sub>o</sub>)<sub>2</sub> and the chloride salt of *N*<sup>1</sup>,*N*<sup>1</sup>-dimethyl-3-oxopiperazinium (dmpd). The dmpd cation is observed in a conjugated amide form and is hydrogen bonded to the anion via an N—H···O bridge [N···O = 3.14 (2) Å].

**Comment**

As part of a program of studies directed towards the preparation of new chelating amine ligands for platinum(II), with the aim of making novel platinum antitumour compounds, the reaction between bromoacetic acid and dimethylethylenediamine followed by crystallization in HCl was carried out. This reaction was found to yield *N*<sup>1</sup>,*N*<sup>1</sup>-dimethyl-3-oxopiperazinium chloride (dmpdCl), and not the

expected *N*<sup>1</sup>,*N*<sup>1</sup>-dimethylethylenediamine-*N*-acetic acid (Fujii, Kyuno & Tsuchiya, 1970). It was considered of interest to investigate whether this cation would undergo a ring-opening reaction with HCl, to allow a reaction with PtCl<sub>2</sub>. Apparently the dmpd ring is quite stable and, in fact, ionic *N*<sup>1</sup>,*N*<sup>1</sup>-dimethyl-3-oxopiperazinium(1+) trichloro(dimethyl sulfoxide-*S*)platinate(1-) (I) was isolated, as shown by the present X-ray study (Fig. 1).



The structure consists of an ionic lattice comprising the unprecedented cation dmpd and the well known anion [PtCl<sub>3</sub>(dms<sub>o</sub>)]<sup>-</sup>. Comparison of the anionic species with those of previous determinations (see *e.g.* Cantoni, Tiripicchio, Tiripicchio-Camellini & Annibale, 1991; Khodadad & Rodier, 1987; Walba, Richards, Hermsmeier & Haltiwanger, 1987) shows that in the present structure the Pt—Cl bonds are all long, especially the *trans* bond [2.388 (4) Å]. This may be caused by substitutional disorder with Br, probably originating from the bromoacetic acid (this was, however, not pursued any further). For Pt—Cl bonds in the literature, *trans*-chlorine bonds are also seen to be slightly longer than the others. The N2—C3—O1 part of the dmpd cation has a conjugated amide form. Weak hydrogen bonding is observed between the N—H group and the O atom of dms<sub>o</sub> [O2···N2 = 3.14 (2) Å].

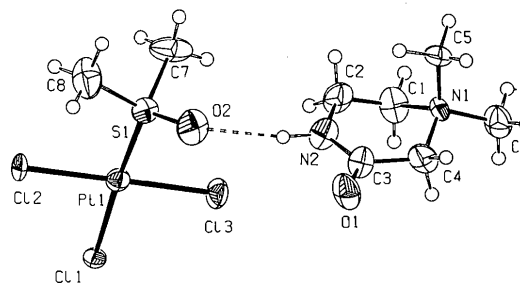


Fig. 1. Thermal motion ellipsoid plot (50% probability level).

**Experimental**

The title compound was crystallized from the reaction mixture of an aqueous chloride solution of the dmpd cation and PtCl<sub>2</sub>(dms<sub>o</sub>)<sub>2</sub> in MeOH.

*Crystal data*

(C<sub>6</sub>H<sub>13</sub>N<sub>2</sub>O)[PtCl<sub>3</sub>-(C<sub>2</sub>H<sub>6</sub>OS)]

Cu Kα radiation  
λ = 1.54184 Å

$M_r = 508.76$   
 Orthorhombic  
 $P2_12_12_1$   
 $a = 7.3225$  (4) Å  
 $b = 9.9618$  (5) Å  
 $c = 21.4130$  (7) Å  
 $V = 1561.98$  (13) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 2.163$  Mg m<sup>-3</sup>

Cell parameters from 25 reflections  
 $\theta = 11-23^\circ$   
 $\mu = 23.05$  mm<sup>-1</sup>  
 $T = 295$  K  
 Transparent needle  
 $0.48 \times 0.18 \times 0.13$  mm  
 Yellowish

C5—N1—C6	113.7 (15)	Cl3—Pt1—S1	86.84 (17)
C2—N2—C3	125 (2)	Pt1—S1—O2	114.6 (6)
N1—C1—C2	111.4 (16)	Pt1—S1—C7	108.9 (7)
N2—C2—C1	115.9 (17)	Pt1—S1—C8	115.5 (10)
O1—C3—N2	122 (2)	O2—S1—C7	106.5 (10)
O1—C3—C4	119.1 (17)	O2—S1—C8	107.9 (11)
N2—C3—C4	118.5 (19)	C7—S1—C8	102.4 (12)
N1—C4—C3	116.1 (16)		

#### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: see below  
 1934 measured reflections  
 1894 independent reflections  
 1750 observed reflections  
 $[I > 2.5\sigma(I)]$

$R_{\text{int}} = 0.058$   
 $\theta_{\text{max}} = 74.89^\circ$   
 $h = -9 \rightarrow 0$   
 $k = 0 \rightarrow 12$   
 $l = -17 \rightarrow 26$   
 3 standard reflections  
 frequency: 60 min  
 intensity variation: 1%

#### Refinement

Refinement on  $F$   
 $R = 0.0470$   
 $wR = 0.0498$   
 $S = 3.57$   
 1750 reflections  
 156 parameters  
 $w = 3.9245/[\sigma^2(F) + 0.000499F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.17$   
 $\Delta\rho_{\text{max}} = 2.03$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.39$  e Å<sup>-3</sup>  
 Extinction correction: none  
 Atomic scattering factors from Cromer & Mann (1968)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

	$x$	$y$	$z$	$U_{\text{eq}}$
O1	0.346 (2)	0.3403 (17)	0.9482 (7)	0.056 (5)
N1	-0.116 (2)	0.4705 (16)	0.9577 (6)	0.033 (4)
N2	0.219 (3)	0.5139 (15)	0.8997 (7)	0.045 (5)
C1	-0.064 (3)	0.6118 (19)	0.9345 (10)	0.049 (7)
C2	0.072 (3)	0.606 (2)	0.8882 (9)	0.052 (7)
C3	0.217 (3)	0.4197 (19)	0.9413 (8)	0.042 (6)
C4	0.053 (3)	0.405 (2)	0.9810 (10)	0.050 (7)
C5	-0.181 (3)	0.386 (3)	0.9049 (8)	0.052 (8)
C6	-0.248 (3)	0.479 (2)	1.0105 (10)	0.051 (7)
Pt1	0.71875 (11)	0.82317 (7)	0.81995 (3)	0.0304 (2)
Cl1	0.8660 (6)	0.9868 (4)	0.88407 (16)	0.0298 (10)
Cl2	0.9362 (6)	0.8644 (5)	0.74324 (17)	0.0379 (13)
Cl3	0.5004 (7)	0.7885 (5)	0.89821 (19)	0.0422 (15)
S1	0.5792 (7)	0.6634 (4)	0.76702 (19)	0.0356 (13)
O2	0.540 (2)	0.5405 (14)	0.8034 (7)	0.056 (5)
C7	0.365 (4)	0.725 (2)	0.7404 (11)	0.062 (9)
C8	0.690 (4)	0.613 (3)	0.6945 (10)	0.069 (9)

Table 2. Selected geometric parameters (Å, °)

O1—C3	1.24 (3)	Pt1—Cl1	2.388 (4)
N1—C1	1.54 (2)	Pt1—Cl2	2.324 (4)
N1—C4	1.49 (3)	Pt1—Cl3	2.342 (5)
N1—C5	1.49 (3)	Pt1—S1	2.205 (4)
N1—C6	1.49 (3)	S1—O2	1.479 (15)
N2—C2	1.44 (3)	S1—C7	1.78 (3)
N2—C3	1.29 (2)	S1—C8	1.82 (2)
C1—N1—C4	107.7 (15)	Cl1—Pt1—Cl2	88.65 (15)
C1—N1—C5	110.5 (15)	Cl1—Pt1—Cl3	89.86 (15)
C1—N1—C6	110.7 (15)	Cl1—Pt1—S1	175.79 (14)
C4—N1—C5	105.9 (16)	Cl2—Pt1—Cl3	178.24 (17)
C4—N1—C6	108.1 (14)	Cl2—Pt1—S1	94.69 (16)

X-ray data were collected for a crystal mounted in a Lindemann glass capillary. A scan angle of  $\Delta\omega = (0.59 + 0.14\tan\theta)^\circ$  was used. Locally modified *CAD-4 Software* (Enraf–Nonius, 1989) was used for data collection. Cell refinement was performed using *SET4* (de Boer & Duisenberg, 1984). *HELENA* (Spek, 1993) was used for data reduction. The structure was solved using *DIRDIF* (Beurskens *et al.*, 1992) and refined with *SHELX76* (Sheldrick, 1976). H atoms were refined riding on their carrier atoms (C—H = 0.98 Å) with two common isotropic displacement parameters. The absolute structure was established by refinement of both enantiomeric structures; that with the lowest  $R$  value was adopted (Flack parameter 0.10).

X-ray data were corrected for absorption with *DIFABS* (Walker & Stuart, 1983). The relatively large correction range ( $T_{\text{min}} = 0.796$ ,  $T_{\text{max}} = 2.624$ ) is in agreement with observed intensity drops of up to 65% for  $360^\circ$   $\psi$  scans of close to axial reflections. A subsequent new data collection carried out on a fragment of the only surviving crystal (one fifth in volume, Mo  $K\alpha$ , 150 K) gave essentially the same structure. Unfortunately, both a refinement based on an absorption correction with *DIFABS* and one based on Gaussian integration gave higher  $R$  values (0.055 and 0.065, respectively). Both *ORTEP* (Johnson, 1965) drawings were indistinguishable.

The material for publication, including Fig. 1, was prepared using *PLATON* (Spek, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1179). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Sels de *S,S'*-(Alcane- $\alpha,\omega$ -diyle)bis-(thiouronium). II. Tétrachloroplatinate(II) de *S,S'*-(Butane-1,4-diyle)bis(thiouronium) Monohydrate

NGUYEN-HUY DUNG ET N. RODIER

Laboratoire de Chimie Physique,  
Minérale et Bioinorganique,  
Faculté des Sciences Pharmaceutiques et Biologiques,  
Université de Paris XI, 5 Rue J.-B. Clément,  
92296 Châtenay-Malabry CEDEX, France

B. VIOSSAT

Laboratoire de Chimie Générale,  
UFR de Médecine et de Pharmacie,  
Université de Poitiers, 34 Rue de Jardin des Plantes,  
86034 Poitiers CEDEX, France

J. C. LANCELOT

Laboratoire de Chimie Thérapeutique,  
UFR de Pharmacie, Université de Caen,  
1 Rue Vaubénard, 14032 Caen CEDEX, France

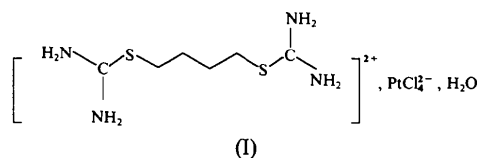
(Reçu le 18 octobre 1993, accepté le 8 février 1994)

### Abstract

The structure of *S,S'*-(1,4-butanediyl)bis(thiouronium) tetrachloroplatinate(II), (C<sub>6</sub>H<sub>16</sub>N<sub>4</sub>S<sub>2</sub>)[PtCl<sub>4</sub>].H<sub>2</sub>O, consists of square-planar PtCl<sub>4</sub><sup>2-</sup> anions and BTUB<sup>2+</sup> cations [where BTUB<sup>2+</sup> is the bis-protonated form of the organic ligand 1,4-butanediylbis(thiourea)]. This ligand exhibits a centre of symmetry and packs in an extended *trans* configuration. The water molecule is involved in an O—H...N hydrogen bond with the BTUB<sup>2+</sup> cation.

### Commentaires

Les tétrahalogénométallates(II) d'alcane- $\alpha,\omega$ -diylebis(ammonium) présentant une structure feuilletée du type perovskite ont fait l'objet de nombreuses études structurales (Tichy, Benes, Kind & Arend, 1980). Leur formule générale peut s'écrire LH<sub>2</sub>, MX<sub>4</sub> [L = H<sub>3</sub>N—(CH<sub>2</sub>)<sub>n</sub>—NH<sub>3</sub>, M = Cu, Mn, Fe, etc., et X = Cl, Br ou I]. La famille à laquelle appartient le produit étudié peut être représentée par la même formule à condition de désigner par L le composé *S,S'*-(alcane- $\alpha,\omega$ -diyle)bis(thiourée). Le nombre n d'atomes de carbone contenus dans L (Lancelot, 1993) peut varier de 4 à 12. Ce mémoire est consacré à [(H<sub>2</sub>N)<sub>2</sub>CS(CH<sub>2</sub>)<sub>4</sub>SC(NH<sub>2</sub>)<sub>2</sub>][PtCl<sub>4</sub>].H<sub>2</sub>O (I). L'étude cristallographique de ce dernier a été entreprise dans le but de préciser la géométrie du cation. Elle fait suite à celle du tétrachloroplatinate(II) de *S,S'*-(octane-1,8-diyl)bis(thiouronium) (Viossat, Nguyen-Huy Dung & Lancelot, 1994).



Le platine étant centre de symétrie, les quatre atomes de chlore auxquels il est lié réalisent un quadrilatère plan. Celui-ci est très proche d'un carré puisque les différences entre les distances Pt—Cl sont de l'ordre des incertitudes et que l'angle Cl(1)—Pt—Cl(2) est égal à 90,65 (6)°.

Comme l'anion, le cation possède la symétrie  $\bar{1}$ . La Fig. 1 et les angles de torsion rapportés dans le Tableau 2 montrent que sa configuration est tout *trans*. Il est approximativement plan puisque les distances des atomes qui le constituent au plan moyen calculé avec les mêmes atomes ne dépassent pas 0,196 (6) Å. Il résulte de la protonation que les distances C(11)—N(12) et C(11)—N(13) sont égales aux incertitudes près, alors que dans le coordination isothiourée présent dans [Au{SC(NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Br (Porter, Fackler, Costamagna & Schmidt, 1992), elles sont longues respectivement de 1,40 (2) et de 1,26 (2) Å. La différence entre S—C(1) [1,799 (7) Å] et S—C(11) [1,734 (5) Å] est due au caractère partiel de double liaison de S—C(11).

Ces distances ne sont pas significativement différentes de leurs homologues respectives dans le *p*-chlorobenzoate de *S*-méthylthiouronium (Kennard & Walker, 1963). Quant aux liaisons C<sub>sp<sup>2</sup></sub>—C<sub>sp<sup>3</sup></sub>, leurs longueurs sont comparables à celles rencontrées dans le butane-1,4-disulfonate d'argent(I) (Charbonnier, Faure & Loiseleur, 1981). Des liaisons hydrogène, N—H...O, O—H...Cl et N—H...Cl, participent à la cohésion cristalline. Leurs caractéristiques géométriques sont rapportées dans le Tableau 2.