# cis/trans Influences on Bond Distances in Square-Planar Complexes. Crystal Structures of trans-Dichlorobis(tetrahydrothiophene)palladium(II) and trans-Dichlorobis(tetrahydrothiophene)platinum(II)

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Crystals of trans-dichlorobis(tetrahydrothiophene)palladium(II) and the corresponding platinum(II) compound were prepared by dissolving the metal chloride in tetrahydrothiophene at 363 K and cooling to room temperature. Crystal data at room temperature (MoKα$_1$, λ=0.70926 Å) are: [PdCl$_2$(C$_4$H$_8$S)$_2$], $M_r$=353.67, monoclinic, C2/c, a=15.648(3), b=9.157(1), c=9.215(2) Å, β=111.94(2)°, V= 1224.8(2) Å$^3$, Z=4, $D_x$=1.918 g cm$^{-3}$, μ=2.22 mm$^{-1}$, F(000)=704, R=0.021 for 872 unique reflections with I⩾3σ(I); [PtCl$_2$(C$_4$H$_8$S)$_2$], $M_r$=442.33, monoclinic, C2/c, a=15.620(4), b=9.146(2), c=9.255(2) Å, β=111.98(2)°, V=1226.0(3) Å$^3$, Z=4, $D_x$=2.396 g cm$^{-3}$, μ=12.29 mm$^{-1}$, F(000)=832, R=0.056 for 779 reflections with I⩾3σ(I). Both compounds consist of van der Waals packed mononuclear trans-[MCl$_2$(C$_4$H$_8$S)$_2$] complexes. The acceptor–donor distances are Pd–Cl 2.296(1); Pd–S 2.323(1); Pt–Cl 2.309(5) and Pt–S 2.305(4) Å. The cis influence of Cl,Cl on a Pd–S or a Pt–S bond length is the same as for I,I. The trans influence of Cl on a Pt–S(thioether) bond is found to be −0.035(16) Å (95% confidence level). It is confirmed that Pt–S(thioether) bonds generally are shorter than corresponding Pd–S bonds.

The trans influence expressed as the extent to which a ligand X in a metal complex lengthens or shortens a bond M–L trans to itself, compared to a reference distance, is expected to be correlated with the trans effect of X, as displayed by the substitution rate. Basolo and Pearson[1] suggested the sum of the hard-sphere covalent radii for M and L as the reference to calculate the bond lengthening of M⋯L. Mason and Towl[2] proposed that the trans influence of X is the relative lengthening of M⋯L, when X is trans to L, as compared to the distance M⋯L when L is in the trans position to itself. However, the M–L bond length is also affected by a cis influence, i.e. by the ligands in the cis position. Therefore, a more adequate reference is the M–L distance in [ML$_4$], as has been put forward previously.[3]

In [ML$_4$] the cis and trans influence operates on each of the four M–L bonds to exactly the same extent and are therefore by definition equal to zero. Thus it may be possible to approximately separate the cis from the trans influence in the following way. The difference between the M–L bond length in trans-[ML$_2$X$_2$] and [ML$_4$] will

give the cis influence of X,X on M–L, while the corresponding difference in [ML$_3$X] gives the trans influence of X. In the case of [MLX$_3$] the bond length M–L reflects the cooperative effect of both influences and will possibly reveal how the cis and trans influences are inter-related.

In recent years most of our work has been focused on sulfur donating ligands, i.e. thioethers and sulfoxides. Only the thioethers gave complexes with all four ligands sulfur bonded. Up till now the Pt–S bond length in [Pt(dms)$_4$]$^{2+}$, [Pt(tx)$_4$]$^{2+}$ and [Pt(tht)$_4$]$^{2+}$ with different cations has been determined[3-5] (dms=dimethyl sulfide, tx=1,4-thioxan, tht=tetrahydrothiophene). The results compared with those of trans-[PtCl$_2$(dms)$_2$],[6] trans-[PtCl$_2$(tx)$_2$],[7] trans-[PtI$_2$(dms)$_2$][8] and trans-[PtI$_2$(tht)$_2$][9] indicate a rather small cis influence of Cl,Cl as well as of I,I on the Pt–S(thioether) bond. The present investigation of trans-[PtCl$_2$(tht)$_2$] was performed to further broaden the knowledge of this matter.

Analogous complexes of palladium(II) and platinum(II) are known to have drastically different kinetical properties in solution. It is therefore of general interest to find out whether the Pd–S(thioether) bond is

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more or less affected than the corresponding Pt–S bond. Since the crystal structure of trans-[PdI₂(tht)₂] has been determined earlier,[9] also trans-[PdCl₂(tht)₂] was included in this study.

## Experimental

*Preparation.* 2.83 mmol PdCl₂ (Johnson & Matthey) was dissolved in 10 ml of hot (363 K) tetrahydrothiophene (tht). At this temperature a clear, dark red solution was obtained. Cooling to room temperature gave many red–brown crystals. They were too small to be used for the diffraction measurements. The crystals were dried between filter papers and then recrystallized from boiling ethylacetate. Cooling to room temperature gave suitable single crystals.

0.89 mmol of PtCl₂ (Johnson & Matthey) was treated as above with 5 ml tht. A clear red–yellow solution was formed. After filtration yellow rod-shaped crystals were obtained upon cooling the solution to room temperature. Single crystals were prepared by recrystallization from boiling ethylacetate.

Both title compounds were analyzed for carbon and hydrogen using an automatic Carbo Erba elemental analyzer. Sulfur and chlorine were determined by the Schöninger flask combustion method. Found, PdCl₂(tht)₂: C 27.20; H 4.49; S 17.55; Cl 19.80. Calc. for PdCl₂C₈H₁₆S₂: C 27.14; H 4.56; S 18.12; Cl 20.04. Found, PtCl₂(tht)₂: C 21.80; H 3.65; S 14.45; Cl 15.75. Calc. for PtCl₂C₈H₁₆S₂: C 21.71; H 3.64; S 14.49; Cl 16.03.

*Structure determination.* Crystal data and information about data collection and least-squares refinements are given in Table 1. The data sets were taken at 295 K on a CAD4 diffractometer with monochromated MoKα radiation, $\lambda(\alpha_1) = 0.709\,26$ Å. Cell dimensions were determined from 50 (Pd) and 39 (Pt) θ-values measured on the diffractometer. Three standard reflection intensities that were checked regularly during the experiment showed no significant variation with time. The observed intensities were corrected for Lorentz polarisation and absorption effects (numerical integration).[10]

The two compounds are isomorphous. The heavy atom positions were found by MULTAN,[11] and the structure models were completed by subsequent electron-density difference calculations assuming the space group C2/c.[10] There are four metal complexes per unit cell.

Both crystals investigated were twinned on (001). It could be estimated from a comparison of equivalent reflections that the minor twin component of the Pd complex was only about 3% of the volume of the major twin. The twinning of the Pd crystal was neglected in the following calculations. In the case of the Pt complex the minor twin component was about 25%. The reciprocal lattices of the two twins are close to or actually coinciding on levels $l = 0, 4, 7$. Furthermore, the background measured for some hk2 reflections were highly asymmetric.

All hk0 and five hk2 reflections were omitted from the Pt complex data. The hk4 and hk7 reflections could be retained because the corresponding minor twin reflections $(-h-5, k, 4$ and $-h-9, k, 7)$ are systematically extinct in space group C2/c.

The structure models were refined by full-matrix least-squares minimizing $\Sigma\, w(|F_o| - |F_c|)^2$ with weights calculated from $w^{-1} = \sigma^2(|F_o|^2)/4|F_o|^2 + (C_1|F_o|)^2 + (C_2 < |F_o| >)^2$. Only reflections with $I \geqslant 3\sigma(I)$ were included. Hydrogen atoms were included with isotropic temperature factors only in the refinement of the Pd complex. All non-hydrogen atoms were assumed to vibrate anisotropically. An isotropic type I extinction correction (Lorentzian mosaicity) was applied. The extinction coefficient $g$ was $0.38(8) \times 10^4$ and $1.9(2) \times 10^4$, corresponding to mosaic spreads of 15.4″ and 3.0″, for the Pd and Pt complexes. The maximum corrections were 1.09 and 2.24, respectively, on the $(\bar{2}02)$ reflection.

Scattering factors with corrections for anomalous dispersion were taken from Ref. 12. Information concerning the collection and reduction of the data is given in Table 1, and final atomic parameters are shown in Table 2.

## Results and discussion

It has been confirmed that trans-dichlorobis-(tetrahydrothiophene)platinum(II) is isostructural with trans-dichlorobis(tetrahydrothiophene)palladium(II), but not with the corresponding iodo compounds.[9] The title compounds belong to space group C2/c and are composed of discrete van der Waals packed trans-[MCl₂(tht)₂] complexes (cf. Figs. 1 and 2). The shortest metal–metal distance is 4.627(1) Å in the platinum compound and 4.608(1) Å in the palladium compound. According to the space-group symmetry the metal atom and the four donor atoms are all in the same plane in both cases. The sulfur atoms bind to the metals through one of the lone pairs, the angle M–S–C being between 103.2 and 112.5°. Bond distances and angles within the tht molecule are normal (Table 3) and in agreement with those previously observed in Ag$^I$,[13] Au$^I$,[14] Pd$^{II}$ and Pt$^{II}$ compounds.[9] Moreover, the geometry of the coordinated tht molecule is essentially the same as in the gaseous phase.[15]

In trans-[PtCl₂(tht)₂] the distance Pt–S is 2.305(4) Å, which is close to the distances previously determined in the corresponding iodo compound; 2.310(1) and 2.309(1) Å.[9] Thus it might be concluded that the cis influence of Cl,Cl and I,I on the Pt–S(thioether) bond is nearly the same. As to the magnitude of this influence one could compare the obtained distances with the average value of the Pt–S bond length in [PtL₄]²⁺, where L denotes a sulfur bonded thioether. Twelve such bond lengths, determined in Refs. 3–5 with different thioethers and CF₃SO₃⁻ or ClO₄⁻ as anions, give a value of 2.315 Å. However, it cannot be assumed that all thio-

*Table 1.* Crystal data, summary of data collections and least-squares refinements.
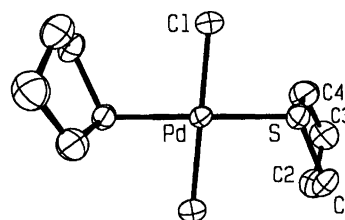
| Compound | *trans*-[PdCl₂(tht)₂] | *trans*-[PtCl₂(tht)₂] |
|---|---|---|
| $M_r$ | 353.67 | 442.33 |
| $a$/Å | 15.648(3) | 15.620(4) |
| $b$/Å | 9.157(1) | 9.146(2) |
| $c$/Å | 9.215(2) | 9.255(2) |
| $\beta$/° | 111.94(2) | 111.98(2) |
| $V$/Å³ | 1224.8(2) | 1226.0(3) |
| Crystal size/mm | 0.04 × 0.12 × 0.33 | 0.09 × 0.30 × 0.38 |
| $[(\sin \theta)/\lambda]_{max}$/Å⁻¹ | 0.595 | 0.595 |
| $h, k, l$ range | ±18, 0⩽10, 0⩽10 | ±18, 0⩽10, 0⩽10 |
| $\omega - 2\theta$ scan width, $\Delta\omega$/° | 0.7 + 0.5 tan θ | 0.55 + 0.5 tan θ |
| Maximum recording time/s | 240 | 180 |
| $\mu$/mm⁻¹ | 2.222 | 12.29 |
| Range of transmission factors | 0.83–0.93 | 0.07–0.32 |
| Number of reflections collected | 1076 | 1078 |
| Number of reflections in final cycle | 872 | 779 |
| Number of parameters refined | 94 | 62 |
| $C_1$ in weighting function | 0.030 | 0.040 |
| $C_2$ in weighting function | 0.042 | 0.036 |
| $(\Delta/\sigma)_{max}$ (non-hydrogen atoms) | 0.01 | 0.02 |
| $(\Delta\rho)_{max}$ (e Å⁻³) | 0.47 | 2.94 |
| $(\Delta\rho)_{min}$ (e Å⁻³) | −0.39 | −2.38 |
| $R$ | 0.0213 | 0.0556 |
| $wR$ | 0.0344 | 0.0794 |
| $S$ | 0.647 | 1.375 |

*Table 2.* Atomic coordinates and equivalent isotropic temperature-factor coefficients of *trans*-[PdCl₂(tht)₂] and *trans*-[PtCl₂(tht)₂].

| | $x$ | $y$ | $z$ | $U_{eq}$/Å² ᵃ |
|---|---|---|---|---|
| [PdCl₂(tht)₂] | | | | |
| Pd | 0 | 0 | 0 | 0.0309(2) |
| Cl | 0.09266(9) | −0.1825(1) | 0.1476(2) | 0.0483(5) |
| S | 0.13624(8) | 0.1325(1) | 0.0726(2) | 0.0402(4) |
| C1 | 0.1166(4) | 0.3251(6) | 0.0219(7) | 0.047(2) |
| C2 | 0.0946(5) | 0.3952(7) | 0.1525(7) | 0.058(3) |
| C3 | 0.1570(5) | 0.3302(7) | 0.3033(8) | 0.060(3) |
| C4 | 0.1646(6) | 0.1675(7) | 0.2818(7) | 0.061(3) |
| H11 | 0.172(4) | 0.358(6) | 0.014(6) | 0.04(1) |
| H12 | 0.072(4) | 0.330(6) | −0.085(7) | 0.05(2) |
| H21 | 0.102(5) | 0.497(8) | 0.150(9) | 0.08(2) |
| H22 | 0.030(5) | 0.369(7) | 0.140(8) | 0.07(2) |
| H31 | 0.215(6) | 0.367(8) | 0.321(9) | 0.09(2) |
| H32 | 0.140(4) | 0.355(7) | 0.396(7) | 0.07(2) |
| H41 | 0.119(5) | 0.117(8) | 0.308(8) | 0.09(2) |
| H42 | 0.215(6) | 0.136(9) | 0.327(9) | 0.09(3) |
| [PtCl₂(tht)₂] | | | | |
| Pt | 0 | 0 | 0 | 0.0313(5) |
| Cl | 0.0928(4) | −0.1835(6) | 0.1496(6) | 0.050(2) |
| S | 0.1360(3) | 0.1305(5) | 0.0753(5) | 0.040(2) |
| C1 | 0.116(1) | 0.323(2) | 0.020(2) | 0.048(7) |
| C2 | 0.093(2) | 0.393(2) | 0.152(3) | 0.058(9) |
| C3 | 0.157(2) | 0.329(3) | 0.305(3) | 0.062(9) |
| C4 | 0.165(2) | 0.168(2) | 0.283(2) | 0.061(9) |

ᵃ $U_{eq} = 1/3 \; \Sigma \; \Sigma \; U_{ij} a_i^* a_j^* a_i \cdot a_j$.



*Fig. 1.* Ortep drawing with atomic numbering of *trans*-[PdCl₂(tht)₂]. The ellipsoids denote 50% probability. Essentially the same picture is obtained for the Pt-compound.

ethers have exactly the same donor capacity. Therefore, the dispersion, calculated as $\sigma = [\Sigma_n(d_n - \bar{d})^2/(n-1)]^{1/2}$, amounts to 0.0055 Å and is used as an error indicator. This results in an error of as much as 0.012 Å for a

confidence level of 95%. This implies that two distances are significantly different at a 95% level if the difference is larger than 0.017 Å. Evidently the *cis* influence for both Cl,Cl and I,I is not significantly different from zero. The same is true for *trans*−[PtCl₂(dms)₂], where the Pt–S bond is 2.309(5) Å.[6] Slightly smaller platinum–sulfur distances are reported for the *trans*-chloro complexes of 1,4-thioxan, 2.298(2) Å,[7] and 7-thiabicyclo[2.2.1]-heptane, 2.286(2) Å.[16] A Cl,Cl *cis* influence of 2.298–2.315 = −0.017(17) Å and 2.286–2.315 = −0.029(17) Å could be calculated in the two cases. The inaccuracy in the differences calculated correspond to a 95% confidence level. (It has been assumed that the errors in the *trans* compounds are the same as for [PtL₄]²⁺.) The obtained result might indicate that a larger influence is followed by increasing complexity of the thioether ligand, which is supported by the Pt–S distance, 2.309(5) Å, found in *trans*-[PtCl₂(dms)₂].[6]

In the present investigation the bond length Pt–Cl is determined to be 2.309(5) Å. For the other thioethers mentioned above,[6,7,15] the values 2.297(5), 2.300(2) and
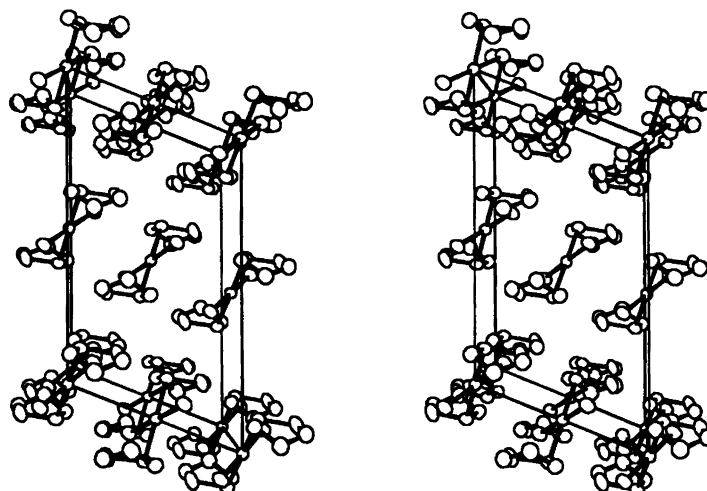
*Fig. 2.* Stereo view of the packing in *trans*-[PdCl₂(tht)₂] and *trans*-[PtCl₂(tht)₂].

*Table 3.* Selected interatomic distances (in Å) and angles (in °), with estimated standard deviations in the last digit given in parentheses.

| *trans*-[PdCl₂(tht)₂] | | | | *trans*-[PtCl₂(tht)₂] | | | |
|---|---|---|---|---|---|---|---|
| (*a*) Coordination geometry around the metal atoms | | | | | | | |
| Pd–2 Cl | 2.296(1) | Cl–Pd–Cl | 180 | Pt–2 Cl | 2.309(5) | Cl–Pt–Cl | 180 |
| Pd–2 S | 2.323(1) | S–Pd–S | 180 | Pt–2 S | 2.305(4) | S–Pt–S | 180 |
| | | Cl–Pd–S | 84.33(5) | | | Cl–Pt–S | 83.9(2) |
| | | Cl–Pd–S | 95.67(5) | | | Cl–Pt–S | 96.1(2) |
| (*b*) Bond angles around the sulfur atoms | | | | | | | |
| Pd–S–C1 | | 112.5(2) | | Pt–S–C1 | | 111.9(7) | |
| Pd–S–C4 | | 103.2(3) | | Pt–S–C4 | | 104.6(8) | |
| C1–S–C4 | | 93.0(3) | | C1–S–C4 | | 93.7(9) | |
| (*c*) Geometry of the tetrahydrothiophene molecules | | | | | | | |
| S–C1 | 1.821(5) | S–C1–C2 | 105.9(4) | S–C1 | 1.83(2) | S–C1–C2 | 104(1) |
| C1–C2 | 1.512(9) | C1–C2–C3 | 108.0(6) | C1–C2 | 1.54(3) | C1–C2–C3 | 108(2) |
| C2–C3 | 1.491(9) | C2–C3–C4 | 109.1(6) | C2–C3 | 1.52(3) | C2–C3–C4 | 108(2) |
| C3–C4 | 1.514(9) | C3–C4–S | 108.0(5) | C3–C4 | 1.50(3) | C3–C4–S | 109(2) |
| C4–S | 1.837(6) | C4–S–C1 | 93.0(3) | C4–S | 1.83(3) | C4–S–C1 | 93.7(9) |

2.300(2) Å are obtained. Thus the Pt–Cl bond length is hardly affected at all by the different nature of the coordinated thioethers.

Several crystal structure investigations of compounds containing the complex cation [PtClL₃]²⁺ (L = dms or tx) have recently been performed. The anions $CF_3SO_3^-$ and $PF_6^-$ were used in the dimethyl sulfide work,[17] while only $CF_3SO_3^-$ was used for the 1,4-thioxane compound.[18] A total of seven independent determinations of the Pt–S bond length *trans* to Cl resulted in a mean value of 2.280 Å with a deviation of 0.010 Å for a confidence level of 95%, calculated as described before. As pointed out in the introduction the *trans* influence (in the ground state) of Cl on the Pt–S(thioether) bond length could now be estimated from the difference 2.280–2.315 = −0.035(16) Å. The error corresponds to a confidence level of 95%. Thus the *trans* influence of Cl shortens significantly the Pt–S(thioether) bond.

The Pt–Cl bond length is somewhat longer than the Pd–Cl bond length, while the opposite is observed for the M–S bond lengths. In the analogous iodo-compounds[9] the M–I bond lengths are about the same, while the Pt–S bond length is 0.013 Å shorter than the Pd–S bond length. The effect is small, but it may indicate that for a soft donor atom like sulfur, the Pt–S bond distance is shorter than the Pd–S bond distance in comparable complexes, which is also found in Refs. 7, 16 and 19. Further support is found in the analogous [M(dmso)₄]²⁺ complexes (dmso = dimethyl sulfoxide),[19,20] where the metal coordinates two S and two O in a *cis* configuration: the average Pt–S distance is 0.038(17) Å shorter (95% confidence level) than the Pd–S distance, due most probably to a stronger σ interaction and a more extensive back-bonding from filled metal *d* orbitals to empty sulfur orbitals of suitable symmetry in the case of platinum. This effect should be

more pronounced in *cis* compounds with a soft donor in *trans* position to a less soft (or hard) one as in the $[M(dmso)_4]^{2+}$ complexes.

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