1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: FG1186). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1921–1924

cis-Dibromobis(dimethyl sulfoxide-*S*)platinum(II) and *trans*-Bis(dimethyl sulfoxide-*S*)diiodoplatinum(II)

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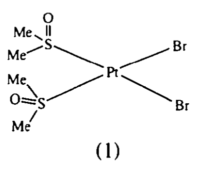
Abstract

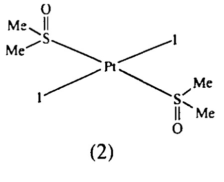
The Pt atom has a slightly distorted square-planar coordination in both title compounds, *cis*-[$PtBr_2(C_2H_6OS)_2$] and *trans*-[$PtI_2(C_2H_6OS)_2$], with the dimethyl sulfoxide ligands bonded *via* their S atoms. The bond distances to platinum in the bromo compound are Pt—Br 2.441 (1) and 2.447 (2), and Pt—S 2.254 (2) and 2.245 (2) Å, and in the centrosymmetric iodo complex are Pt—I 2.6111 (9) and Pt—S 2.289 (2) Å.

Comment

With the thioethers dimethyl sulfide and 1,4-thioxane, both the *cis*- and *trans*-[$PtCl_2$(thioeter)$_2$] isomers can be synthesized and crystallized (Horn, Kumar, Maverick, Fronczek & Watkins, 1990; Kukushkin, Lövqvist, Norén, Oskarsson & Elding, 1992; Bugarcic, Lövqvist & Oskarsson, 1993). For iodo complexes, however, only a *trans*-thioether compound has been reported previously (Oskarsson, Norén, Svensson & Elding, 1990), indicating that the *trans* configuration might be the preferred isomer for iodide. Also, with sulfoxide ligands, both *cis* and *trans* isomers could be obtained for the dichloro complexes of platinum(II). The *cis* isomer seems to be the thermodynamically more stable complex as the preparation of *trans*-[$PtCl_2$(dmso)$_2$] [dmso is dimethyl sulfoxide, $(CH_3)_2SO$] results in rapid isomerization to the *cis* isomer. *trans*-[$PtCl_2$(dmso)$_2$] has been prepared by a bridge-splitting reaction and the *trans*-to-*cis* isomerization rate was followed with ^1H NMR by Annibale, Bonivento, Canovese, Cattalini, Michelon & Tobe (1985), who claimed that complexes of the type [MX_2L_2] adopt the *trans* configuration when *M* is Pd, but that the *cis* configuration is preferred when *M* is Pt, except for very sterically demanding sulfoxides. Melanson & Rochon (1987, 1988) were able to prepare and determine the structures of both *cis* and *trans* isomers of [$PtCl_2$(di-*n*-propyl sulfoxide)$_2$]. The crystal structure of *cis*-[$PtCl_2$(dmso)$_2$] has been reported (Melanson & Rochon, 1975; Shibaeva, 1983), but investigations of the bromo and iodo complexes of [PtX_2(dmso)$_2$] have, so far, not resulted in any reported crystal structures, though the structure of *cis*-[$PtBr_2$(dmso)$_2$] was referred to by Kukushkin *et al.* (1991). For *cis* isomers, steric repulsion increases in the series Cl < Br < I and it is of interest to investigate the isomerism of the different halides in [PtX_2(dmso)$_2$]. Hence, halides of platinum(II) (X = Cl, Br, I) were dissolved in dimethyl sulfoxide. This resulted in *cis* isomers for Cl and Br, (1), and a *trans* isomer for I, (2), both in the solid state and in solution.



(1)



(2)

cis-[$PtBr_2$(dmso)$_2$], (1), is isostructural with *cis*-[$PtCl_2$(dmso)$_2$]. The coordination around platinum is distorted square planar and the dimethyl sulfoxide molecules are bonded to platinum *via* the S atom. The closest contact between the complexes is O(2)···C(1)($\frac{3}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) of 2.99 (1) Å. One of the dimethyl sulfoxide molecules has the O(2) atom in an eclipsed conformation with respect to the S(1) atom of the other ligand (Fig. 1). The C(1) methyl group on the other dimethyl sulfoxide molecule is in an eclipsed conformation with respect to the Br(2) atom. The Pt—Br distances (Table 3) of 2.441 (1) and 2.447 (2) Å are similar to that observed *trans* to S in K[$PtBr_3$(diethyl sulfoxide)] of 2.452 (2) Å (Belsky, Konovalov & Kukushkin, 1993), but they are somewhat longer than those found in *cis*-[$PtBr_2$(dmso)(MeCN)], which were 2.429 (2) and 2.427 (2) Å *trans* to S, and 2.397 (2) and 2.394 (2) Å *trans* to N (Belsky, Konovalov, Kukushkin & Moiseev, 1990). The shorter Pt—Br distance *trans* to MeCN indicates that the *trans* influence of dimethyl sulfoxide is greater than that of MeCN. The Pt—S distances in *cis*-[$PtBr_2(dmso)_2$] of 2.254 (2) and 2.245 (2) Å are not significantly different from those found in *cis*-[$PtCl_2(dmso)_2$] [2.229 (2)–2.251 (3) Å; Melanson & Rochon, 1975; Shibaeva, 1983].

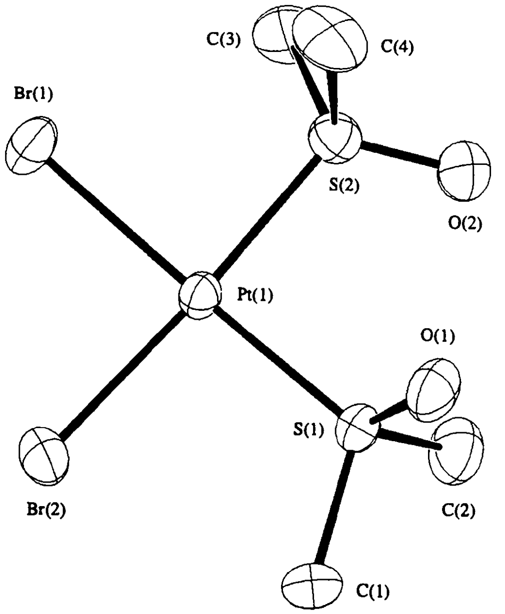


Fig. 1. An *ORTEP* (Johnson, 1965) drawing of *cis*-[$PtBr_2(dmso)_2$]. Displacement ellipsoids are at the 50% probability level.

In *trans*-[$PtI_2(dmso)_2$], (2), two S and two I atoms form a distorted square-planar coordination (Fig. 2). The PtI_2S_2 moiety is centrosymmetric and thus strictly planar. The I—Pt—S angles of 86.64 (6) and 93.36 (6)° (Table 3) deviate from the ideal value of 90°. The larger angle may be caused by steric repulsion between the methyl group C(1) and I atoms, since they are in an eclipsed conformation [I—Pt—S—C(1) 1.5 (4)° and C(1)···I 3.39 (1) Å]. The shortest Pt···Pt distance is equal to the shortest unit-cell axis [a = 5.2789 (9) Å] and the closest contact between the complexes is O···C(1)($x-1$, y, z) of 3.28 (1) Å. The Pt—I distance of 2.6111 (9) Å is similar to that found in *trans*-[PtI_2(dimethyl sulfide)$_2$] of 2.6039 (8) Å (Lövqvist, Wendt & Leipoldt, 1996), in *trans*-[PtI_2{*O*-ethyl (*N*-ethyl)thiocarbamate}$_2$] of 2.610 (2) Å (Bardi, Piazzeri, Del Pra & Trincia, 1987), in *trans*-[PtI_2(methylphenyl telluride)$_2$] of 2.604 (1) and 2.607 (1) Å (Levason, Webster & Mitchell, 1992), in *trans*-[$PtI_2(PPh_3)_2$] of 2.603 (1) Å (Boag, Mohan Rao & Terrill, 1991) and in *trans*-[PtI_2(tetrahydrothiophene)$_2$] of 2.606 (1) and 2.616 (1) Å (Oskarsson, Norén, Svensson & Elding, 1990). This indicates that the *cis* influence on the Pt—I bond is about the same for the different donor atoms. The Pt—S distance of 2.289 (2) Å is somewhat shorter than in both *trans*-[PtI_2(tetrahydrothiophene)$_2$] [2.310 (1) and 2.309 (1) Å] and the corresponding dimethyl sulfide compound [2.310 (2) Å]. The bond distance is, however, not significantly different from that found in *trans*-[$PtCl_2$(di-*n*-propyl sulfoxide)$_2$] [2.292 (2) Å]. It has been observed previously (Bugarcic, Lövqvist & Oskarsson, 1993) that Pt—S(sulfoxide) distances are about 0.03–0.07 Å shorter than the corresponding Pt—S(thioether) distances. In *trans*-[$PtI_2(dmso)_2$], the Pt—S distances are only 0.021 (3) Å shorter than in *trans*-[PtI_2(dimethyl sulfide)$_2$]. An explanation might be that the *trans* influence opposes the differences in bond strength and/or that both effects are small.

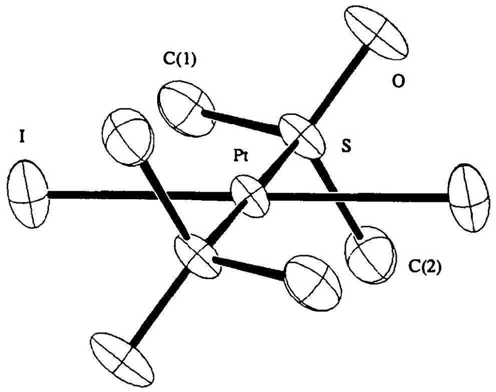


Fig. 2. An *ORTEP* (Johnson, 1965) drawing of *trans*-[$PtI_2(dmso)_2$]. Displacement ellipsoids are at the 50% probability level.

Experimental

An excess of dimethyl sulfoxide was added to the respective platinum halide ($PtCl_2$, $PtBr_2$, PtI_2). The mixture was heated and stirred until the halide was dissolved. Crystals were grown either by cooling a warm solution or by natural evaporation. The crystals of *cis*-[$PtCl_2(dmso)_2$] were pale yellow, while those of *cis*-[$PtBr_2(dmso)_2$], (1), were yellow and those of *trans*-[$PtI_2(dmso)_2$], (2), were red. IR spectra were measured on a Bio-Rad FTS 6000 spectrometer using polyethene pellets.

Raman spectra were measured on a Bio-Rad FT Raman spectrometer on both the solid sample and in dimethyl sulfoxide solution. The IR analysis of (2) gave ν(Pt—I) at 192 cm^{-1} and Raman gave ν(Pt—I) at 151 and 150 cm^{-1} for the solid and the solution, respectively. IR analysis of (1) gave ν(Pt—Br) at 200 and 217 cm^{-1} and Raman gave ν(Pt—Br) peaks at 200 and 224 cm^{-1} for the solid and at 206 and 222 cm^{-1} in dimethyl sulfoxide solution.

Compound (1)

Crystal data

$[\mathrm{PtBr_2(C_2H_6OS)_2}]$
M_r = 511.16
Monoclinic
$P2_1/n$
a = 8.959 (3) Å
b = 13.677 (8) Å
c = 9.777 (3) Å
β = 108.78 (2)°
V = 1134 (1) Å^3
Z = 4
D_x = 2.993 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 23 reflections
θ = 13.89–27.12°
μ = 19.79 mm^{-1}
T = 295 K
Prismatic
0.43 × 0.21 × 0.12 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: by integration from crystal shape (*TEXSAN*; Molecular Structure Corporation, 1989)
T_{min} = 0.014, T_{max} = 0.176
2980 measured reflections
2826 independent reflections

2092 observed reflections [$I \geq 3\sigma(I)$]
R_{int} = 0.0741
θ_{max} = 28°
$h = -11 \rightarrow 11$
$k = -18 \rightarrow 0$
$l = 0 \rightarrow 12$
3 standard reflections monitored every 120 reflections intensity decay: 1.6%

Refinement

Refinement on F
R = 0.0324
wR = 0.0413
S = 1.713
2092 reflections
101 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F)]$
$(\Delta/\sigma)_{\mathrm{max}}$ = 0.0006

$\Delta\rho_{\mathrm{max}}$ = 1.33 e Å^{-3}
$\Delta\rho_{\mathrm{min}}$ = −1.33 e Å^{-3}
Extinction correction: Zachariasen (1963) type 2, Gaussian isotropic
Extinction coefficient: 22.4 × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)*

$$U_{\mathrm{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pt(1)	0.47936 (4)	0.01502 (2)	0.21528 (3)	0.0260 (1)
Br(1)	0.1928 (1)	−0.00149 (7)	0.1317 (1)	0.0454 (4)
Br(2)	0.4888 (1)	−0.15115 (7)	0.1258 (1)	0.0461 (4)
S(1)	0.7432 (3)	0.0232 (2)	0.3185 (2)	0.0311 (7)
S(2)	0.4541 (3)	0.1672 (2)	0.2912 (2)	0.0321 (7)
O(1)	0.7907 (8)	0.0400 (5)	0.4744 (6)	0.044 (3)
O(2)	0.5947 (8)	0.2280 (5)	0.3359 (8)	0.048 (3)
C(1)	0.849 (1)	−0.0831 (7)	0.294 (1)	0.049 (4)
C(2)	0.833 (1)	0.1130 (7)	0.238 (1)	0.048 (4)
C(3)	0.304 (1)	0.2352 (7)	0.161 (1)	0.050 (4)
C(4)	0.379 (1)	0.1595 (8)	0.439 (1)	0.054 (5)

Compound (2)

Crystal data

$[\mathrm{PtI_2(C_2H_6OS)_2}]$
M_r = 605.16
Triclinic
$P\bar{1}$
a = 5.2789 (9) Å
b = 7.089 (2) Å
c = 8.709 (3) Å
α = 110.42 (2)°
β = 94.50 (2)°
γ = 93.48 (2)°
V = 303.1 (3) Å^3
Z = 1
D_x = 3.315 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 14.08–27.98°
μ = 17.03 mm^{-1}
T = 295 K
Thin prism
0.27 × 0.19 × 0.07 mm
Orange–red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: by integration from crystal shape (*TEXSAN*; Molecular Structure Corporation, 1989)
T_{min} = 0.113, T_{max} = 0.353
2892 measured reflections
1446 independent reflections

1332 observed reflections [$I \geq 3\sigma(I)$]
R_{int} = 0.024
θ_{max} = 28°
$h = -6 \rightarrow 6$
$k = -9 \rightarrow 9$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 120 reflections intensity decay: −0.3%

Refinement

Refinement on F
R = 0.0471
wR = 0.0568
S = 2.67
1332 reflections
52 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F)]$
$(\Delta/\sigma)_{\mathrm{max}}$ = 0.0008

$\Delta\rho_{\mathrm{max}}$ = 3.35 e Å^{-3}
$\Delta\rho_{\mathrm{min}}$ = −4.51 e Å^{-3}
Extinction correction: Zachariasen (1963) type 2, Gaussian isotropic
Extinction coefficient: 20.1 × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

$$U_{\mathrm{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pt	0	0	0	0.0230 (2)
I	0.2975 (1)	0.1974 (1)	−0.12976 (8)	0.0437 (3)
S	0.0442 (3)	0.2567 (3)	0.2511 (3)	0.0278 (7)
O	−0.199 (1)	0.324 (1)	0.3158 (9)	0.045 (2)
C(1)	0.238 (2)	0.479 (2)	0.267 (1)	0.040 (3)
C(2)	0.230 (2)	0.178 (2)	0.396 (1)	0.043 (4)

Table 3. *Selected bond distances (Å) and angles (°) for the two title compounds*

cis-[PtBr$_2$(dmso)$_2$]		*trans*-[PtI$_2$(dmso)$_2$]	
Pt—Br(1)	2.441 (1)	Pt—I	2.6111 (9)
Pt—Br(2)	2.447 (2)		
Pt—S(1)	2.254 (2)	Pt—S	2.289 (2)
Pt—S(2)	2.245 (2)		
S(1)—O(1)	1.463 (6)	S—O	1.482 (6)
S(1)—C(1)	1.793 (9)	S—C(1)	1.78 (1)
S(1)—C(2)	1.783 (10)	S—C(2)	1.79 (1)
S(2)—O(2)	1.455 (7)		
S(2)—C(3)	1.789 (9)		
S(2)—C(4)	1.780 (9)		
Br(1)—Pt—Br(2)	87.02 (4)		
Br(1)—Pt—S(1)	173.03 (6)	I—Pt—S	93.36 (6)
Br(1)—Pt—S(2)	89.39 (6)		
Br(2)—Pt—S(1)	93.11 (6)		
Br(2)—Pt—S(2)	176.38 (6)		
S(1)—Pt—S(2)	90.50 (8)		
Pt—S(1)—O(1)	112.7 (3)	Pt—S—O	114.8 (3)
Pt—S(1)—C(1)	115.1 (3)	Pt—S—C(1)	116.3 (3)
Pt—S(1)—C(2)	113.2 (4)	Pt—S—C(2)	108.4 (4)
O(1)—S(1)—C(1)	105.9 (5)	O—S—C(1)	106.5 (4)
O(1)—S(1)—C(2)	109.2 (4)	O—S—C(2)	109.9 (4)
Pt—S(2)—O(2)	117.4 (3)		
Pt—S(2)—C(3)	112.3 (4)		
Pt—S(2)—C(4)	108.6 (3)		
O(2)—S(2)—C(3)	107.3 (5)		
O(2)—S(2)—C(4)	107.8 (5)		

The structure of *cis*-[PtCl$_2$(dmso)$_2$] has previously been determined by Melanson & Rochon (1975) and Shibaeva (1983). The characterization of the chloro compound was therefore made by comparing the unit-cell parameters only. The position of the Pt atom in the bromo complex was found by the Patterson method and in *trans*-[PtI$_2$(dmso)$_2$], the Pt atom was placed on the origin. Difference-Fourier calculations revealed the rest of both structures, which were refined by full-matrix least-squares calculations. All non-H atoms were refined anisotropically. The H atoms could not be located in the difference-Fourier maps and were not included in the calculations. The high max./min. residuals due to the presence of heavy elements are situated 1.56/0.86 Å and 1.03/0.81 Å from the Pt atom in the bromo and iodo complexes, respectively.

For both compounds, data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989); cell refinement: *DETTH* (Enraf-Nonius, 1989); data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *TEXSAN*; program(s) used to refine structures: *TEXSAN LS*; software used to prepare material for publication: *TEXSAN FINISH*.

The author thanks Bertil Norén for valuable discussions of this work. Ola F. Wendt is acknowledged for help with the spectroscopic measurements. Financial support from the Swedish Natural Science Research Council and the Crafoord Foundation are gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1349). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Three Metal (1,4,8,11-Tetraazacyclotetradecane) Halide Salts

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Abstract

Attempts to synthesize [M([14]aneN$_4$)][$M'X_4$] chain systems (M,M' = divalent metal ion, [14]aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane, X = Cl, Br) yielded three M([14]aneN$_4$)X_2.xH$_2$O salts. The structures of these