Molecular and crystal structures of *cis*-Pt(DMSO)(C_2H_5CN)Cl_2 and Cl(DMSO)Pt(μ-N(CH_3)CHO)$_2$Pt(DMSO)Cl

Fernande D. Rochon, Pi-Chang Kong and Robert Melanson
Département de Chimie, Université du Québec à Montréal, C P. 8888, Succ A, Montreal, Que, H3C 3P8 (Canada)

(Received June 30, 1993; revised September 28, 1993)

Abstract

The aqueous reaction of K[Pt(DMSO)Cl_3] with propionitrile at normal pH (~2.4), gave the product Pt(DMSO)(C_2H_5CN)Cl_2 which was studied by X-ray diffraction methods. The crystals belongs to the monoclinic $P2_1$ space group, with $a = 8.188(3)$, $b = 7.193(3)$, $c = 10.325(4)$ Å, $\beta = 116.76(3)°$ and $Z = 2$. The results have confirmed the *cis* geometry of the complex The coordination around the Pt atom is square planar, but there are important distortions towards a square pyramidal structure The bond distances are: Pt–Cl, 2.337(5), 2.328(3), Pt–S, 2.217(4); Pt–N, 1.951(6) Å The aqueous reaction of K[Pt(DMSO)Cl_3] with *N*-methylformamide at neutral pH (adjusted with NaOH) produced the *N*-methylformamido-bridged dimer Cl(DMSO)Pt(μ-N(CH_3)CHO)$_2$Pt(DMSO)Cl whose crystal structure was determined. The compound belongs to the monoclinic $P2_1/c$ space group, with $a = 8.482(3)$, $b = 10.512(5)$, $c = 24.124(10)$ Å, $\beta = 124.52(2)°$ and $Z = 4$. The results have shown that the dimer is the head-to-tail isomer with the DMSO ligands located in *trans* position to the *O*-formamido atoms. The bond distances are: Pt–Cl, 2.314(3), 2.305(4); Pt–S, 2.183(3), 2.198(3), Pt–O, 2.049(7), 2.040(9); Pt–N, 2.018(9), 2.019(9) Å. The dihedral angle between the two Pt(II) planes is 42°.

Key words: Crystal structures; Platinum complexes; Nitrile complexes; Formamido complexes

Introduction

When K[Pt(DMSO)Cl_3] is dissolved in water, the pH of the solution is 2.35 (0.025 M) indicating some hydrolysis reactions. Its reaction with CH_3CN produced *cis*-Pt(DMSO)(CH_3CN)Cl_2, which was studied by X-ray diffraction [1, 2]. A systematic study of the aqueous reaction of K[Pt(DMSO)Cl_3] with no adjustment of pH and at neutral pH was made with several other alkyl and halo acetonitrile derivatives [3]. The products of these reactions were analyzed by IR and by ^{195}Pt and ^{1}H NMR spectroscopy. The results of the study have shown that at normal pH, the product of the reactions with R–CN (R = alkyl group) is Pt(DMSO)(R–CN)Cl_2. The IR spectra of the compounds suggested *cis* isomers. We have now crystallized the product with C_2H_5CN and have studied its crystal structure by X-ray diffraction methods. The results are discussed in this publication.

When the pH of the K[Pt(DMSO)Cl_3] solution is adjusted with NaOH to about 7 before adding the nitrile ligand (R–CN), acetamido-bridged dimers can be obtained. ^{195}Pt NMR [3] and the determination of the crystal structures of {Pt(DMSO)Cl(μ-NHC(R)O)}$_2$ where R = CH_3 [1], CH(CH_3)$_2$ and C(CH_3)$_3$ [3], have shown that the dimers formed are the head-to-tail isomers. The acetamido ligands were formed from the hydrolysis of R–CN. In these reactions, a blue solution was observed. This blue compound which is very soluble in water, is probably an analogue of platinblau reported in 1907 [4] and whose exact structure is still unknown. It was suggested that it contains deprotonated acetamido ligands bound to platinum(II), the acetamide being produced from the reaction of water with coordinated acetonitrile [5–7]. But attempts to obtain platinblau by direct combination of platinum(II) with acetamide were not successful. The acetamido-bridged dimers can also be formed without adjusting the pH. If the reacting mixture (pH ~2.4) is left at room temperature for several weeks, a blue solution gradually forms and the acetamido-bridged dimer can be eventually obtained. When diacetamide was added to an aqueous solution of K[Pt(DMSO)Cl_3], we also isolated the same dimer as the one obtained with CH_3CN.

We have now studied the aqueous reaction of K[Pt(DMSO)Cl_3] with an N-substituted formamide ligand at neutral pH. We were interested to know if these types of molecules could also form bridged dimers. We have chosen the simplest molecule, *N*-methylformamide for this study. The results are discussed below.

SSDI 0020-1693(93)03723-N

Experimental

The pH values were measured on a pH-meter Radiometre pHM 28 with a Graphic-Controls microelectrode (13-620-253). K_2PtCl_4 was bought from Johnson Matthey Inc. and was purified by crystallization from water before use. The nitrile ligands were obtained from Aldrich.

K[Pt(DMSO)Cl$_3$] was prepared by the published method [8].

cis-Pt(DMSO)(C$_2$H$_5$CN)Cl$_2$ (**I**) was prepared as already reported [3].

{Cl(DMSO)Pt(μ-N(CH$_3$)CHO)}$_2$ (II). K[Pt(DMSO)-Cl$_3$] (0.2 g) was dissolved in 5 ml of distilled water and the pH of the solution was adjusted to 6.7 with 0.1 M NaOH. A quantity of 0.5 ml of *N*-methylformamide was dissolved in 5 ml of ethanol and the solution added slowly to the Pt salt solution. The beaker was sealed with wax paper and the mixture was left at room temperature until crystals were formed (about 10 days).

Crystallographic measurements and structure resolution

The two crystals were selected after examination under a polarizing microscope for homogeneity. The unit cell parameters and the reflection data were measured on a Syntex P$\bar{1}$ diffractometer using graphite-monochromatized Mo Kα radiation. The crystal data and the experimental details are listed in Table 1. Corrections were made for Lorentz–polarization effects and the anomalous dispersion terms of Pt, S and Cl were included in the calculations [9].

The coordinates of the Pt atoms for the two crystals were determined from a three-dimensional Patterson map and the positions of all the other non-hydrogen atoms were found by the usual Fourier methods. The refinement was done by block cascade procedure [10] for **I** and by full-matrix least-squares calculations for **II**. The refinement of the other enantiomorphic structure of crystal **I** gave higher R values ($R=0.040$ and $R_w=0.038$). Isotropic secondary-extinction corrections [11] were included in the calculations of **II**. The H atoms could not be located, and they were fixed at their calculated positions with $U_{eq}=1.2\times U_{eq}$ of the C to which they are bonded for **I** and $U=0.076$ for **II**. See also 'Supplementary material'.

The scattering curves from the International Tables [9] were used. The calculations for crystal **I** were done on a SHELXTL system [10] and those of crystal **II** on a Cyber 830 with programs already described [12].

Results and discussion

The refined atomic parameters of the two structures are listed in Table 2. Labelled diagrams are shown in Figs. 1 and 2. The The bond distances and angles are reported in Table 3.

cis-Pt(DMSO)(C$_2$H$_5$CN)Cl$_2$

The reaction of K[Pt(DMSO)Cl$_3$] with C_2H_5CN, without adjusting the pH, gave the yellow compound Pt(C_2H_5CN)(DMSO)Cl$_2$.

$$K[Pt(DMSO)Cl_3] + C_2H_5CN \xrightarrow[\text{pH} \sim 2.4]{H_2O} Pt(DMSO)(C_2H_5CN)Cl_2$$

The IR spectrum of the product showed two ν(Pt–Cl) bands at 322 and at 340 cm^{-1} suggesting a *cis* isomer [3]. The crystal structure determination of the compound has now confirmed the *cis* geometry of the complex.

The formation of *cis* isomers might seem surprising because of the large *trans* effect of DMSO. We have suggested that the aqueous reaction of K[Pt(DMSO)Cl$_3$] with the nitrile ligand first produces the *trans* isomer, which would then isomerize to the more stable *cis* compound [3]. The multiple nature of the Pt–S and Pt–N bonds is an important factor for *trans–cis* isomerization The complex Pt(DMSO)$_2$Cl$_2$, which is obtained in aqueous solution, is also a *cis* isomer [12]. It is now known that the first compound formed is *trans*-Pt(DMSO)$_2$Cl$_2$ which rapidly isomerizes to the *cis* isomer. It was suggested that the enhanced π(d–d) bonding is more efficient in the *cis* isomer compared to the *trans* compound [13]. Similarly, since nitriles are capable of accepting π electrons from Pt, the formation of π bonds in the Pt–N and Pt–S bonds in Pt(DMSO)(RCN)Cl$_2$ would be more efficient in the *cis* configuration.

The coordination around the Pt atom is square planar, but there are quite important distortions. The *trans* bonds S–Pt–Cl(1) and Cl(2)–Pt–N form angles of only 165.4(2), and 157.4(2)° respectively. The best (weighted) plane was calculated through the five atoms. The deviations are Pt, −0.1265(2); Cl(1), 0.133(6); Cl(2), 0.126(5); S, 0.161(8); and N, 0.413(7) Å, indicating important distortions towards a square pyramidal structure. No such distortions were observed for *cis*-Pt(DMSO)(CH$_3$CN)Cl$_2$ [1], *cis*-Pt(CH$_3$CN)$_2$Cl$_2$ [14] or Pt(DMSO)$_2$Cl$_2$ [12]

The DMSO ligand is bonded through its S atom and propionitrile through its lone pair of electrons on the N atom. The Pt–Cl(1) bond located in *trans* position to the DMSO ligand is 2.337(5) Å, close to the value observed for *cis*-Pt(DMSO)(CH$_3$CN)Cl$_2$ (2.324(2) Å [1]), while the Pt–Cl(2) bond located in *trans* position to the nitrile ligand (2.328(3) Å) is significantly longer than the one reported for *cis*-Pt(DMSO)(CH$_3$CN)Cl$_2$ (2.282(2) Å [1]). Short Pt–Cl bonds located in *trans* positions to CH$_3$CN were also observed for *cis*-Pt(CH$_3$CN)$_2$Cl$_2$ (2.263–2.277 Å [14]). The Pt–S bond

TABLE 1. Experimental details of the X-ray studies of *cis*-Pt(DMSO)(C_2H_5CN)Cl_2 (**I**) and Cl(DMSO)Pt(μ-N(CH_3)CHO)$_2$Pt(DMSO)Cl (**II**)

	I	**II**
Formula	$C_5H_{11}NOSCl_2Pt$	$C_8H_{20}N_2O_4S_2Cl_2Pt_2$
Formula weight	399.21	733.47
Space group	$P2_1$	$P2_1/c$
a (Å)	8.188(3)	8.482(3)
b (Å)	7.193(3)	10.512(5)
c (Å)	10.325(4)	24.124(10)
β (°)	116.76(3)	124.52(2)
Volume (Å^3)	543.0(4)	1772(1)
Z	2	4
F(000)	368	1344
ρ_{calc} (Mg m^{-3})	2.462	2.748
λ (Mo Kα) (Å)	0.71069	0.71069
μ (Mo Kα) (mm)	13.806	16.47
Crystal faces and distance from center (mm)	(0 0 1), (0 0 −1) (0.082) (0 1 0), (0 −1 0) (0.212) (1 0 −1), (−1 0 1) (0.039)	(1 1 −2), (−1 −1 2) (0.058) (−1 1 2), (1 −1 −2) (0.077) (−1 0 0), (0 −1 2), (0 −1 −2) (0.25)
Absorption	based on crystal faces	based on crystal faces
Transmission factor range	0.092–0.369	0.093–0.208
$2\theta_{max}$ (°)	55	55
Octants	$h, k, l, h, k, -l$	$h, k, l, h, k, -l$
h, k, l	$0 \rightarrow 10$, $0 \rightarrow 8$, $-13 \rightarrow 12$	$0 \rightarrow 11$, $0 \rightarrow 13$, $-31 \rightarrow 25$
Scan technique and rate (°/min)	$2\theta/\theta$, 1–24	$2\theta/\theta$, 1.5–24
Temperature (°)	295	295
No. independent reflections	1451	4095
No. observed reflections	1146 ($I > 2.6\sigma(I)$)	2653 ($I > 3.0\sigma(I)$)
Weight	$1/\sigma^2(F) + 0.0001F^2$	$1/\sigma^2(F)$
R	0.038	0.031
R_w	0.036	0.032
S	1.9	1.35
$(\Delta/\sigma)_{max}$	0.02	0.08
$(\Delta\rho)_{max}$ (e Å^3)	1.2 (close to Pt)	0.95 (close to Pt)

(2.217(4) Å) is normal, while the Pt–N bond is shorter (1.951(6) Å) than a Pt–N(amine) bond, but close to the values observed for *cis*-Pt(CH_3CN)$_2$$Cl_2$ (1.95–1.99 Å [14]) and for *cis*-Pt(DMSO)(CH_3CN)Cl_2 (1.976(7) Å [1]). Nitriles contain empty π^* orbitals which can accept electron density from the metal.

The Pt–N≡C(1)–C(2) segment is almost linear as expected with angles Pt–N–C = 171.3(9)° and N–C(1)–C(2) = 170(1)°. The nitrile bond is normal (1.125(10) Å). The angle Pt–S–O (118.7(6)°) is larger than the Pt–S–C angles (104.2(5) and 110.8(4)°) and O–S–C angles (97.9(6) and 108.6(6)°) as observed for other Pt–DMSO complexes. The S–O and S–C bond lengths are normal, 1.446(12), 1.804(9) and 1.765(12) Å. [12, 15].

Cl(DMSO)Pt(μ-N(CH₃)CHO)₂Pt(DMSO)Cl

The reaction of K[Pt(DMSO)Cl_3] in neutral solution (pH adjusted to ~7 with NaOH) with *N*-methylformamide produced the *N*-methylformamido-bridged dimer as shown by the results of the crystal structure determination.

$$\mathrm{K[(DMSO)Cl_3] + (CH_3)NHCOH \xrightarrow{pH\sim7} Cl(DMSO)Pt(\mu\text{-}N(CH_3)CHO)_2Pt(DMSO)Cl}$$

The structural analysis of the dimer has shown that the compound is the head-to-tail isomer, with the DMSO molecules in *trans* position to the *O*-formamido atoms. This geometry is similar to the structures of the three reported Pt(II) acetamido-bridged dimers [1, 3] synthesized with nitrile ligands. The relatively short Pt---Pt distance (3.031(0.5) Å) is produced by the geometric requirements imposed by the two bridging ligands.

The coordination around each platinum atom is square planar, but there are some slight square-pyramidal distortions. The two Pt atoms are out of their respective plane formed by the four coordinating atoms by −0.1166(4) and 0.1010(4) Å towards each other. The tilt angle between the two weighted Pt planes is 42°.

The Pt–Cl bonds (2.314(3), 2.305(4) Å) are normal. The Pt–S bonds (2.183(3), 2.198(3) Å) are slightly shorter than the average value (2.21 Å) reported for Pt–DMSO complexes [12, 15], but similar to those

TABLE 2. Positional parameters with their e.s.d.s and temperature factors ($\times 10^4$)

Atom	x	y	z	U_{eq}[a]
cis-Pt(DMSO)(C_2H_5CN)Cl_2 (I)				
Pt	1352(1)	3000	6243(1)	409(2)
Cl(1)	2871(5)	3624(8)	4842(4)	687(9)
Cl(2)	4019(5)	3832(7)	8281(4)	559(9)
S	2(4)	3178(11)	7680(3)	518(8)
O	356(13)	4784(14)	8611(11)	821(12)
N	−890(10)	3360(10)	4448(8)	252(11)
C(1)	−2212(12)	3379(15)	3350(11)	573(12)
C(2)	−3776(12)	3756(14)	1962(11)	465(12)
C(3)	−5428(13)	3945(15)	2239(12)	682(12)
C(4)	−2434(12)	3483(14)	6631(12)	580(12)
C(5)	761(14)	1174(14)	8778(13)	578(12)
Cl(DMSO)Pt(μ-N(CH_3)CHO)$_2$Pt(DMSO)Cl (II)				
Pt(1)	2535.5(5)	1695.9(3)	719.3(2)	215(2)
Pt(2)	5590.7(5)	3369.6(4)	1840.9(2)	266(2)
Cl(1)	4399(4)	−7(2)	812(1)	332(11)
Cl(2)	6284(5)	4746(3)	1263(2)	491(13)
S(1)	1991(3)	2237(2)	−249(1)	247(10)
S(2)	8370(3)	2428(3)	2279(1)	372(10)
O(1)	2667(9)	1000(6)	1538(3)	276(16)
O(2)	3178(10)	4401(6)	1516(4)	422(18)
O(3)	691(11)	3302(7)	−612(4)	305(17)
O(4)	10037(10)	3176(8)	2778(4)	603(18)
N(1)	860(10)	3112(7)	675(4)	302(17)
N(2)	4890(11)	2330(7)	2375(4)	278(17)
C(1)	1480(15)	4104(9)	1054(5)	308(18)
C(2)	3647(12)	1417(8)	2134(4)	265(18)
C(3)	−1192(15)	3005(11)	196(6)	438(19)
C(4)	5733(17)	2713(12)	3077(5)	512(19)
C(5)	4128(16)	2545(11)	−196(6)	408(18)
C(6)	1093(18)	889(10)	−782(5)	489(19)
C(7)	8690(18)	1998(14)	1637(6)	629(19)
C(8)	8450(16)	922(12)	2619(6)	475(19)

$U_{eq} = \frac{1}{3} \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

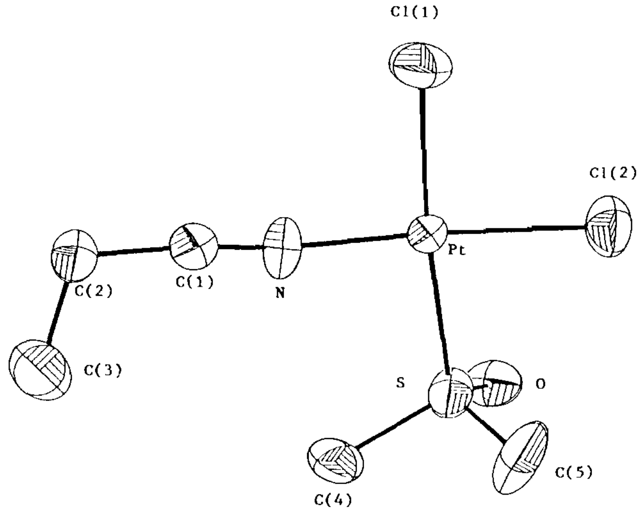

Fig. 1. Labeled diagram of *cis*-Pt(DMSO)C_2H_5CN)Cl_2 (I)

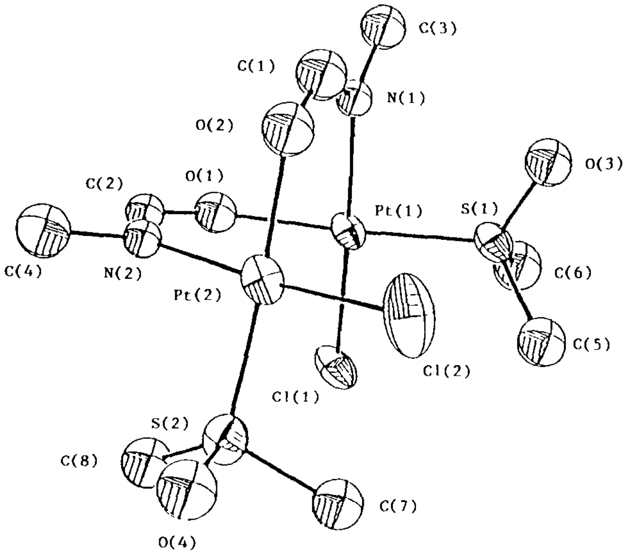

Fig. 2. Labeled diagram of Cl(DMSO)Pt(μ-N(CH_3)CHO)$_2$Pt(DMSO)Cl (II)

reported for the three Pt(II) acetamido-bridged dimers (2.173–2.198 Å) [1, 3]. The results on these dimers are different from those observed in α-pyridonate bridged platinum complexes where the Pt–N (amine or ethylenediamine) distances *trans* to pyridonate oxygen atoms were significantly longer than those *trans* to pyridonate nitrogen atoms, revealing a larger *trans* influence of the O atom. Lippard and co-workers suggested that this *trans* influence originated in more extensive σ-overlap of the Pt–N (pyridonate) bond relative to the Pt–O (amidate) bond [16, 17]. For our dimers, the Pt–S bonds which are located in *trans* position to the Pt–O (acetamido or formamido) bonds are slightly shorter than normal, probably indicating a greater π character of the Pt–S bond.

The Pt–O (2.049(7), 2.040(9) Å) and Pt–N (2.018(9), 2.019(9) Å) bonds are normal and agree well with values found in the acetamido, pyridonate and uracilate dimeric complexes mentioned above. The bond lengths and angles in the two bridging ligands are also normal. The N–C bond distances are 1.29(1), 1.30(1) Å while the O–C bond lengths are 1.26(1), 1.26(1) Å. The angles around C(1) and C(2) are 129(1) and 128(1)°, indicating an sp^2 hybrid. The internal angles at N(1), N(2), O(1) and O(2) are similar varying from 124.5(8) to 127.9(6)°. The moieties N(C)–C–O are planar with the two amido planes almost perpendicular to each other.

The packing of the molecules in the crystal was examined, see 'Supplementary material'. No hydrogen bonding is expected in this type of structure.

Supplementary material

The following are available from the authors on request: anisotropic temperature factors (Table S1),

TABLE 3. Bond distances (Å) and angles (°)

cis-Pt(DMSO)(C_2H_5CN)Cl_2 (**I**)			
Pt–S	2.217(4)	S–Pt–Cl(1)	165.4(2)
Pt–Cl(1)	2.337(5)	S–Pt–Cl(2)	85.8(1)
Pt–Cl(2)	2.328(3)	S–Pt–N	95.1(3)
Pt–N	1.950(6)	Cl(1)–Pt–Cl(2)	88.1(1)
S–O	1.450(12)	Cl(1)–Pt–N	85.5(3)
S–C(4)	1.803(9)	Cl(2)–Pt–N	157.4(2)
S–C(5)	1.763(12)	Pt–S–O	118.7(6)
N–C(1)	1.124(10)	Pt–S–C(4)	110.8(4)
C(1)–C(2)	1.493(11)	Pt–S–C(5)	104.2(5)
C(2)–C(3)	1.509(17)	O–S–C(4)	97.9(6)
		O–S–C(5)	108.6(6)
		C(4)–S–C(5)	117.3(6)
		Pt–N–C(1)	171.3(9)
		N–C(1)–C(2)	170.0(10)
		C(1)–C(2)–C(3)	110.0(10)
Cl(DMSO)Pt(μ-N(CH_3)CHO)$_2$Pt(DMSO)Cl (**II**)			
Pt(1)–Cl(1)	2.314(3)	Pt(2)–Cl(2)	2.305(4)
Pt(1)–S(1)	2.183(3)	Pt(2)–S(2)	2.198(3)
Pt(1)–N(1)	2.018(9)	Pt(2)–N(2)	2.019(9)
Pt(1)–O(1)	2.049(7)	Pt(2)–O(2)	2.040(9)
S(1)–O(3)	1.464(8)	S(2)–O(4)	1.463(9)
S(1)–C(5)	1.77(2)	S(2)–C(7)	1.78(2)
S(1)–C(6)	1.77(1)	S(2)–C(8)	1.77(1)
O(1)–C(2)	1.26(1)	O(2)–C(1)	1.26(1)
N(1)–C(1)	1.29(1)	N(2)–C(2)	1.30(1)
N(1)–C(3)	1.45(2)	N(2)–C(4)	1.47(1)
Pt(1)---Pt(2)	3.031(0.5)		
Cl(1)–Pt(1)–S(1)	91.3(1)	Cl(2)–Pt(2)–S(2)	90.1(1)
Cl(1)–Pt(1)–O(1)	88.3(2)	Cl(2)–Pt(2)–O(2)	88.7(3)
Cl(1)–Pt(1)–N(1)	176.1(3)	Cl(2)–Pt(2)–N(2)	173.9(3)
S(1)–Pt(1)–O(1)	170.7(2)	S(2)–Pt(2)–O(2)	173.4(2)
S(1)–Pt(1)–N(1)	92.0(3)	S(2)–Pt(2)–N(2)	94.2(3)
O(1)–Pt(1)–N(1)	88.1(3)	O(2)–Pt(2)–N(2)	86.5(3)
Pt(1)–S(1)–O(3)	118.1(4)	Pt(2)–S(2)–O(4)	115.3(4)
Pt(1)–S(1)–C(5)	112.5(4)	Pt(2)–S(2)–C(7)	110.4(5)
Pt(1)–S(1)–C(6)	108.2(4)	Pt(2)–S(2)–C(8)	112.0(5)
O(3)–S(1)–C(5)	107.2(6)	O(4)–S(2)–C(7)	107.5(6)
O(3)–S(1)–C(6)	108.0(6)	O(4)–S(2)–C(8)	109.6(6)
C(5)–S(1)–C(6)	101.5(6)	C(7)–S(2)–C(8)	101.1(7)
Pt(1)–O(1)–C(2)	127.9(6)	Pt(2)–O(2)–C(1)	127.0(8)
Pt(1)–N(1)–C(1)	124.5(8)	Pt(2)–N(2)–C(2)	125.1(7)
Pt(1)–N(1)–C(3)	118.5(7)	Pt(2)–N(2)–C(4)	117.3(7)
C(1)–N(1)–C(3)	116.9(10)	C(2)–N(2)–C(4)	117.4(9)
N(1)–C(1)–O(2)	129(1)	N(2)–C(2)–O(1)	128(1)

coordinates of the H atoms (Table S2), weighted least-squares planes (Table S3), stereoscopic views of the unit cell of the two crystals (Figs. 3 and 4), observed and calculated structure factor amplitudes (Table S4) (30 pages).

Acknowledgement

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of the project.

References

1 F D. Rochon, P.C Kong and R. Melanson, *Inorg Chem, 29* (1990) 1352.

2 V.K Belsky, V E Konovalov, V K. Kukushkin and A.I Moiseev, *Inorg Chim Acta, 169* (1990) 101.

3 F D. Rochon, R. Boughzala and R. Melanson, *Can J Chem, 70* (1992) 2476

4 K.A Hoffman and G Bugge, *Berichte, 40* (1907) 1772; *41* (1908) 312.

5 I.I Chernyaev and L.A Nazarova, *Izv Sekt Platiny Drugikh Blagorodn Met., Inst Obshch Neorg Khim, Akad Nauk SSSR, 26* (1951) 101; V.F. Barkovskii and L M Kul'berg, *Izv Sekt Platiny Drugikh Blagorodn Met, Inst Obshch. Neorg Khim, Akad Nauk SSSR, 28* (1954) 235.

6 R D. Gillard and G Wilkinson, *J Chem Soc*, (1964) 2835.

7 D B. Brown, R.D Burbank and M B Robin, *J Am. Chem Soc, 91* (1969) 2895.

8 Y.N. Kukushkin, Y E Vyazmenskii and L I. Zorina, *Russ J. Inorg Chem, 13* (1968) 1573.

9 D T. Cromer, *Acta Crystallogr, 18* (1965) 17; *International Tables for X-ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974.

10 G M. Sheldrick, *SHELXTL,* Revision 4.1, Nicolet XRD Corporation, Madison, WI, USA, 1984

11 P Coppens and W C Hamilton, *Acta Crystallogr, Sect. A, 26* (1970) 71

12 R. Melanson and F.D. Rochon, *Can J Chem., 53* (1975) 2371.

13 J.H Price, A N. Williamson, R.F. Schramm and B B. Wayland, *Inorg Chem., 11* (1972) 1280.

14 F.D Rochon, R. Melanson, H E. Howard-Lock, C J.L. Lock and G Turner, *Can J. Chem, 62* (1984) 860.

15 L.I. Elding and A. Oskarsson, *Inorg Chim Acta, 130* (1987) 209, R Melanson, J. Hubert and F.D. Rochon, *Acta Crystallogr, Sect. B, 32* (1976) 1914; F.D Rochon, P.C Kong and R Melanson, *Acta Crystallogr., Sect C, 41* (1985) 1602, R. Melanson and F D Rochon, *Inorg. Chem, 17* (1978) 679, *Acta Crystallogr, Sect B, 33* (1978) 3571; *34* (1978) 1125; *34* (1978) 941; *Sect. C, 40* (1984) 793; B. Viosset, P. Khodadad and N. Rodier, *Acta Crystallogr, Sect C, 47* (1991) 1317.

16 T.V. O'Halloran, P.K Mascharak, I D. Williams, M.M Roberts and S.J. Lippard, *Inorg Chem., 26* (1987) 1261.

17 A.P. Ginsberg, T V. O'Halloran, P. Fanwick, L.S. Hollis and S.J. Lippard, *J Am Chem Soc, 106* (1984) 5430.