

## *Cis–Trans* Influences in Pt Complexes. Crystal Structures of *cis*-[PtCl<sub>2</sub>(1,4-thioxane)<sub>2</sub>] and *trans*-[PtCl<sub>2</sub>(1,4-thioxane)<sub>2</sub>]

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The crystal structures of *cis*- and *trans*-[dichloro-bis(1,4-thioxane)platinum(II)] have been determined from X-ray intensity data collected at room temperature on a CAD 4 diffractometer with  $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$ . The *cis* compound crystallizes in the space group  $P2_1/n$  with  $Z = 4$ ,  $a = 10.614(2)$ ,  $b = 11.283(2)$ ,  $c = 11.015(2) \text{ \AA}$ ,  $\beta = 93.33(1)^\circ$  and  $V = 1316.9(2) \text{ \AA}^3$ . The refinement converged to  $R = 0.057$ . The *trans* compound crystallizes in  $Pbca$  with  $Z = 4$ ,  $a = 7.959(5)$ ,  $b = 8.972(1)$ ,  $c = 18.590(6) \text{ \AA}$ ,  $V = 1327.5(6) \text{ \AA}^3$  and  $D_x = 2.37 \text{ g cm}^{-3}$ . The refinement converged to  $R = 0.031$ . The coordination geometry is square planar in both compounds. In the *cis* compound the Pt–Cl distances are in the range 2.321–2.327 Å and the Pt–S distances are both 2.273 Å. In the *trans* compound the Pt–Cl and Pt–S distances are 2.300(2) and 2.298(2) Å, respectively. A literature survey of platinum thioether compounds gives the following *trans* influence series on the Pt–S (thioether) bond distance;  $\text{Cl} < \text{S} < \text{C}$ .

The structure of a crystal is determined by the sum of the forces present in it and thus represents an observable property important for the characterization of chemical bonding. In molecular compounds the molecular structure is determined predominantly by the covalent bonding between its constituent atoms, whereas the molecular packing is determined by molecular shape and van der Waals forces. This should also be a reasonable approximation in coordination compounds, and it was shown in an earlier paper<sup>1</sup> that torsion- and bond-angles, but not bond distances, are significantly affected by packing forces in the complex ion di- $\mu$ -hydroxo-bis[bis(dimethyl sulfoxide)platinum(II)]<sup>2+</sup>. It is thus reasonable to assume that the bond distances to Pt in a square-planar complex [PtLXYZ] are mainly determined by intramolecular forces, i.e. the affinity of Pt to the donor atoms as well as the relative positions of LXYZ in the complex (the *cis–trans* influence). This approximation has been used previously to discuss *cis–trans* influences in Pt(II) complexes.<sup>2,3</sup>

The structures of [Pt(tx)<sub>4</sub>]<sup>2+</sup> (tx = 1,4-thioxane) and [Pt(dms)<sub>4</sub>]<sup>2+</sup> (dms = dimethyl sulfide) show no significant differences in the Pt–S distances, indicating a negligible influence of packing forces as well as a very similar affinity of Pt to the S atoms in dms and tx, respectively.<sup>3</sup> The crystal structures of *cis*- and *trans*-[Pt(dms)<sub>2</sub>Cl<sub>2</sub>]

have been reported in the literature.<sup>4–6</sup> In order to study further the affinity of Pt to S in different types of ligands we have synthesized and determined the crystal structures of the analogous compounds of 1,4-thioxane. We have also compiled literature data of geometries for complexes [PtS(thioether)XYZ] in order to analyse the *cis–trans* influence of different ligands on the Pt–S(thioether) distance.

### Experimental

*Cis*-[PtCl<sub>2</sub>(tx)<sub>2</sub>] was synthesized by mixing a 20 ml water solution of 0.8778 g K<sub>2</sub>[PtCl<sub>4</sub>] with a solution of 0.4 ml 1,4-thioxane in 10 ml water and 10 ml ethanol. The solution was stirred for 5 h at room temperature. The yellow crystals of the complex *cis*-[PtCl<sub>2</sub>(tx)<sub>2</sub>] were separated by filtration and washed with water, ethanol and acetone. The compound was recrystallized from nitromethane. Yellow rhombic crystals were formed.

*Trans*-[PtCl<sub>2</sub>(tx)<sub>2</sub>] was prepared from 0.4 g PtCl<sub>2</sub> mixed with 5.3 ml 1,4-thioxane. The mixture was heated to 70°C; almost all PtCl<sub>2</sub> dissolved and a white precipitate was formed. The precipitate and excess PtCl<sub>2</sub>(s) were filtered off to give a yellow solution. The solution was evaporated at room temperature and orange crystals were formed. The compound was recrystallized from ethylacetate, in which it is only slightly soluble. A few orange crystals precipitated from the solution.

The intensity data sets were collected at room temperature on a CAD 4 diffractometer using graphite-

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Table 1. Crystal data, collection and reduction of intensity data and least-squares refinement.

Compound	<i>cis</i> -[Pt(tx) <sub>2</sub> Cl <sub>2</sub> ]	<i>trans</i> -[Pt(tx) <sub>2</sub> Cl <sub>2</sub> ]
Mol.wt	474.32	474.32
Space group	<i>P2</i> <sub>1</sub> / <i>n</i>	<i>Pbca</i>
<i>a</i> /Å	10.614(2)	7.959(5)
<i>b</i> /Å	11.283(2)	8.972(1)
<i>c</i> /Å	11.015(2)	18.590(6)
β/°	93.33(1)	
<i>V</i> /Å <sup>3</sup>	1316.9(2)	1327.5(6)
<i>Z</i>	4	4
<i>D<sub>x</sub></i> /g cm <sup>-3</sup>	2.39	2.37
μ/mm <sup>-1</sup>	11.46	11.06
Crystal size/mm	0.15 × 0.33 × 0.10	0.13 × 0.13 × 0.18
λ/Å	0.71069	0.71069
Range of transmission factors	0.227–0.525	0.219–0.323
θ-Interval/°	3.00–28.00	3.00–24.00
ω–2θ scan width, Δω/°	0.7 + 0.5 tan θ	0.9 + 0.5 tan θ
σ( <i>I</i> )/ <i>I</i> requested in a scan	0.028	0.030
Maximum recording time/s	150	100
Number of measured reflexions	3295	2298
Number of reflexions used in the refinements, <i>m</i>	2785	1232
<i>hkl</i> range	0 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 14, –14 ≤ <i>l</i> ≤ 14	0 ≤ <i>h</i> ≤ 12, 0 ≤ <i>k</i> ≤ 17, –11 ≤ <i>l</i> ≤ 11
$R = \sum ( F_o  -  F_c ) / \sum  F_o $	0.057	0.031
$R_w = [\sum w( F_o  -  F_c )^2 / \sum  F_o ^2]^{1/2}$	0.072	0.038
$S = [\sum w( F_o  -  F_c )^2 / (m - n)]^{1/2}$	0.99	1.22
Δρ <sub>max/min</sub> /e Å <sup>-3</sup>	3.49/–3.87	2.33/–1.30
δ <i>R</i> slope	1.07	0.98
δ <i>R</i> intercept	–0.08	–0.17
<i>C</i> <sub>1</sub> (weighting scheme)	0.07	0.10
<i>C</i> <sub>2</sub> (weighting cheme)	0.0	5.0

monochromated Mo *K*α radiation. The ω–2θ scan technique was employed and the scan interval, Δω, was extended 25% at both ends for the background measurement. Two standard reflexions were measured at regular intervals. No systematic variation in their intensities was observed. Information on the collection and reduction of the data is given in Table 1. The values of *I* and σ(*I*) were corrected for Lorentz, polarization and absorption effects, the latter by numerical integration [σ(*I*) is based on counting statistics]. Reflexions with *I* < 3σ(*I*) for the *cis*

compound and *I* < 2σ(*I*) for the *trans* compound were considered insignificantly different from the background and were excluded from all subsequent calculations. Cell dimensions were obtained from least-squares calculation of 25 and 24 θ-values for *cis*-[PtCl<sub>2</sub>(tx)<sub>2</sub>] and *trans*-[PtCl<sub>2</sub>(tx)<sub>2</sub>], respectively, determined as θ<sub>*hkl*</sub> = (ω<sub>*hkl*</sub> – ω<sub>*h̄k̄l̄*</sub>)/2 with ω<sub>*h̄k̄l̄*</sub> measured at negative θ-angle. For *cis*-[PtCl<sub>2</sub>(tx)<sub>2</sub>] the Laue class is 2/*m* and systematic extinctions *h*0*l*, *h* + *l* ≠ 2*n* and 0*k*0 ≠ 2*n* are consistent with the space group *P2*<sub>1</sub>/*n*, while Laue class *mmm* and systematic extinctions 0*kl*, *k* ≠ 2*n*; *h*0*l*, *l* ≠ 2*n* and *hk*0, *h* ≠ 2*n* uniquely determines the space group as *Pbca* for *trans*-[PtCl<sub>2</sub>(tx)<sub>2</sub>].

Both structures were solved by Patterson and difference Fourier methods and refined by full-matrix least-

Table 2. Atomic coordinates and *U*<sub>eq</sub> with e.s.d.s for *cis*-[Pt(tx)<sub>2</sub>Cl<sub>2</sub>].

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> /Å <sup>2a</sup>
Pt	0.11819(2)	0.11159(2)	0.07861(2)	0.0244(1)
S(1)	0.1967(2)	0.0016(2)	–0.0724(2)	0.0263(5)
S(2)	0.1984(2)	–0.0071(2)	0.2309(2)	0.0300(5)
Cl(1)	0.0224(2)	0.2340(2)	0.2154(2)	0.0433(6)
Cl(2)	0.0529(2)	0.2384(2)	–0.0794(2)	0.0382(6)
O(1)	0.4449(6)	–0.1223(6)	–0.1445(6)	0.043(2)
C(11)	0.2611(8)	–0.1394(8)	–0.0218(7)	0.035(2)
C(12)	0.3374(8)	–0.1925(8)	–0.1231(8)	0.042(2)
C(13)	0.4120(9)	–0.0109(9)	–0.1957(8)	0.048(3)
C(14)	0.3416(8)	0.0705(8)	–0.1082(8)	0.040(2)
O(2)	0.2029(7)	–0.0089(6)	0.5137(5)	0.047(2)
C(21)	0.2830(8)	0.0912(8)	0.3373(7)	0.038(2)
C(22)	0.314(1)	0.026(1)	0.4546(9)	0.054(3)
C(23)	0.139(1)	–0.1020(9)	0.4450(9)	0.049(3)
C(24)	0.0767(8)	–0.0539(9)	0.3262(8)	0.042(2)

$$^a U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j.$$

Table 3. Atomic coordinates and *U*<sub>eq</sub> with e.s.d.s for *trans*-[Pt(tx)<sub>2</sub>Cl<sub>2</sub>].

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> /Å <sup>2a</sup>
Pt	0.00000	0.00000	0.00000	0.0352(2)
Cl	0.0000(4)	0.2013(3)	0.0765(1)	0.0569(9)
S	0.0674(3)	–0.1419(3)	0.0988(1)	0.0387(7)
O	–0.0836(9)	–0.3806(7)	0.2043(4)	0.056(3)
C(1)	–0.100(1)	–0.119(1)	0.1642(5)	0.047(4)
C(2)	–0.070(1)	–0.229(1)	0.2262(5)	0.053(4)
C(3)	0.044(1)	–0.421(1)	0.1545(5)	0.056(4)
C(4)	0.029(1)	–0.339(1)	0.0825(5)	0.049(4)

$$^a U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j.$$

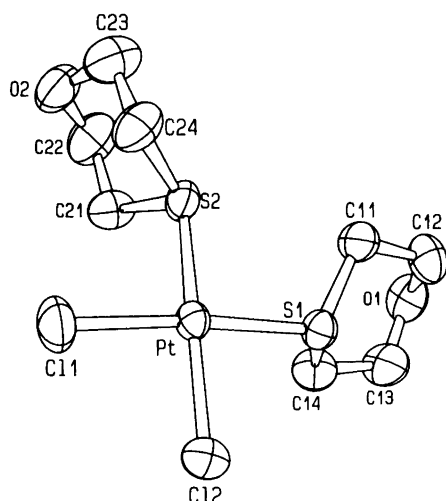


Fig. 1. Atomic numbering in *cis*-[Pt(tx)<sub>2</sub>Cl<sub>2</sub>].

squares calculations. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , with weights  $w^{-1} = [\sigma_o^2/4 |F_o|^2 + (C_1 |F_o|)^2 + C_2]$ ;  $C_1$  and  $C_2$  are given in Table 1. Anisotropic temperature factors were applied to all non-H atoms. Scattering factors with correction for anomalous dispersion were taken from Ref. 7. The positions of the H atoms were calculated with C-H distances equal to 0.95 Å. These were not refined, but only included in the structure-factor calculations. Details of the refinements are given in Table 1 and the final atomic parameters in Tables 2 and 3. Selected interatomic distances and angles are given in Tables 4 and 5. Computer programs used were those compiled and amended by Lundgren.<sup>8</sup>

### Description of the structures

Both compounds are composed of [PtCl<sub>2</sub>(tx)<sub>2</sub>] complexes. The packing efficiencies are very similar: the

Table 4. Distances (in Å), bond angles (in °) and torsion angles (in °) with e.s.d.s in *cis*-[Pt(tx)<sub>2</sub>Cl<sub>2</sub>].<sup>a</sup>

Pt-Cl(1)	2.321(2)	S(1)-Pt-S(2)	94.63(6)
Pt-Cl(2)	2.327(2)	S(1)-Pt-Cl(1)	173.29(7)
Pt-S(1)	2.273(2)	S(1)-Pt-Cl(2)	83.94(7)
Pt-S(2)	2.273(2)	S(2)-Pt-Cl(1)	91.79(7)
S(1)-C(11)	1.806(9)	S(2)-Pt-Cl(2)	175.29(7)
S(1)-C(14)	1.788(9)	Cl(1)-Pt-Cl(2)	89.82(7)
C(11)-C(12)	1.54(1)	Pt-S(1)-C(11)	113.8(3)
C(14)-C(13)	1.55(1)	Pt-S(1)-C(14)	106.3(3)
C(12)-O(1)	1.42(1)	C(11)-S(1)-C(14)	97.8(4)
C(13)-O(1)	1.41(1)	S(1)-C(11)-C(12)	109.0(6)
S(2)-C(21)	1.813(9)	C(11)-C(12)-O(1)	111.4(7)
S(2)-C(24)	1.791(9)	C(12)-O(1)-C(13)	112.4(7)
C(21)-C(22)	1.51(1)	O(1)-C(13)-C(14)	113.3(7)
C(24)-C(23)	1.53(1)	C(13)-C(14)-S(1)	109.3(6)
C(22)-O(2)	1.43(1)	Pt-S(2)-C(21)	105.5(3)
C(23)-O(2)	1.44(1)	Pt-S(2)-C(24)	110.7(3)
Pt...S(1) <sup>i</sup>	3.575(2)	C(21)-S(2)-C(24)	98.5(4)
Pt...C(23) <sup>ii</sup>	4.15(1)	S(2)-C(21)-C(22)	109.2(7)
		C(21)-C(22)-O(2)	112.2(8)
		C(22)-O(2)-C(23)	109.5(7)
		O(2)-C(23)-C(24)	110.9(8)
		C(23)-C(24)-S(2)	108.3(7)
		S(1)-Pt...S(1) <sup>i</sup>	99.97(5)
		S(1)-Pt...C(23) <sup>ii</sup>	97.1(2)
		S(1) <sup>i</sup> ...Pt...C(23) <sup>ii</sup>	149.3(2)
		Cl(1)-Pt-S(2)-C(21)	-53.5(3)
		Cl(1)-Pt-S(2)-C(24)	52.1(3)
		Cl(2)-Pt-S(1)-C(11)	-174.4(3)
		Cl(2)-Pt-S(1)-C(14)	79.1(3)

<sup>a</sup>Symmetries: <sup>i</sup> -x, -y, -z; <sup>ii</sup> 1/2 - x, 1/2 + y, 1/2 - z.

volumes per complex are 329.2 and 331.9 Å<sup>3</sup> for the *cis* and *trans* complexes respectively.

*Cis*-[PtCl<sub>2</sub>(tx)<sub>2</sub>]. The platinum atom is coordinated to two chlorine and two sulfur atoms (Fig. 1 and Table 4). The coordination around Pt is distorted square planar with angles around Pt from 83.9 to 94.6°. S(2) shows the largest deviation from the least-squares plane through S<sub>2</sub>PtCl<sub>2</sub>, 0.123(2) Å. The deviation from the expected bond angles of 90° around the Pt atom is probably caused

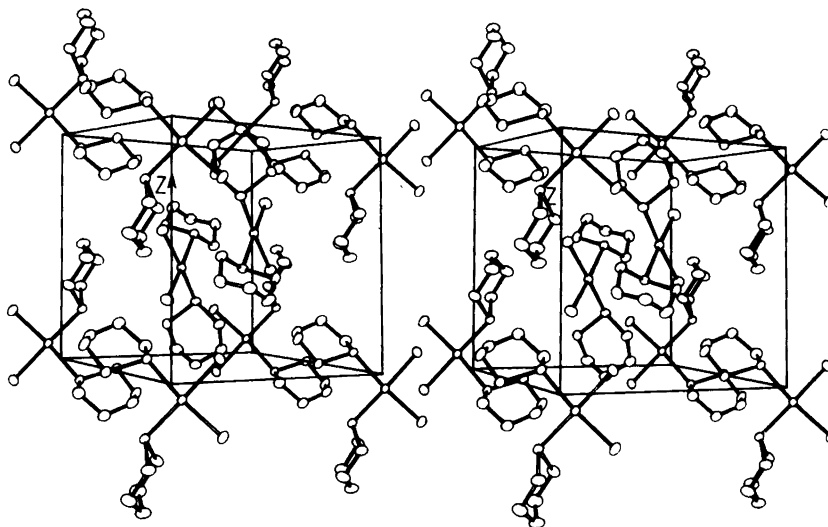


Fig. 2. Stereoscopic view of the crystal packing of *cis*-[Pt(tx)<sub>2</sub>Cl<sub>2</sub>].

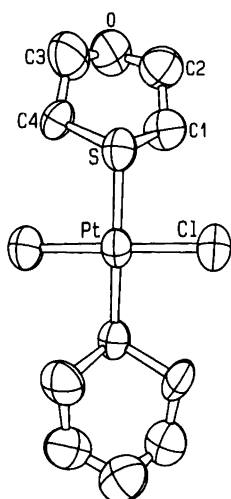


Fig. 3. Atomic numbering in *trans*-[Pt(tx)<sub>2</sub>Cl<sub>2</sub>].

by the intramolecular interactions H1(C21)⋯Cl(1) = 2.75, H1(C24)⋯Cl(1) = 2.88 and H1(C11)⋯S(2) = 2.77 Å, which are somewhat smaller than the sum of the van der Waals radii, 3.00 for H⋯Cl and 3.05 Å for H⋯S. The two Pt–Cl distances are slightly different, while the Pt–S distances are equal. The sulfur atoms bind to the metal through the lone pairs, the angles Pt–S–C are between 106–114°.

Both thioxane molecules adopt the chair conformation (Fig. 1, Table 4) with bond distances and bond angles in agreement with those observed in [Pt(tx)<sub>4</sub>]<sup>2+</sup>.<sup>3</sup> The complexes are packed as dimers (Fig. 2) with two Pt⋯S(1)<sup>i</sup> distances of 3.575(2) Å per dimer. The shortest Pt⋯Pt distance is 3.8897(7) Å and the second shortest Pt⋯Pt distance is 5.997(2) Å, owing to the symmetry. The Pt atom has another atom, C(23)<sup>ii</sup>, from

Table 5. Distances (in Å), bond angles (in °) and torsion angles (in °) with e.s.d.s in *trans*-[Pt(tx)<sub>2</sub>Cl<sub>2</sub>].<sup>a</sup>

Pt–Cl	2.300(2)	S–Pt–S	180.0
Pt–S	2.298(2)	S–Pt–Cl	86.61(9)
S–C(1)	1.82(1)	S–Pt–Cl	93.39(9)
S–C(4)	1.819(9)	Cl–Pt–Cl	180.0
C(1)–C(2)	1.53(1)	Pt–S–C(1)	107.6(3)
C(4)–C(1)	1.53(1)	Pt–S–C(4)	111.5(3)
C(2)–O	1.42(1)	C(1)–S–C(4)	96.6(5)
C(1)–O	1.42(1)	S–C(1)–C(2)	108.5(7)
Pt⋯C(4) <sup>iii</sup>	4.30(1)	C(1)–C(2)–O	112.7(8)
		C(2)–O–C(1)	112.0(8)
		O–C(1)–C(4)	113.3(8)
		C(1)–C(4)–S	108.0(6)
		C(1)–S–Pt–Cl	59.4(4)
		C(4)–S–Pt–Cl <sup>iv</sup>	17.07(4)

<sup>a</sup>Symmetries: <sup>iii</sup>1/2 + x, 1/2 – y, –z; <sup>iv</sup>–x, –y, –z.

a neighbouring complex in the approximate octahedral position with Pt⋯C(23)<sup>ii</sup> = 4.15(1), Pt⋯H1(C23)<sup>ii</sup> = 3.22 Å and S(1)<sup>i</sup>⋯Pt⋯C(23)<sup>ii</sup> = 149° (Table 3). The S(1)–thioxane molecule is rotated about 50° around the Pt–S(1) axis relative to the orientation found in [Pt(tx)<sub>4</sub>]<sup>2+</sup> and in the other thioxane moiety of the present molecule. The free electron pair of S(1) is pointing towards the neighbouring platinum atom (dihedral angles are given in Table 4).

*Trans*-[PtCl<sub>2</sub>(tx)<sub>2</sub>]. Platinum is coordinated to two chlorine atoms and two sulfur atoms in a centrosymmetric *trans* arrangement (Fig. 3). One Pt atom is surrounded by four other Pt atoms at equal distances, 5.997(2) Å, owing to the symmetry. The 1,4-thioxane molecule adopts the same chair conformation as in *cis*-

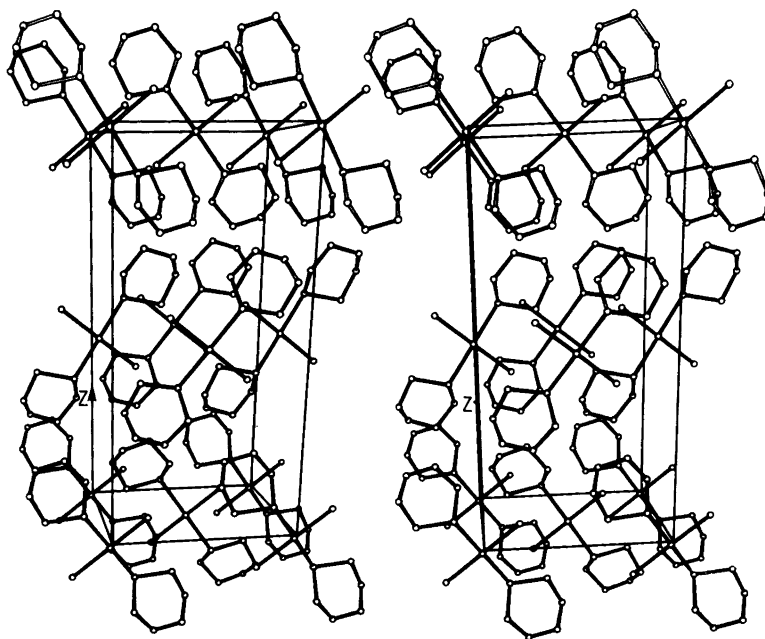


Fig. 4. Stereoscopic view of the crystal packing of *trans*-[Pt(tx)<sub>2</sub>Cl<sub>2</sub>].

[PtCl<sub>2</sub>(tx)<sub>2</sub>] and [Pt(tx)<sub>4</sub>]<sup>2+</sup>.<sup>3</sup> The coordination is distorted square planar with S–Pt–Cl angles 86.61(9) and 93.39(9)°. The deviations from 90° are probably also in this compound caused by intramolecular interactions (Fig. 4). The thioxane molecule is rotated somewhat around the Pt–S bond, relative to the orientation found in [Pt(tx)<sub>4</sub>]<sup>2+</sup> (torsion angles are given in Table 5); the closest contacts between the two chlorine atoms and the thioxane molecule are Cl<sup>iii</sup>...H2(C4) = 2.95, Cl<sup>iii</sup>...H1(C4) = 2.99 and Cl...H1(Cl) = 2.90 Å, and are smaller than the sum of the corresponding van der Waals radii.

## Discussion

The Pt–S distances in *cis*-[PtCl<sub>2</sub>(tx)<sub>2</sub>], 2.273(2), and *trans*-[PtCl<sub>2</sub>(tx)<sub>2</sub>], 2.298(2) Å, are significantly smaller than the average value, 2.319(2) Å,<sup>3</sup> observed in thioether complexes of the type [PtS<sub>4</sub>]<sup>2+</sup>. Thus the combined *cis*(Cl/S) and *trans*(Cl) influence shortens the Pt–S bond 0.046(3) Å in *cis*-[PtCl<sub>2</sub>(tx)<sub>2</sub>], and the *cis* influence from (Cl/Cl) in *trans*-[PtCl<sub>2</sub>(tx)<sub>2</sub>] shortens the Pt–S distance there [0.021(4) Å compared to the average Pt–S bond

distance, 2.319(2) Å]. The average Pt–Cl distance in *cis*-[PtCl<sub>2</sub>(tx)<sub>2</sub>], 2.324(3) Å, on the other hand, is larger than the average value, 2.304(7) Å, calculated from ten [PtCl<sub>4</sub>]<sup>2-</sup> complexes determined from crystal structures.<sup>9</sup> The combined *cis*(Cl/S) and *trans*(S) influence thus increases the Pt–Cl bond by 0.018(8) Å, while the Pt–Cl distance in *trans*-[PtCl<sub>2</sub>(tx)<sub>2</sub>], 2.300(2) Å, is not significantly different from the reference value.

In Table 6 Pt–S bond distances for complexes of the type [PtS(thioether)XYZ] are given in the order of increasing Pt–S bond length. Chelate and bridged complexes are not included.

The large range observed for the Pt–S distances, 2.25–2.39 Å, reflects not only experimental errors but also packing forces, *cis*–*trans* influences and steric requirements of the ligands. The 12 distances with Cl *trans* to S, i.e. a constant *trans* influence, have an average of 2.275 and a dispersion of 0.011 Å. The dispersion, *s*, is calculated from  $s = [\sum (d_n - \bar{d})^2 / (n - 1)]^{1/2}$ . The same calculation restricted to the six complexes with *trans*-(Cl) and *cis*-(Cl/S), i.e. constant *trans* and *cis* influences, results in an average of 2.276 and a dispersion 0.008 Å. The increase in the number of distances from six to twelve

Table 6. Comparison of the Pt–S bond distance in some Pt(thioether) complexes.

Pt–S(thioether)/Å	<i>trans</i> -Partner	<i>cis</i> -Partners	Compound	Ref.
2.246(2)	Cl	Cl/Cl	(Ph <sub>3</sub> PBzI)[PtCl <sub>3</sub> (dms)]	6
2.269(1)	Cl	Cl/S	<i>cis</i> -[PtCl <sub>2</sub> (dms) <sub>2</sub> ]	4
2.272(1)	Cl	Cl/S	<i>cis</i> -[PtCl <sub>2</sub> (dms) <sub>2</sub> ]	4
2.273(2)	Cl	Cl/S	<i>cis</i> -[PtCl <sub>2</sub> (tx) <sub>2</sub> ]	This work
2.273(2)	Cl	Cl/S	<i>cis</i> -[PtCl <sub>2</sub> (tx) <sub>2</sub> ]	This work
2.273(4)	Cl	Cl/P	<i>cis</i> -[PtCl <sub>2</sub> (Et <sub>2</sub> S)(Bz <sub>2</sub> PMe)]	14
2.277(2)	Cl	S/S	[PtCl(dms) <sub>3</sub> ](CF <sub>3</sub> SO <sub>3</sub> )	6
2.277(2)	Cl	S/S	[PtCl(dms) <sub>3</sub> ](CF <sub>3</sub> SO <sub>3</sub> )	6
2.278(7)	Cl	Cl/S	<i>cis</i> -[PtCl <sub>2</sub> (S(p-ClC <sub>6</sub> H <sub>4</sub> )) <sub>2</sub> ]	15
2.281(3)	S	Br/Br	<i>trans</i> -[PtBr <sub>2</sub> (tx) <sub>2</sub> ]	16
2.282(2)	Cl	S/S	[PtCl(tx) <sub>3</sub> ](CF <sub>3</sub> SO <sub>3</sub> )	*
2.282(6)	Cl	S/S	[PtCl(dms) <sub>3</sub> ](PF <sub>6</sub> )	6
2.290(3)	S	Cl/S	[PtCl(dms) <sub>3</sub> ](PF <sub>6</sub> )	6
2.291(4)	S	Cl/C	<i>trans</i> -[PtCl(dms) <sub>2</sub> (phenyl)]	*
2.292(6)	Cl	Cl/S	<i>cis</i> -[PtCl <sub>2</sub> (S(p-ClC <sub>6</sub> H <sub>4</sub> )) <sub>2</sub> ]	15
2.298(3)	S	Cl/Cl	<i>trans</i> -[PtCl <sub>2</sub> (tx) <sub>2</sub> ]	This work
2.298(3)	S	Cl/C	<i>trans</i> -[PtCl(dms) <sub>2</sub> (phenyl)]	*
2.301(2)	S	Cl/S	[PtCl(dms) <sub>3</sub> ](CF <sub>3</sub> SO <sub>3</sub> )	6
2.301(2)	S	Cl/S	[PtCl(dms) <sub>3</sub> ](CF <sub>3</sub> SO <sub>3</sub> )	6
2.302(1)	S	S/S	<i>trans</i> -[Pt(SC <sub>6</sub> F <sub>6</sub> ) <sub>2</sub> (Et <sub>2</sub> S) <sub>2</sub> ]	17
2.304(2)	S	Cl/S	[PtCl(tx) <sub>3</sub> ](CF <sub>3</sub> SO <sub>3</sub> )	*
2.309(1)	S	I/I	<i>trans</i> -[PtI <sub>2</sub> (tht) <sub>2</sub> ]	2
2.309(5)	S	Cl/Cl	<i>trans</i> -[PtCl <sub>2</sub> (dms) <sub>2</sub> ]	6
2.310(1)	S	I/I	<i>trans</i> -[PtI <sub>2</sub> (tht) <sub>2</sub> ]	2
2.316(2)	S	Cl/S	[PtCl(tx) <sub>3</sub> ](CF <sub>3</sub> SO <sub>3</sub> )	*
2.316(7)	S	Cl/S	[PtCl(dms) <sub>3</sub> ](PF <sub>6</sub> )	6
2.317(3)	S	S/S	[Pt(dms) <sub>4</sub> ](CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	3
2.318(2)	S	Cl/S	[PtCl(dms) <sub>3</sub> ](CF <sub>3</sub> SO <sub>3</sub> )	6
2.318(2)	S	S/S	[Pt(tx) <sub>4</sub> ](CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	3
2.318(3)	S	S/S	[Pt(dms) <sub>4</sub> ](CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	3
2.320(2)	S	Cl/S	[PtCl(dms) <sub>3</sub> ](CF <sub>3</sub> SO <sub>3</sub> )	6
2.321(2)	S	S/S	[Pt(tx) <sub>4</sub> ](CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	3
2.370(2)	C	S/C	<i>cis</i> -[Pt(dms) <sub>2</sub> (phenyl) <sub>2</sub> ]	18
2.389(2)	C	S/C	<i>cis</i> -[Pt(dms) <sub>2</sub> (phenyl) <sub>2</sub> ]	18

\*To be published.

does not decrease the dispersion, which most probably is due to the different *cis* influences. However, the dispersion caused by the packing forces, sterical requirements and experimental errors, 0.008 Å, is too large for a more quantitative discussion of the *cis* influences.

A similar analysis for *trans*-(S) complexes results in 2.307(11) Å (20 distances), for *trans*-(S) and *cis*-(Cl/S) in 2.308(11) Å (eight distances) and for *trans*-(S) and *cis*-(S/S) in 2.315(8) Å (five distances) (Table 6). The different *cis* influences are thus also noticeable in this case, but the dispersion due to packing forces, sterical requirements of the ligands and experimental errors, are too large for a quantitative discussion.

From a comparison of the distances in the complexes *trans*-(Cl) and *cis*-(Cl/S) 2.276(8) Å with those in *trans*-(S) and *cis*-(Cl/S), 2.308(11) Å (constant *cis* influence) it may be concluded that the *trans* influence of S on S is significantly larger than that of Cl on S. There are no complexes *trans*-(C) and *cis*-(S/Cl) reported in the literature. However, the large increase in Pt-S distances between *trans*-(S), 2.307(11) Å, and *trans*-(C), 2.380(13) Å, implies a very large *trans* influence of C, and the following series of *trans* influence is obtained: Cl < S < C.

Boström *et al.*<sup>10</sup> have reported a corresponding compilation for complexes of the type [PtS(dmsO)XYZ] (dmsO = dimethyl sulfoxide, (CH<sub>3</sub>)<sub>2</sub>SO). With the same *cis-trans* partners the Pt-S(dmsO) distance is 0.03–0.07 Å shorter than the corresponding Pt-S(thioether) distance. Such a difference between Pt-S(thioether) and Pt-S(sulfoxide) distances has previously been reported by Kukushkin *et al.*<sup>19</sup>

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