Synthesis and Crystal Structure of Platinum(II) Dichlorodimethylsulfoxide Complex of Tenonitrozole, a 2-Amino-5-nitrothiazole Derivative, an Antimycotic and Trichomonacid Agent

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The crystal structure of *trans*-dichlorodimethylsulfoxide–Tenonitrozole (synthesized from *cis*-$PtCl_2(DMSO)_2$ and tenonitrozole in methanol) was determinated by X-ray analysis.

Keywords X-ray analysis; crystal structure determination; platinum(II) complex; (2′-thenoyl)-2-amino-5-nitrothiazole.

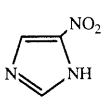
Farrell *et al.* have described the synthesis and properties of some nitroimidazole complexes of platinum(II) and palladium(II): *cis*-(MCl_2L_2) complexes were obtained from L = 5-nitroimidazole ligands whereas *trans*-(MCl_2L_2) were synthesized for 2-nitroimidazole and misonidazole ligands.[1]

On the other hand, the 2-amino-5-nitrothiazole is characterizd by several possible centres of coordination, the nitrogen ring, the nitro group, the sulphur ring, π electrons of the ring and the exocyclic nitrogen. Therefore, metal complexes of this ligand with Co(II), Ni(II), Cu(II), Cd(II), Cu(I), Ag(I)[2] or with palladium salts[3] and rhodium(II) carboxylates[4] were synthesized. The crystal structure of the later complex was confirmed by three dimensional X-ray structure analysis.

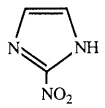
To our knowledge, the complexation by metal ions of tenonitrozole (which includes an aminonitrothiazole moiety) has not been described. We report here the synthesis and crystal structure of dichlorodimethylsulfoxide platinum(II) with tenonitrozole, the chemical formula of which is (2′-thenoyl)-2-amino-5-nitrothiazole.

Tenonitrozole is an antimycotic and trichomonacid drug. It may be solvated (or not) by dimethylformamide, the crystal structures of which were solved by our group.[5,6] We thought it would be of interest to extend our research on Pt(II) complexes.

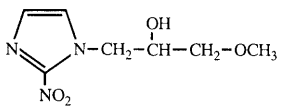
Equimolar amounts of each reactant (Tenonitrozole and *cis*-$PtCl_2(DMSO)_2$) were used and dissolved in methanol at 60 °C. The mixture was mechanically stirred for 5 h at the same temperature. The precipitate was filtered, washed with a methanol solution and then dried with diethyloxide and air. The neutral adduct was recrystallized in dichloromethane.



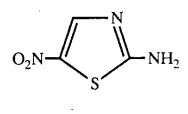
5-nitroimidazole



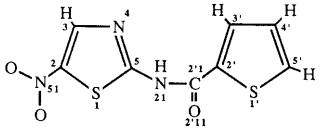
2-nitroimidazole



misonidazole



2-amino-5-nitrothiazole



tenonitrozole

Anal. Calcd for $C_{10}H_{11}Cl_{12}N_3O_4PtS_3$ (yellow parallelepipeds): C, 20.04; H, 1.85; N, 7.01. Found: C, 19.92; H, 1.83; N, 6.95. *cis*-$PtCl_2(DMSO)_2$ was synthesized by a method similar to that reported by Kukushkin *et al.*[7]

The crystallographic data was as follows: space group $Pna2_1$; $Z=4$; cell constants: $a=10.120(1)$, $b=22.660(1)$, $c=7.6312(3)$ Å; density, $D_x=2.27$, $D_m=2.23(2)$ g·cm^{-3}. All data were collected on an Enraf Nonius CAD4 diffractometer using graphite-monochromatized Mo$K\alpha$ radiation.

The structure was solved by using the standard Patterson techniques to find the Pt atom and the normal sequence of least-squares and difference Fourier cycles to locate all other atoms with Crystals.[8] Atomic scattering factors were taken from "International Tables for X-Ray crystallography" and anomalous corrections were applied to the curves for platinum and chloride. 1600 reflections satisfying the criterion $F>3\sigma(F)$ were retained; a final refinement led to $R=0.034$ and $R_w=0.037$. The computations were carried out on a VAX 11/725 computer. The final atomic coordinates are listed in Table II. Bond lengths and

TABLE I

Atom	*x*	*y*	*z*	*U*(eqv)
Pt	0.1679 (5)	0.24217 (2)	−0.0002 (5)	0.0327
Cl(1)	0.0328 (6)	0.2673 (2)	0.2495 (9)	0.0591
Cl(2)	0.2788 (5)	0.2206 (2)	−0.2366 (8)	0.0526
S(1)	0.1718 (5)	0.4409 (2)	−0.1031 (8)	0.0405
S(1′)	0.4498 (5)	0.4616 (2)	0.522 (1)	0.0524
S(11)	0.1723 (5)	0.1508 (2)	0.1151 (8)	0.0393
O(2′11)	0.296 (1)	0.4674 (5)	0.186 (2)	0.0519
O(12)	0.055 (1)	0.1161 (6)	0.090 (2)	0.0566
O(511)	−0.002 (2)	0.4002 (7)	−0.533 (3)	0.0815
O(512)	0.072 (2)	0.4823 (6)	−0.432 (2)	0.0712
N(3)	0.145 (1)	0.3272 (5)	−0.080 (2)	0.0332
N(21)	0.255 (1)	0.3692 (6)	0.164 (2)	0.0417
N(51)	0.050 (2)	0.4303 (8)	−0.420 (2)	0.0503
C(2)	0.195 (1)	0.3750 (6)	0.002 (4)	0.0283
C(4)	0.091 (2)	0.3422 (7)	−0.239 (2)	0.0369
C(5)	0.098 (2)	0.3990 (8)	−0.267 (2)	0.0418
C(2′)	0.364 (2)	0.4064 (7)	0.418 (2)	0.0423
C(3′)	0.371 (1)	0.3530 (6)	0.509 (4)	0.0395
C(4′)	0.443 (2)	0.3599 (8)	0.674 (3)	0.0463
C(5′)	0.492 (2)	0.4162 (8)	0.691 (2)	0.0466
C(2′1)	0.304 (2)	0.4178 (8)	0.247 (2)	0.0422
C(23)	0.310 (2)	0.1113 (7)	0.035 (3)	0.0518
C(24)	0.215 (2)	0.1509 (8)	0.344 (2)	0.0417

U(eqv) = 1/3 trace (*U*).

Table II. Bond Lengths (Å) and Angles (°) with Their e.s.d.'s in Parentheses

Distance (Å)		Angles (°)	
Pt–Cl(1):	2.3761 (7)	Cl(2)–Pt–Cl(1):	178.6 (3)
Pt–Cl(2):	2.216 (7)	S(11)–Pt–Cl(1):	86.2 (2)
Pt–S(11):	2.253 (5)	S(11)–Pt–Cl(2):	95.0 (2)
Pt–N(3):	2.03 (1)	N(3)–Pt–Cl(1):	88.2 (4)
S(1)–C(2):	1.71 (2)	N(3)–Pt–Cl(2):	90.5 (4)
S(1)–C(5):	1.74 (2)	N(3)–Pt–S(11):	174.2 (5)
C(2)–N(3):	1.35 (2)	C(5)–S(1)–C(2):	85.5 (11)
N(3)–C(4):	1.38 (2)	S(1)–C(2)–N(3):	115.4 (19)
C(4)–C(5):	1.31 (2)	C(2)–N(3)–C(4):	111.3 (15)
C(5)–N(51):	1.45 (2)	N(3)–C(4)–C(5):	111.0 (16)
S(11)–O(12):	1.44 (1)	C(4)–C(5)–S(1):	116.7 (15)
S(11)–C(13):	1.76 (2)	N(51)–C(5)–C(4):	126.1 (19)
S(11)–C(14):	1.80 (2)	N(51)–C(5)–S(1):	117.2 (14)
N(51)–O(511):	1.22 (2)	C(5)–N(51)–O(511):	116.3 (16)
N(51)–O(512):	1.20 (2)	O(511)–N(51)–O(512):	118.3 (18)
C(2)–N(21):	1.38 (3)	O(512)–N(51)–C(5):	125.2 (18)
N(21)–C(2′1):	1.36 (2)	S(1)–C(2)–N(21):	124.4 (16)
C(2′1)–O(2′11):	1.22 (2)	N(3)–C(2)–N(21):	120.1 (14)
C(2′1)–C(2′):	1.46 (3)	C(2)–N(21)–C(2′1):	119.8 (15)
C(2′)–C(3′):	1.40 (3)	N(21)–C(24)–C(2′):	115.1 (16)
C(3′)–C(4′):	1.47 (3)	N(21)–C(2′1)–O(2′11):	122.7 (17)
C(4′)–C(5′):	1.38 (2)	O(2′11)–C(2′1)–C(2′):	122.2 (17)
C(5′)–S(1′):	1.71 (2)	C(2′1)–C(2′)–S(1′):	119.6 (14)
S(1′)–C(2′):	1.72 (2)	C(2′1)–C(2′)–C(3′):	128.1 (17)
		S(1′)–C(2′)–C(3′):	112.0 (15)
		C(2′)–C(3′)–C(4′):	111.1 (14)
		C(3′)–C(4′)–C(5′):	111.2 (16)
		C(4′)–C(5′)–S(1′):	113.4 (15)
		C(5′)–S(1′)–C(2′):	92.2 (9)
		Pt–S(11)–O(12):	114.2 (6)
		Pt–S(11)–C(13):	111.8 (7)
		Pt–S(11)–C(14):	113.0 (7)
		O(12)–S(11)–C(13):	109.2 (9)
		O(12)–S(11)–C(14):	109.1 (9)
		C(13)–S(11)–C(14):	98.5 (11)

Table III. Torsion Angles (°)

	In the title complex	In the free ligand
N(3)–C(2)–N(21)–C(2′1):	−179 (2)	179.0 (3)
S(1)–C(2)–N(21)–C(2′1):	−2 (2)	−0.9 (4)
C(2)–N(21)–C(2′1)–C(2′):	180 (2)	179.6 (6)
C(2)–N(21)–C(2′1)–O(2′1):	1 (3)	−0.3 (7)
N(21)–C(2′1)–C(2′)–C(3′):	−4 (3)	15.1 (5)
N(21)–C(2′1)–C(2′)–S(1′):	171 (1)	167.5 (2)

distances are given in Table III.[9] The figure was drawn by using the program ORTEP.[10]

The platinum atom is in nearly-square planar coordination and is bonded to tenonitrozole through the N(3) position of the thiazole ring, to sulfur of the dimethylsulfoxide (DMSO) molecule, and to two chlorine atoms in a *trans*-square configuration (Figure). The Pt–Cl(2) bond is shorter that of the Pt–Cl(1) and falls below the range of the reported values for the Pt(II)–Cl bond in the related compounds (2.30—2.42 Å).[11] The other distances, Pt–N and Pt–S, are as expected from previous X-ray studies. The

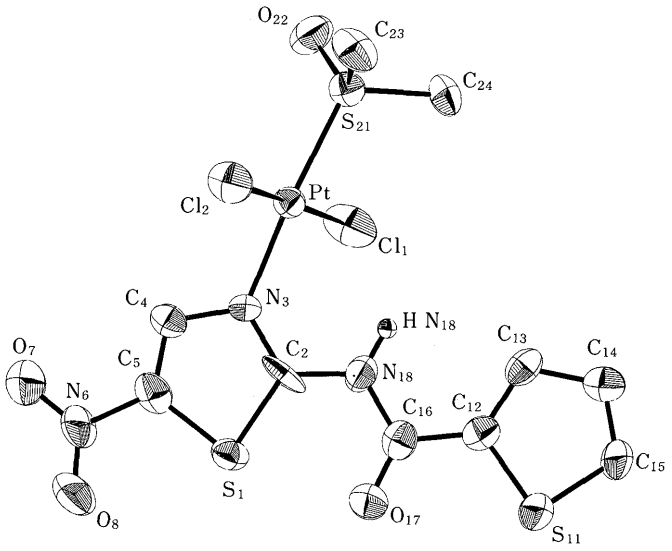


Fig. 1

"mean plane" of the heterocyclic thiazole ring is twisted 119.4° with respect to the $PtCl_2NS$ "mean plane": this value is in accordance with that found by Farrell *et al.*[1] in *trans*-dichloro bis(misonidazole) platinum(II) (dihedral angle: 124°). In the title compound, the NO_2 group lies almost in the "mean plane" of the thiazole ring with a dihedral angle of 5.4°, while in the complex,[1] the same NO_2 group lies out of the "mean plane" of the imidazole ring with a loss of coplanarity.

As shown by the torsion angles (Table III), the ligand in the title complex exhibits the same conformation as in the free ligand.

The closest non-bonded contact between non-hydrogen atoms in the unit-cell is: 2.91(2) Å.

References and Notes

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