Inorganica Chimica Acta, 130 (1987) 209–213

Synthesis and Crystal Structure of Tetrakis(dimethylsulfoxide) Platinum(II) Bis(trifluoromethanesulfonate)

LARS I. ELDING

Department of Inorganic Chemistry, Chalmers University of Technology, S-41296 Gothenburg, Sweden

and ÅKE OSKARSSON

Department of Chemistry, University College of Sundsvall-Härnösand, P.O. Box 860, S-851 24 Sundsvall, Sweden

(Received November 24, 1986)

Abstract

Crystals of $Pt(DMSO)_4(TFMS)_2$ have been prepared by dissolution of platinum(II) hydroxide in a solution of CF_3SO_3H in DMSO and subsequent evaporation. The structure was determined by use of a CAD-4 diffractometer with monochromatic Mo Kα radiation. The space group is $P\bar{1}$ with $Z = 2$, $a = 8.630(2)$, $b = 9.557(3)$, $c = 16.659(3)$ Å, $\alpha = 73.33(2)$, $\beta = 77.38(2)$ and $\gamma = 79.19(3)°$. The refinement converged to $R = 0.056$. The coordination around platinum is distorted square-planar with two S- and two O-bonded DMSO ligands in a *cis*-arrangement. The four donor atoms and the platinum are coplanar within 0.03 Å. There is a severe steric crowding between the two S-bonded DMSO molecules, which gives rise to a distortion of the bond angles around the platinum. The crowding is minimized as much as possible by a staggered arrangement of oxygen atoms and methyl groups of adjacent ligands. Pt–S bond lengths 2.208(3) and 2.205(4) Å are significantly shorter than those in the corresponding palladium complex, in accordance with a much stronger bond in the case of platinum. Bond length comparisons also indicate that ground state *trans*-influence of S-bonded DMSO probably is about the same in platinum and palladium complexes.

Introduction

Dimethylsulfoxide coordinates to metal ions either via the oxygen or the sulfur atoms [1], which was realized very early [2]. In palladium(II) and platinum(II) complexes sulfur-bonding is predominant. Thus, both Ir [2, 3] and direct structure determinations [4–14] of complexes containing one or two DMSO ligands all indicate S-bonding.

Early spectroscopic studies of solutions of the tetrasolvated cations $M(DMSO)_4^{2+}$, M = Pd, Pt showed that there is probably both O- and S-bonded DMSO ligands in those complexes, due to a balance between steric and electronic factors [15–17]. When the steric crowding increases due to bulky substituents on the sulfoxide, oxygen bonding is predominant in the palladium(II) complexes [18]. A recent structure determination of $Pd(DMSO)_4(BF_4)_2 \cdot DMSO$ verifies those early suggestions: there are two O- and two S-bonded ligands in a *cis*-arrangement in the solid state [19].

Preparation of $Pt(DMSO)_4(ClO_4)_2$ was reported in 1972 [16], but there seems to be no further studies of the structure of compounds of this complex since then. A recent attempt to prepare crystals of $Pt(DMSO)_4(ClO_4)_2$ for a structure determination resulted in $[Pt_2(DMSO)_4(OH)_2](ClO_4)_2$ which contains a hydroxo-bridged dimer [20]. We here report a single crystal X-ray determination of the structure of the trifluoromethanesulfonate salt of the monomeric tetrakis-DMSO platinum(II) cation.

Experimental

Synthesis

150 ml 1.00 M NaOH (Merck p.a.) was added to a stirred solution of 150 ml 9.8 mM $Pt(H_2O)_4(ClO_4)_2$ in 1.00 M $HClO_4$ prepared as described elsewhere [21]. The resulting solution was rapidly titrated to pH = 7.1 (Orion pH-electrode) with 0.100 M NaOH. The light yellow–green precipitate of $Pt(OH)_2 \cdot xH_2O$ (described previously [21]) was allowed to settle for a few min. It was separated from the solution on a Millipore filter (HVLP 02500) and washed quickly with 4 × 1 ml ice-cold water under suction. It was immediately dissolved on the filter by addition of 1.25 ml of a cooled solution, obtained by mixing 2 ml DMSO (Merck Uvasol) and 1 ml CF_3SO_3H (Fluka, purum), and stirring with a stream of nitrogen.

The resulting solution was first yellow–brown and changed within a few minutes to bright yellow.

0020-1693/87/$3.50

It was passed through the filter together with 5 ml DMSO. To remove residual water, it was distilled at *ca.* 65 °C under reduced pressure to a volume of *ca.* 2 ml, whereafter 5 ml DMSO was added and distillation repeated twice. The solution was allowed to cool in an open evaporation dish. Light yellow crystals separated from the now almost colourless solution. The crystals are stable in contact with the supernatant solution.

Structure Determination

A single crystal with the dimensions 0.15 X 0.263 X 0.063 mm was used for the data collection on an Enraf-Nonius CAD-4 diffractometer employing graphite monochromatized Mo Kα radiation (λ = 0.7107 Å). Since the crystal decomposes when exposed to air, it was mounted in a Lindemann glass capillary. Laue symmetry $\bar{1}$ give $P1$ and $P\bar{1}$ as possible choices for the space group ($Z = 2$). Cell dimensions (Table I) were obtained by least-squares calculations of 25 θ-values. The intensity of 4436 reflections in one half of the reflection sphere obeying $3 < \theta < 25°$ were measured with the ω–2θ technique ($\Delta\omega = 0.85 + 0.5 \tan \theta$). The scan interval was extended 25% at both ends for the background measurement. The ratio $\sigma(I)/(I)$ requested in a scan was 0.028 and the maximum recording time was 150 s. Three standard reflections were recorded at regular intervals. The intensity of these reflections decreased 10% during the data collection, most probably due to a slight decomposition of the crystal. The intensities were corrected according to the decrease of the standard reflections. I and $\sigma(I)$ were corrected for Lorentz, polarization and absorption effects, the latter by numerical integration (μ = 63.52 cm^{-1}, transmission factors 0.339–0.675). Only the 3869 reflections with $I > 3\sigma(I)$ were considered significantly different from the background and used in the calculations.

TABLE I. Crystal Data for $Pt(DMSO)_4(CF_3SO_3)_2$

a (Å)	8.630(2)
b (Å)	9.557(3)
c (Å)	16.659(3)
α (°)	73.33(2)
β (°)	77.38(2)
γ (°)	79.19(3)
V (Å^3)	1272.8
D (g cm^{-3})	2.10

The structure was solved by Patterson and difference Fourier methods. The parameters of the non-H atoms were refined in space group $P\bar{1}$ using full-matrix least-squares. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = [\sigma^2/4|F_o|^2 + (0.03|F_o|)^2 + 3.0)]^{-1}$. In the final refinement anisotropic temperature factors were applied to the atoms in the coordination sphere (Pt, S1, S2, O3, O4). The total number of parameters refined was 161. Scattering factors with corrections for anomalous dispersion were taken from International Tables for X-ray Crystallography [22]. The final agreement indices $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_W = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ were 0.056 and 0.080, respectively. A δR-plot resulted in a straight line with a slope of 0.93 and an intercept of –0.08. Computer programs compiled and amended by Lundgren [23] were used. The final positional and thermal parameters are given in Table II. See also 'Supplementary Material'.

Results and Discussion

The compound contains discrete ions $Pt(DMSO)_4^{2+}$ and $CF_3SO_3^-$. Selected interatomic distances and angles within the platinum complex are given in Table III. The coordination geometry is distorted square-planar as shown by Fig. 1. As expected, platinum coordinates two S and two O atoms from different unidentate DMSO-molecules in a *cis*-arrangement. This causes a severe steric crowding in the coordination sphere, as shown by several short van der Waals distances between atoms of adjacent DMSO molecules, *cf.* Table III. However, this does not affect the planarity of the complex: Pt, S1, S2, O3 and O4 are coplanar within 0.03 Å. Instead, the steric repulsion causes distortions of the bond angles around the central platinum within the coordination plane. The largest distortion is observed for the S1–Pt–S2 angle, 95.1°, and it is the result of van der Waals repulsions between O1 and C21, C22 and S2 (Table III). Noteworthy, the repulsions between adjacent DMSO molecules are minimized by a staggered arrangement of O1 and C21, C22 and O4 and C11, C12. O1 and O2 both lie very close to the coordination plane (Table IV), whereas the distances from C11, C12, C21 and C22 to that plane are very similar (1.37 to 1.43 Å, Table IV). All the four distances O4/C11, C12 and O1/C21, C22 lie in the interval 3.05 to 3.25 Å; the sum of the covalent radii of oxygen and methyl is 3.4 Å. Similarly, the distances between O2 and O3, S3 and C32, and between O3, O4 and S4 are equal to or smaller than the sum of the van der Waals radii.

The sulfur atoms S3 and S4 in the two O-bonded DMSO ligands have a free electron pair. The orientation of those two ligands in the coordination sphere is such that both the interatomic repulsions and the interaction between the free electron pair and the other atoms in adjacent DMSO molecules is minimized (Fig. 1).

TABLE II. Atomic Coordinates and Isotropic Temperature Factors with Standard Deviations[a]

Atom	x/a	y/b	z/c	U_{iso} (Å^2)
Pt	0.3291(1)	0.1574(1)	0.2343(1)	0.0313(2)
S1	0.4360(4)	0.0881(4)	0.1164(2)	0.0379(12)
O1	0.3548(13)	−0.0084(13)	0.0912(7)	0.0583(27)
C11	0.4576(21)	0.2482(20)	0.0306(11)	0.0598(41)
C12	0.6398(22)	0.0078(21)	0.1211(12)	0.0652(45)
S2	0.1207(4)	0.0371(4)	0.2646(2)	0.0413(12)
O2	0.0120(13)	0.0604(12)	0.3411(7)	0.0557(26)
C21	0.1774(19)	−0.1545(18)	0.2767(10)	0.0565(40)
C22	0.0146(18)	0.0846(17)	0.1794(9)	0.0476(34)
S3	0.0921(4)	0.3212(4)	0.3618(2)	0.0446(8)
O3	0.2588(10)	0.2279(10)	0.3436(5)	0.0370(32)
C31	0.1471(22)	0.4808(21)	0.3768(12)	0.0661(46)
C32	0.0125(22)	0.2383(21)	0.4706(12)	0.0676(47)
S4	0.5299(4)	0.3882(4)	0.2514(2)	0.0399(8)
O4	0.5245(12)	0.2638(12)	0.2115(6)	0.0524(42)
C41	0.6434(23)	0.5062(22)	0.1671(12)	0.0699(48)
C42	0.6751(24)	0.3123(23)	0.3186(13)	0.0742(51)
S5	0.6703(6)	0.7293(6)	0.3543(3)	0.0676(12)
O51	0.5762(18)	0.7037(18)	0.3028(10)	0.0933(44)
O52	0.7560(24)	0.6026(24)	0.3988(13)	0.1305(65)
O53	0.7603(27)	0.8461(26)	0.3163(14)	0.1449(75)
C51	0.5311(33)	0.7905(33)	0.4339(17)	0.1028(75)
F51	0.4328(23)	0.9067(23)	0.4085(12)	0.1553(67)
F52	0.4239(26)	0.6956(25)	0.4717(13)	0.1712(76)
F53	0.4163(21)	0.1872(21)	0.5042(12)	0.1387(57)
S6	0.1587(6)	0.5556(6)	0.1087(3)	0.0712(12)
O61	0.0689(20)	0.4382(20)	0.1430(11)	0.1038(49)
O62	0.2561(23)	0.5903(23)	0.1536(12)	0.1211(59)
O63	0.2441(26)	0.5626(26)	0.0223(14)	0.1457(75)
C61	0.0192(24)	0.7152(22)	0.0838(13)	0.0702(48)
F61	0.9136(16)	0.7086(15)	0.0411(9)	0.1011(39)
F62	0.0848(18)	0.8361(18)	0.0485(10)	0.1155(45)
F63	0.9301(21)	0.7362(21)	0.1592(12)	0.1415(59)

[a] U_{eq} is given for the anisotropic atoms (Pt, S1, S2, O3, O4) under the heading of U_{iso}. U_{eq} is the equivalent isotropic temperature factor coefficient calculated from the average of the anisotropic temperature factor over all directions.

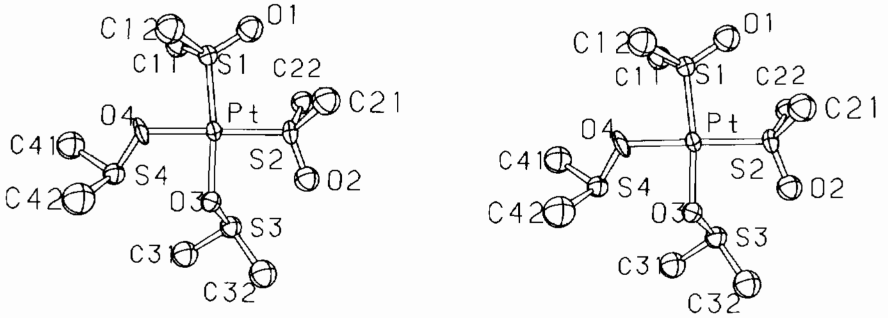

Fig. 1. Stereoscopic view of the cation Pt(DMSO)$_4$$^{2+}$.

A comparison with the previously studied Pd(DMSO)$_4$(BF$_4$)·DMSO structure [19] shows that the arrangement of the DMSO molecules around the two metal ions is very similar, as may be seen from Table IV. In the palladium compound also, there are several short distances between atoms of adjacent DMSO molecules, which give rise to steric crowding. The palladium complex is also planar, with a very similar distortion of the bond angles [19].

The M–S bond lengths in the platinum compound (2.208 and 2.205 Å), however, are significantly shorter than those in the palladium analog

TABLE III. Selected Interatomic Distances (Å) and Angles (°) with Standard Deviations

Pt–S1	2.208(3)	S1–Pt–S2	95.1(1)
Pt–S2	2.205(4)	S2–Pt–O3	91.9(3)
Pt–O3	2.051(9)	O3–Pt–O4	86.6(4)
Pt–O4	2.040(10)	O4–Pt–S1	86.2(3)
		S1–Pt–O3	172.6(3)
		S2–Pt–O4	177.5(3)
S1–O1	1.453(12)	O1–S1–C11	107.6(7)
S1–C11	1.776(18)	O1–S1–C12	109.4(8)
S1–C12	1.791(19)	C11–S1–C12	102.3(8)
		O1–S1–Pt	118.5(5)
S2–O2	1.454(11)	O2–S2–C21	108.8(7)
S2–C21	1.769(17)	O2–S2–C22	109.5(7)
S2–C22	1.761(15)	C21–S2–C22	101.7(7)
		O2–S2–Pt	112.1(5)
S3–O3	1.561(9)	O3–S3–C31	101.9(7)
S3–C31	1.777(19)	O3–S3–C32	104.7(7)
S3–C32	1.794(19)	C31–S3–C32	98.3(9)
		S3–O3–Pt	121.1(5)
S4–O4	1.532(11)	O4–S4–C41	101.6(8)
S4–C41	1.763(20)	O4–S4–C42	103.8(8)
S4–C42	1.777(20)	C41–S4–C42	99.6(9)
		S4–O4–Pt	123.5(6)
O1–C21	3.178(19)		
O1–C22	3.074(19)		
O1–S2	3.233(12)		
O2–C32	3.107(22)		
O2–S3	2.838(12)		
O2–O3	2.908(14)		
O3–S4	2.933(9)		
O3–O4	2.807(3)		
O4–C11	3.238(20)		
O4–C12	3.129(22)		
O4–S1	2.906(11)		

TABLE IV. Selected Distances (Å) from the Coordination Plane through the Metal Ion and the Donor Atoms S1, S2, O3, O4 for $M(DMSO)_4^{2+}$, M = Pd, Pt. Values for M = Pd Calculated from Ref. 19.

	O1	O2	C11	C12	C21	C22
Pt	0.06	–0.06	–1.42	1.36	1.44	–1.29
Pd	0.07	–0.17	–1.47	1.24	1.43	–1.35

(2.249 and 2.240 Å) [19]. This reflects a stronger σ-interaction and more extensive back-bonding from filled metal d-orbitals to empty sulfur orbitals of suitable symmetry in the case of platinum. In agreement with this observation platinum complexes of DMSO in solution have been found to be much more stable than those of palladium. For instance, the stability constant of $Pt(DMSO)(H_2O)_3^{2+}$ is $>10^7$ M^{-1} [24], whereas that of the corresponding palladium complex is only 9 M^{-1} [25].

The two Pt–S distances *trans* to oxygen-bonded DMSO are somewhat shorter than the observed Pt–DMSO distances *trans* to nitrogen (2.21 to 2.22 Å) [8–11], *trans* to chlorine (2.23 to 2.25 Å) [14, 19] and *trans* of phenyl-carbon (2.32 Å) [13], which gives a *trans*-influence order for platinum of $O < N < Cl < C$

The M–O bond lengths *trans* to the sulfur-bonded DMSO in the two compounds, on the other hand, are very similar, 2.05 and 2.06 Å or M = Pt and Pd, respectively. This is very similar to the Pd–O distance of 2.066 Å observed in *cis*-$Pd(DMSO)_2(NO_3)_2$ [4]. For comparison, the M–O distances in $M(NO_3)_4^{2-}$ are 2.01 for M = Pt [26] and 2.00 for M = Pd [27]. Similarly, Pt–O bond lengths *trans* to oxygen in other square-planar oxalato and squarato complexes also lie in the interval 1.99 to 2.01 Å [28, 29]. Thus, there is a slight lengthening of the M–O bonds *trans* to sulfur-bonded DMSO, reflecting a ground-state *trans*-influence which seems to be of similar magnitude in the palladium and platinum complexes.

As observed and discussed previously [5, 13, 19, 30], the structures of the DMSO ligands are changed slightly on coordination. Bonding to the metal via the sulfur results in significantly shorter S–O distances (here 1.45 Å) as compared to coordination via O (1.55 Å). The coordination mode also has a slight effect on the bond angles around the sulfur; the O–S–C angles are larger in the S-coordinated DMSO molecules, *cf.* Table III.

Bond distances and angles within the trifluoromethanesulfonate ions are normal [31, 32], and there are no short distances between the atoms of the anions and the platinum complex. The nature of the anion does not seem to have any importance for the coordination geometry around the metal ion: the two compounds $Pt(DMSO)_4(CF_3SO_3)_2$ and $Pd(DMSO)_4(BF_4)_2 \cdot DMSO$ have almost identical coordination geometries around the metal ions.

Supplementary Material

Tables of $|F_o|$, $\sigma(|F_o|)$, $|F_c|$ are available on request from the authors.

Acknowledgements

Thanks are due to Eva Bredenfeldt for experimental assistance, to Dr. Bertil Norén for help with the ORTEP drawings, and to the Swedish Natural Science Research Council for financial support.

References

1 J. A. Davies, *Adv. Inorg. Chem. Radiochem., 24,* 115 (1981).

2 F. A. Cotton and R. Francis, *J. Am. Chem. Soc., 82,* 2986 (1960).

3 F. A. Cotton, R. Francis and W. D. Horrocks, Jr., *J. Phys. Chem., 64,* 1534 (1960).

4 D. A. Langs, C. R. Hare and R. G. Little, *Chem. Commun.,* 1080 (1967).

5 M. J. Bennett, F. A. Cotton, D. L. Weaver, R. J. Williams, and W. H. Watson, *Acta Crystallogr., 23,* 788 (1967).

6 R. Melanson, J. Hubert and F. D. Rochon, *Acta Crystallogr., Sect. B, 32,* 1914 (1976).

7 R. Melanson and F. D. Rochon, *Acta Crystallogr., Sect. B, 34,* 941 (1978).

8 R. Melanson and F. D. Rochon, *Acta Crystallogr., Sect. B, 34,* 1125 (1978).

9 N. B. Pahor, M. Calligaris, L. Randaccio and R. Romeo, *Inorg. Chim. Acta, 26,* L13 (1978).

10 R. Melanson and F. D. Rochon, *Inorg. Chem., 17,* 679 (1978).

11 F. Caruso, R. Spagna and L. Zambonelli, *Acta Crystallogr., Sect. B, 36,* 713 (1980).

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

13 R. Bardi, A. DelPra and A. M. Piazzesi, *Cryst. Struct. Commun., 10,* 301 (1981).

14 R. P. Shibaeva, *Koord. Khim., 11,* 129 (1985).

15 B. B. Wayland and R. F. Schramm, *Chem. Commun.,* 1465 (1968).

16 B. B. Wayland and R. F. Schramm, *Inorg. Chem., 8,* 971 (1969).

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

18 J. H. Price, R. F. Schramm and B. B. Wayland, *Chem. Commun.,* 1377 (1970).

19 B. F. G. Johnson, J. Puga and P. R. Raithby, *Acta Crystallogr., Sect. B, 37,* 953 (1981).

20 F. D. Rochon, P. C. Kong and R. Melanson, *Acta Crystallogr., Sect. C, 41,* 1602 (1985).

21 L. I. Elding, *Inorg. Chim. Acta, 20,* 65 (1976).

22 'International Tables for X-Ray Crystallography', Vol. 4, Kynoch Press, Birmingham, 1974.

23 J. O. Lundgren, 'Crystallographic Computer Programs', *Report No. UUIC-B13-4-05,* Uppsala University, Sweden, 1982.

24 L. I. Elding and Ö. Gröning, *Inorg. Chem., 17,* 1872 (1978).

25 Y. Ducommun, A. E. Merbach, B. Hellquist and L. I. Elding, *Inorg. Chem., 26* (1987) in press.

26 L. I. Elding and Å. Oskarsson, *Inorg. Chim. Acta, 103,* 127 (1985).

27 L. I. Elding, B. Norén and Å. Oskarsson, *Inorg. Chim. Acta, 114,* 71 (1986).

28 A. Kobayashi, Y. Sasaki and H. Kobayashi, *Bull. Chem. Soc. Jpn., 52,* 3682 (1979).

29 O. Simonsen and H. Toftlund, *Inorg. Chem. 20,* 4044 (1981).

30 J. A. Davies, *Adv. Inorg. Chem. Radiochem., 24,* 136 (1981).

31 J. Brock Spencer and J. O. Lundgren, *Acta Crystallogr., Sect. B, 29,* 1923 (1973).

32 J. O. Lundgren, *Acta Crystallogr., Sect. B, 34,* 2428 (1978).