Acta Cryst. (1990). **B46**, 748–752

trans Influence on Bond Distances. Structures of *trans*-Diiodobis(tetrahydrothiophene)palladium(II) and *trans*-Diiodobis(tetrahydrothiophene)platinum(II)

By Å. Oskarsson*

Inorganic Chemistry, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

and B. Norén, C. Svensson and L. I. Elding

Inorganic Chemistry, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden

(*Received* 30 *March* 1990; *accepted* 29 *May* 1990)

Abstract

Crystals of *trans*-diiodobis(tetrahydrothiophene)palladium(II) and *trans*-diiodobis(tetrahydrothiophene)platinum(II) were prepared by dissolving the appropriate metal iodide in tetrahydrothiophene at 353 K and cooling to room temperature. Crystal data at room temperature (Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å) are: $[PdI_2(C_4H_8S)_2]$, $M_r = 536{\cdot}54$, triclinic, $P\bar{1}$, $a = 8{\cdot}4920\,(8)$, $b = 8{\cdot}8248\,(1)$, $c = 9{\cdot}4580\,(11)$ Å, $\alpha = 97{\cdot}595\,(9)$, $\beta = 91{\cdot}963\,(9)$, $\gamma = 99{\cdot}482\,(9)°$, $V = 691{\cdot}8\,(1)$ Å^3, $Z = 2$, $D_x = 2{\cdot}576$ Mg m^{-3}, $\mu = 5{\cdot}997$ mm^{-1}, $F(000) = 496$, $R = 0{\cdot}028$ for 2090 unique reflections with $I > 3\sigma(I)$; $[PtI_2(C_4H_8S)_2]$, $M_r = 625{\cdot}24$, triclinic, $P\bar{1}$, $a = 7{\cdot}889\,(2)$, $b = 8{\cdot}676\,(1)$, $c = 10{\cdot}616\,(2)$ Å, $\alpha = 103{\cdot}75\,(1)$, $\beta = 90{\cdot}36\,(1)$, $\gamma = 94{\cdot}70\,(2)°$, $V = 703{\cdot}2\,(2)$ Å^3, $Z = 2$, $D_x = 2{\cdot}953$ Mg m^{-3}, $\mu = 14{\cdot}67$ mm^{-1}, $F(000) = 560$, $R = 0{\cdot}024$ for 3988 reflections with $I > 3\sigma(I)$. Both compounds consist of van-der-Waals-packed mononuclear *trans*-$[MI_2(C_4H_8S)_2]$ complexes. There are two centrosymmetric metal complexes in the asymmetric unit of the Pt compound but only one pseudoplanar complex in the Pd compound. The acceptor–donor distances are Pd—I 2·603 (1), 2·625 (1); Pd—S 2·316 (2), 2·329 (2); Pt—I 2·606 (1), 2·616 (1); and Pt—S 2·309 (1), 2·310 (1) Å. A literature survey of compounds in which ligand-I or -S (in thioethers) atoms are *trans* to themselves shows average *M*—I and *M*—S distances of Pd—I 2·605 (20), Pd—S 2·324 (15), Pt—I 2·609 (9) and Pt—S 2·313 (13) Å. The spread of the *M*—I and *M*—S distances is significantly increased if complexes are included where I or S are not *trans* to themselves, indicating that for some donor atoms the *trans* influence dominates over other factors such as the *cis* influence and packing forces.

Introduction

Pidcock, Richards & Venanzi (1966) have defined the *trans influence* of a ligand *L* in a metal complex as the extent to which that ligand weakens the bond *trans* to itself in the ground state of the complex. It may be anticipated that such bond weakening should result in an increase of the bond length $M\cdots X$, for example in a square-planar complex *trans*-$[MA_2LX]$, and it is also expected to parallel an increase in the kinetic *trans* effect of *L*, *i.e.* the substitution rate of *X*. Such a relationship was established by Basolo & Pearson as early as 1962 for Pt^{II} complexes, and Bürgi (1989) has proposed a model of the reaction profile for series of related compounds undergoing the same type of reaction which rationalizes the observation that rather small structural changes in the ground state affect the reaction rate dramatically. Hard-sphere covalent radii for *M* and *X* are normally used as the reference to calculate the bond lengthening of $M\cdots X$ (Basolo & Pearson, 1962). Mason & Randaccio (1971) pointed out the inadequacy of using a fixed metal radius for different types of ligands and suggested that the *trans* influence of *L* is instead defined as the relative lengthening of $M\cdots X$ when *L* is *trans* to *X*, as compared to the distance $M\cdots X$ when *X* is in a *trans* position to itself (Mason & Towl, 1970). However, with this choice of reference point the *trans* influence could not only increase a bond length but also shorten it in some cases and in fact it is easy to find examples where the bond lengthening is much smaller than the bond shortening. For instance, a comparison of bond distances in $K[PtCl_3(DMSO)]$, DMSO = dimethyl sulfoxide (Melanson, Hubert & Rochon, 1976), and *trans*-$[PtCl_2(DPSO)_2]$, DPSO = di-*n*-propyl sulfoxide (Melanson & Rochon, 1988), gives a bond lengthening for Pt—Cl in S—Pt—Cl of 0·02 Å while the corresponding bond shortening of Pt—S is as large as 0·11 Å. Therefore we have rephrased the definition

---

* Present address: Inorganic Chemistry, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden.

0108-7681/90/060748-05$03.00

of Mason & Towl (1970) in the following way: the *trans* influence of L on the bond length $M \cdots X$, when L is in a *trans* position to X, is the shortening or lengthening of the $M \cdots X$ distance as compared to the distance $M \cdots X$ when X is in a *trans* position to itself. The *trans* influence may thus also assume negative values. This operational definition will only be useful if the distribution of $M \cdots X$ distances is significantly smaller when X is in a *trans* position to itself as compared to other cases, *i.e.* the *trans* influence should be substantially larger than other effects on the bond distances. In order to check the validity of this condition we have determined the crystal structures of *trans*-[$PdI_2(THT)_2$] and *trans*-[$PtI_2(THT)_2$], THT = tetrahydrothiophene, and compared the M—I and M—S distances of these compounds with distances for related complexes compiled in the Cambridge Structural Database of January 1988 (Allen, Kennard & Taylor, 1983).

Experimental

Preparation

Aqueous complexes $M(H_2O)_n^{2+}$, M = Pd, Pt, were prepared as described by Elding (1972, 1976). Addition of a potassium iodide solution gave $MI_2(s)$. Dissolution of the metal iodide in THT at 353 K and then cooling to room temperature gave single crystals with composition $MI_2(THT)_2$. The crystals were washed with ethyl acetate at about 283 K and analyzed for carbon and hydrogen using an automatic Carlo Erba elemental analyzer. Sulfur and iodine were determined by the Schöniger flask combustion method. The following results were obtained (calculated values are given in parentheses). $PdI_2(THT)_2$: C 17·35 (17·91), H 3·01 (3·01), S 12·30 (11·95), I 46·6 (47·30)%. $PtI_2(THT)_2$: C 15·20 (15·37), H 2·60 (2·58), S 10·50 (10·25), I 40·4 (40·59)%.

Structure determination

Information about crystal data, data collection, structure solution and refinements is given in Table 1. The intensity-data sets were collected at room temperature with the aid of a CAD-4 diffractometer. Both compounds show Laue class $\bar{1}$ and the absence of systematic extinctions gave $P1$ and $P\bar{1}$ as possible space groups. For both compounds, cell dimensions were obtained from least-squares calculations of 50 θ values determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$ with $\omega_{\bar{h}\bar{k}\bar{l}}$ measured at negative θ angle (Pd compound: $8 < \theta < 25°$; Pt compound: $7 < \theta < 23°$). For each data-set collection three standard reflections were measured at regular intervals. No systematic variation of the intensities was observed. The values of I and $\sigma(I)$ were corrected for Lorentz, polarization and absorption effects, the latter by numerical integration [$\sigma(I)$ is based on counting statistics]. Reflections with $I < 3\sigma(I)$ were considered insignificantly different from the background and excluded from all subsequent calculations.

Table 1. *Crystal data, summary of the collection and reduction of intensity data, and results of the least-squares refinements*

	trans-[$PdI_2(THT)_2$]	*trans*-[$PtI_2(THT)_2$]
a (Å)	8·4920 (8)	7·889 (2)
b (Å)	8·8248 (1)	8·676 (1)
c (Å)	9·4580 (11)	10·616 (2)
α (°)	97·595 (9)	103·75 (1)
β (°)	91·963 (9)	90·36 (1)
γ (°)	99·482 (9)	94·70 (2)
V (Å^3)	691·8 (1)	703·2 (2)
Z	2	2
Crystal size (mm)	0·29 × 0·14 × 0·09	0·08 × 0·10 × 0·33
Radiation (graphite-monochromated)	Mo $K\alpha$	Mo $K\alpha$
θ interval (°)	3–25	3–25
$[(\sin\theta)/\lambda]_{max}$ (Å^{-1})	0·595	0·595
h,k,l range	$-10 \le 0, \pm 10, \pm 11$	$\pm 9, \pm 10, \pm 12$
ω–2θ scan width, $\Delta\omega$ (°)	$0·6 + 0·5\tan\theta$	$0·7 + 0·5\tan\theta$
Maximum recording time (s)	180	180
μ (mm^{-1})	5·997	14·67
Range of transmission factors	0·41–0·63	0·26–0·34
Number of measured reflections	2414	4913
Number of reflections used in final refinements [$I > 3\sigma(I)$]	2090	3988
Number of parameters refined	183	186
C_1 in weighting function	0·015	0·020
C_2 in weighting function	1·00	0·50
$(\Delta/\sigma)_{max}$ (non-hydrogen atoms)	0·09	0·16
$(\Delta\rho)_{max}$ (e Å^{-3})	1·19	2·23
$(\Delta\rho)_{min}$ (e Å^{-3})	−0·44	−2·19
R_{int}	0·049*	0·026
R	0·028	0·024
wR	0·035	0·031
S	1·06	1·00
δR plot,† slope	1·14	1·07
δR plot, intercept	−0·11	−0·05

* Calculated from the few non-unique reflections.
† Abrahams & Keve (1971).

Both structures were solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and difference Fourier methods assuming the space group $P\bar{1}$. The structures were refined by full-matrix least-squares calculations. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with empirical weights $w = [\sigma^2/4|F_o|^2 + (C_1|F_o|)^2 + C_2]^{-1}$. An isotropic extinction correction was applied in both cases. The extinction coefficient g was $0·73\,(2) \times 10^4$ (mosaic spread 8·0″) and $0·24\,(1) \times 10^4$ (mosaic spread 24·4″) for the palladium and the platinum compound, respectively. The maximum correction, on F_o, was 1·44 ($1\bar{2}0$) and 1·21 ($10\bar{1}$), respectively. Scattering factors with corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final atomic parameters are given in Table 2.*

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53228 (66 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates and equivalent isotropic temperature-factor coefficients* (*calculated from the average of the anisotropic temperature factors over all directions for the non-hydrogen atoms*) *with standard deviations*

	x	*y*	*z*	U_{eq}(Å^2)†
[$PdI_2(THT)_2$]				
Pd	0·40123 (5)	0·67445 (5)	0·21537 (4)	0·0325 (2)
I1	0·62028 (5)	0·76099 (5)	0·04281 (5)	0·0487 (2)
I2	0·17018 (5)	0·59971 (6)	0·38382 (5)	0·0554 (2)
S1	0·19418 (17)	0·61475 (18)	0·04077 (16)	0·0383 (4)
S2	0·59829 (20)	0·68752 (19)	0·39608 (17)	0·0466 (5)
C11	0·2435 (8)	0·6201 (8)	−0·1453 (6)	0·043 (2)
C12	0·2092 (9)	0·7716 (9)	−0·1842 (7)	0·053 (2)
C13	0·0661 (9)	0·8089 (10)	−0·1033 (7)	0·050 (3)
C14	0·0995 (9)	0·7868 (9)	0·0508 (7)	0·049 (2)
C21	0·7653 (10)	0·8507 (14)	0·4056 (9)	0·080 (4)
C22	0·8040 (14)	0·9027 (17)	0·5612 (10)	0·094 (4)
C23	0·6554 (15)	0·8891 (14)	0·6371 (10)	0·095 (4)
C24	0·5455 (10)	0·7469 (12)	0·5780 (8)	0·070 (3)
H111	0·347 (9)	0·596 (8)	0·848 (7)	0·02 (2)
H112	0·162 (11)	0·517 (11)	0·806 (10)	0·06 (3)
H121	0·310 (11)	0·872 (10)	0·842 (9)	0·05 (2)
H122	0·178 (10)	0·766 (9)	0·714 (9)	0·04 (2)
H131	0·040 (8)	0·895 (9)	0·887 (7)	0·02 (2)
H132	−0·018 (8)	0·744 (8)	0·859 (7)	0·01 (2)
H141	0·011 (9)	0·784 (8)	0·096 (8)	0·03 (2)
H142	0·184 (11)	0·867 (10)	0·091 (10)	0·05 (3)
H211	0·857 (15)	0·865 (14)	0·361 (13)	0·10 (4)
H212	0·710 (11)	0·964 (10)	0·384 (9)	0·04 (2)
H221	0·855 (20)	0·819 (20)	0·599 (18)	0·15 (8)
H222	0·871 (12)	0·982 (12)	0·581 (10)	0·06 (3)
H231	0·667 (12)	0·933 (12)	0·701 (11)	0·05 (3)
H232	0·687 (17)	1·009 (16)	0·558 (15)	0·11 (5)
H241	0·455 (18)	0·853 (18)	0·542 (16)	0·14 (5)
H242	0·465 (22)	0·670 (21)	0·610 (21)	0·17 (7)
[$PtI_2(THT)_2$]				
Pt1	0·00	0·00	0·00	0·0338 (1)
Pt2	0·50	0·00	0·50	0·0308 (1)
I1	0·14373 (5)	0·27965 (4)	−0·00557 (4)	0·0600 (2)
I2	0·63147 (4)	0·27089 (4)	0·64554 (4)	0·0514 (1)
S1	−0·27626 (15)	0·07117 (15)	0·01266 (12)	0·0400 (4)
S2	0·21953 (14)	0·05907 (14)	0·51157 (11)	0·0374 (4)
C11	−0·3056 (8)	0·2785 (7)	0·0140 (6)	0·051 (2)
C12	−0·3079 (9)	0·3663 (8)	0·1559 (7)	0·063 (2)
C13	−0·4034 (9)	0·2555 (9)	0·2251 (7)	0·060 (2)
C14	−0·3300 (8)	0·0953 (8)	0·1849 (6)	0·052 (2)
C21	0·1837 (8)	0·2572 (7)	0·6060 (6)	0·054 (2)
C22	0·1922 (11)	0·3617 (8)	0·5115 (8)	0·069 (3)
C23	0·1030 (10)	0·2707 (8)	0·3895 (8)	0·068 (3)
C24	0·1684 (7)	0·1056 (7)	0·3568 (8)	0·047 (2)
H111	−0·232 (10)	0·302 (9)	−0·031 (7)	0·05 (2)
H112	−0·422 (8)	0·279 (7)	−0·035 (6)	0·03 (2)
H121	−0·196 (11)	0·397 (10)	0·181 (8)	0·07 (3)
H122	−0·372 (7)	0·477 (7)	0·171 (5)	0·02 (1)
H131	−0·526 (8)	0·249 (7)	0·208 (6)	0·03 (2)
H132	−0·409 (12)	0·287 (11)	0·306 (10)	0·08 (3)
H141	−0·391 (8)	0·033 (7)	0·189 (6)	0·02 (2)
H142	−0·217 (7)	0·089 (6)	0·240 (5)	0·02 (1)
H211	0·081 (8)	0·224 (7)	0·651 (6)	0·02 (2)
H212	0·269 (8)	0·288 (7)	0·656 (6)	0·03 (2)
H221	0·156 (10)	0·449 (10)	0·536 (8)	0·05 (2)
H222	0·304 (9)	0·405 (8)	0·511 (7)	0·04 (2)
H231	0·116 (9)	0·309 (9)	0·317 (8)	0·05 (2)
H232	−0·020 (10)	0·265 (9)	0·406 (8)	0·06 (2)
H241	0·274 (9)	0·111 (8)	0·309 (7)	0·05 (2)
H242	0·086 (8)	0·020 (7)	0·306 (6)	0·03 (2)

†$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Computer programs used were those compiled and amended by Lundgren (1982).

Results and discussion

Both compounds are composed of discrete van-der-Waals-packed *trans*-[$MI_2(THT)_2$] complexes (Fig. 1).

The Pd complex has no internal symmetry and is only pseudoplanar (Fig. 2*a*). The atoms Pd, S1, S2, I1 and I2 are coplanar within 0·2 Å. The two Pd—I distances are slightly different while there is no significant difference in the Pd—S distances (Table 3). The deviation from centrosymmetry of the complex can be checked by the value of Δ/σ, where Δ is the parameter shift necessary to achieve centrosymmetry and σ the e.s.d. of that parameter. The largest Δ/σ is 100 within the coordination sphere (I) and it is as large as 182 for some carbon atoms in the THT ring (C13, C22).

Each of the two Pt complexes in the asymmetric unit is centrosymmetric (Figs. 2*b* and 2*c*). As for the Pd compound, the two independent metal–sulfur distances are equal within experimental error but there is a slight difference in the two Pt—I distances.

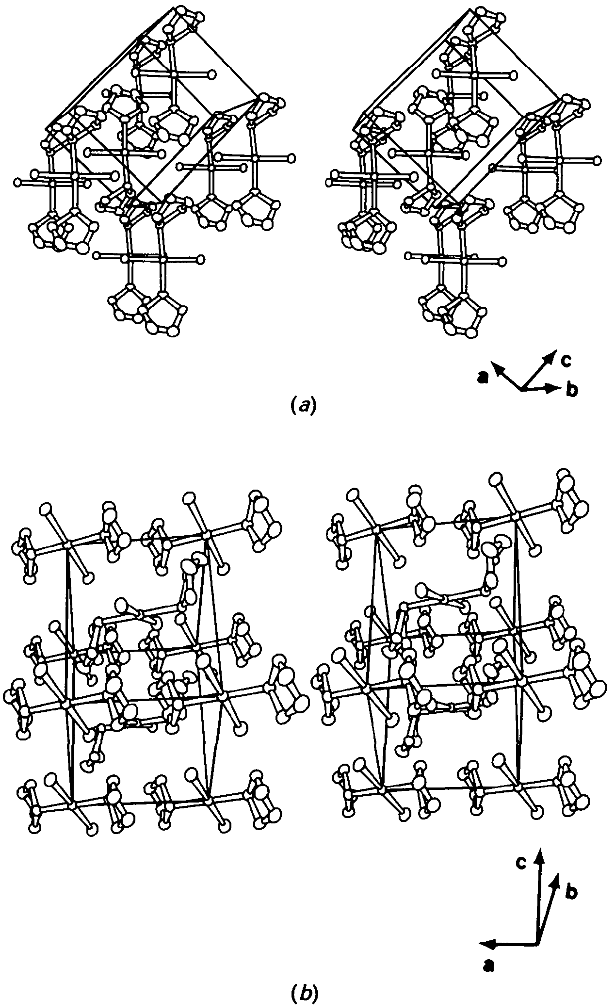
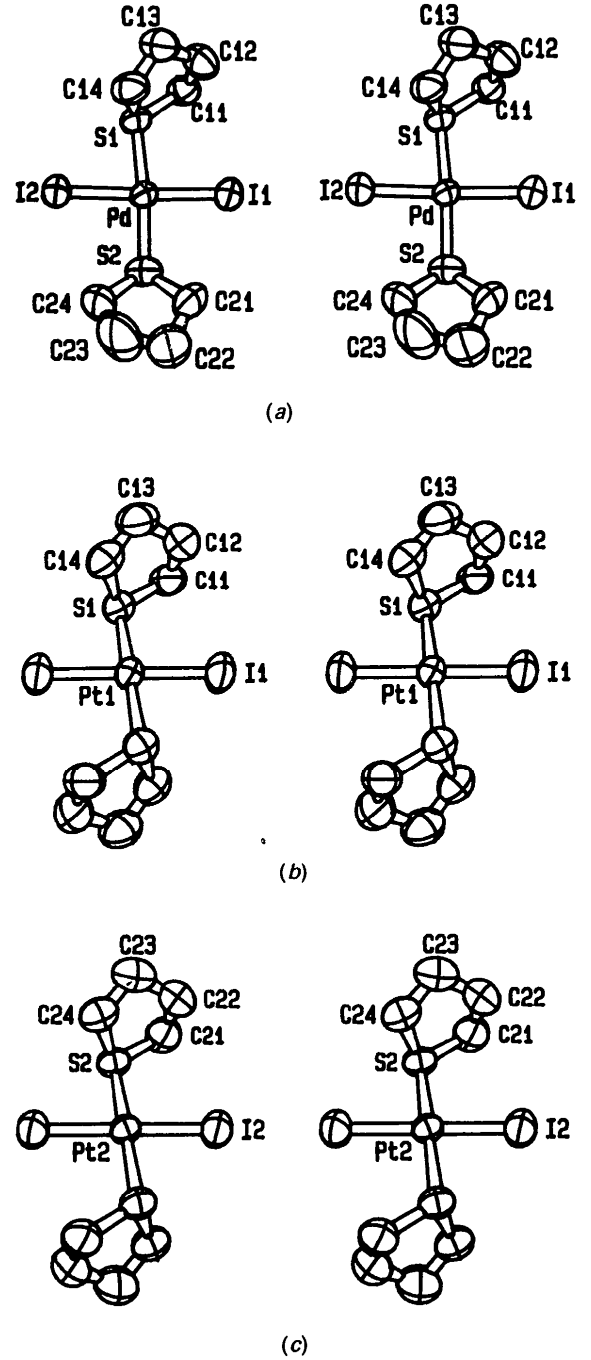


Fig. 1. Packing diagram of (*a*) the $PdI_2(THT)_2$ and (*b*) the $PtI_2(THT)_2$ molecules.

In all complexes the sulfur atoms bind to the metal through one of the lone pairs, the angle M—S—C being between 118·2 and 105·1°. Bond distances and angles within the THT molecule are normal (Table 3) and in agreement with those observed in Ag^I (Norén & Oskarsson, 1984) and Au^I compounds (Ahrland, Norén & Oskarsson, 1985). In the two compounds the closest distances between different complexes are normal van der Waals contacts.



(a)

(b)

(c)

Fig. 2. Stereoview and numbering of (a) the $PdI_2(THT)_2$ molecule and (b), (c) two $PtI_2(THT)_2$ molecules.

The distribution of M—A bond lengths in a series of square-planar *trans*-$[MA_2LX]$ complexes is affected by intramolecular (*cis* influence of L and X, steric requirements of the ligands) and intermolecular forces. These factors may both increase and decrease the M—A distances and it is reasonable to use the average distance observed for a series of compounds as the reference in calculating the *trans* influence for other donor atoms. Table 4(*a*) gives the average and the distribution of M—I and M—S distances in mononuclear *trans*-$[MI_2LX]$ and *trans*-$[MS_2LX]$ compounds. Since sulfur may have different bonding properties in different molecules only data for thioether sulfurs have been included.

In compounds containing *trans*-$[MI_2L_2]$ complexes both M—I distances are affected by the same *cis* influence and differences in M—I distances for complexes with the same L should be due to intermolecular forces only. The distribution of M—I distances in this type of compound will thus indicate the effect of such forces on the M—I distances. The largest differences for Pt—I distances are observed in $K_2[PtI_4].2H_2O$, 2·606–2·616 Å (Olsson & Oskarsson, 1989), and in *trans*-$[PtI_2(THT)_2]$, 2·606–2·616 Å. For Pd—I the largest differences are found in *trans*-$[PdI_2\{P(CH_3)_2H\}_2]$, 2·592–2·638 Å (Bailey & Mason, 1968), and in *trans*-$[PdI_2(THT)_2]$, 2·603–2·625 Å. These differences are much larger than the e.s.d.'s, 0·001–0·003 Å, and can mainly be ascribed to changes in intermolecular forces. Furthermore, the spread of the Pd—I distances is much larger than that of the Pt—I distances (Table 4*a*) which might be explained by the fact that Pd—I bonds are softer than Pt—I bonds and therefore more sensitive to changes in intermolecular forces.

The distributions of bond distances in Table 4(*a*) may be compared to those including complexes were the donor atom, I or S, is not in a *trans* position to itself, Table 4(*b*). In this case the average value is affected not only by *cis* effects and intermolecular forces, but also by changes in *trans* influence. The distributions, calculated in units of 1σ, are increased 1·3, 5·2, 4·0 and 3·2 times for Pd—I, Pd—S, Pt—I and Pt—S, respectively. In conclusion, with the exception of Pd—I, the effects of *cis* influence and intermolecular forces on these bond distances are several times smaller than the effect of donor atoms with a large *trans* influence.

Experimental assistance from Mrs Bodil Eliasson and financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

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

trans-[PdI$_2$(THT)$_2$]				*trans*-[PtI$_2$(THT)$_2$]			
(*a*) Coordination geometry around the metal atoms							
Pd—I1	2·603 (1)	I1—Pd—I2	176·43 (2)	Pt1—I1	2·606 (1)	I1—Pt1—S1	96·45 (4)
Pd—I2	2·625 (1)	I1—Pd—S1	95·09 (4)	Pt2—I2	2·616 (1)	I2—Pt2—S2	97·17 (4)
Pd—S1	2·316 (2)	I1—Pd—S2	89·97 (4)	Pt1—S1	2·310 (1)		
Pd—S2	2·329 (2)	I2—Pd—S1	82·85 (4)	Pt2—S2	2·309 (1)		
		I2—Pd—S2	92·52 (4)				
		S1—Pd—S2	169·67 (6)				
(*b*) Bond angles around the sulfur atoms							
Pd—S1—C11	118·2 (2)	Pd—S2—C24	116·5 (3)	Pt1—S1—C11	116·6 (2)	Pt2—S2—C24	105·8 (2)
Pd—S1—C14	105·5 (2)	C11—S1—C14	93·9 (3)	Pt1—S1—C14	105·1 (2)	C11—S1—C14	93·6 (3)
Pd—S2—C21	115·7 (3)	C21—S2—C24	92·7 (4)	Pt2—S2—C21	115·3 (2)	C21—S2—C24	93·4 (3)
(*c*) Geometry of the tetrahydrothiophene molecules							
S1—C11	1·83 (1)	S1—C11—C12	107·0 (5)	S1—C11	1·83 (1)	S1—C11—C12	106·1 (4)
C11—C12	1·50 (1)	C11—C12—C13	107·1 (6)	C11—C12	1·52 (1)	C11—C12—C13	106·6 (5)
C12—C13	1·52 (1)	C12—C13—C14	106·7 (6)	C12—C13	1·50 (1)	C12—C13—C14	107·6 (6)
C13—C14	1·52 (1)	C13—C14—S1	105·3 (5)	C13—C14	1·52 (1)	C13—C14—S1	105·7 (4)
C14—S1	1·83 (1)	C14—S1—C11	93·9 (3)	C14—S1	1·85 (1)	C14—S1—C14	93·6 (3)
S2—C21	1·84 (1)	S2—C21—C22	105·2 (7)	S2—C21	1·82 (1)	S2—C21—C22	105·7 (5)
C21—C22	1·49 (1)	C21—C22—C23	109·3 (9)	C21—C22	1·50 (1)	C21—C22—C23	107·7 (6)
C22—C23	1·47 (2)	C22—C23—C24	110·6 (9)	C22—C23	1·49 (1)	C22—C23—C24	107·1 (6)
C23—C24	1·47 (2)	C23—C24—S2	108·3 (6)	C23—C24	1·53 (1)	C23—C24—S2	106·7 (4)
C24—S2	1·82 (1)	C24—S2—C21	92·7 (4)	C24—S2	1·83 (1)	C24—S2—C21	93·4 (3)

Table 4. *The average and distribution of M*—I *and M*—S *distances* (Å)

The data are collected mainly from the Cambridge Structural Database, release January 1988 (Allen, Kennard & Taylor, 1983). The references are given in Codens-type notation according to *Checklist for Authors* (1985). The distribution has been calculated as $\sigma = [\sum_n (d_n - \bar{d})^2/(n-1)]^{1/2}$.

	Average and σ	No. of distances	References
(*a*) Compounds of the type *trans*-[MI_2LX] and *trans*-[MS_2LX] (S = thioether sulfur)			
Pd—I	2·605 (20)	14	(1)–(8)
Pt—I	2·609 (9)	14	(1), (9)–(17)
Pd—S	2·320 (15)	11	(1), (18)–(22)
Pt—S	2·313 (13)	9	(1), (23)–(24)
(*b*) Compounds including those where the donor atom, I or S, is not in a *trans* position to itself			
Pd—I	2·612 (25)	23	(1)–(8), (25)–(29)
Pt—I	2·623 (36)	26	(1), (9)–(17), (30)–(46)
Pd—S	2·315 (79)	36	(1), (18)–(22), (47)–(56)
Pt—S	2·299 (42)	26	(1), (23), (57)–(65)

References: (1) this paper; (2)–(8) ASBSDK 29 1283, ASBSDK 26 1655, JORCAI 37 C49, JCSIAP 1968 2594, INOCAJ 23 2572, JCDTBI 1986 2289, ACSCEE 43 21; (9)–(17) ACAPCT 43 811, JCDTBI 1974 1834, JCDTBI 1977 2038, CHBEAM 111 3162, JCDTBI 1979 948, INOCAJ 23 4309, ACSCEE 42 1743, ASBSDK 38 1133, ACSCEE 43 1281; (18)–(22) ASBSDK 34 1711, ASBSDK 34 1712, JCDTBI 1980 2309, JCDTBI 1980 2312, ACSCEE 39 993; (23)–(24) ACAPCT Bugarcic, Z. *et al.*, submitted, JCDTBI 1977 458; (25)–(29) INOCAJ 20 1702, JORCAI 215 121, ACSCEE 39 877, ZNBAD2 38 1295, AJCHAS 35 2193; (30)–(46) INOCAJ 14 1628, JORCAI 71 299, JORCAI 133 273, CJCHAG 58 664, JCCCAT 1981 698, JORCAI 228 C71, JACSAT 104 6609, JCDTBI 1983 1619, JCDTBI 1983 1583, ACSCEE 41 513, JCDTBI 1986 595, JCDTBI 1986 151, JACSAT 108 322, ICHAA3 115 L35, ICHAA3 124 213, ICHAA3 117 17, ZSTKAI 1985 955; (47)–(56) ASBSDK 26 1402, JCDTBI 1973 821, ASBSDK 35 1465, ACSCEE 39 877, JCDTBI 1980 137, ASBSDK 29 762, ASBSDK 30 1889, ASBSDK 30 753, JACSAT 97 1275, JORCAI 215 121; (57)–(65) INOCAJ 10 2309, INOCAJ 26 185, JCDTBI 1970 1523, ICHAA3 22 69, JACSAT 98 6159, JCDTBI 1979 434, ICHAA3 89 L9, ACSCEE 41 1750, CJCHAG 64 1474.

References

Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* **A27**, 157–165.

Ahrland, S., Norén, B. & Oskarsson, Å. (1985). *Inorg. Chem.* **24**, 1330–1333.

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Bailey, N. A. & Mason, R. (1968). *J. Chem. Soc. A*, pp. 2594–2605.

Basolo, F. & Pearson, R. G. (1962). *Prog. Inorg. Chem.* **4**, 381–453.

Bürgi, H. B. (1989). 12th Eur. Crystallogr. Meet., Moscow. Collected Abstracts, Vol. 3, p. 397.

Checklist for Authors (1985). *Acta Cryst.* **B41**, 1–4.

Elding, L. I. (1972). *Inorg. Chim. Acta*, **6**, 647–651.

Elding, L. I. (1976). *Inorg. Chim. Acta*, **20**, 65–69.

Lundgren, J. O. (1982). Report No. UUIC-B13-4-05. Univ. of Uppsala, Sweden.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Mason, R. & Randaccio, L. (1971). *J. Chem. Soc. A*, pp. 1150–1154.

Mason, R. & Towl, D. C. (1970). *J. Chem. Soc. A*, pp. 1601–1613.

Melanson, R., Hubert, J. & Rochon, F. D. (1976). *Acta Cryst.* **B32**, 1914–1916.

Melanson, R. & Rochon, F. D. (1988). *Acta Cryst.* **C44**, 1893–1895.

Norén, B. & Oskarsson, Å. (1984). *Acta Chem. Scand. Ser. A*, **38**, 479–484.

Olsson, L.-F. & Oskarsson, Å. (1989). *Acta Chem. Scand.* **43**, 811–812.

Pidcock, A., Richards, R. E. & Venanzi, L. M. (1966). *J. Chem. Soc. A*, pp. 1707–1710.