

$a = 7.5815(8) \text{ \AA}$
 $b = 9.9861(9) \text{ \AA}$
 $c = 10.2413(12) \text{ \AA}$
 $\alpha = 78.417(9)^\circ$
 $\beta = 88.559(9)^\circ$
 $\gamma = 71.491(8)^\circ$
 $V = 719.66(14) \text{ \AA}^3$
 $Z = 1$
 $D_x = 1.5493 \text{ Mg m}^{-3}$
 D_m not measured

$\mu = 0.671 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 Rod
 $0.30 \times 0.25 \times 0.25 \text{ mm}$
 Pink

son, 1976). Software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of a CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey, and are grateful to the Kafkas University Research Fund for the financial support of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1013). Services for accessing these data are described at the back of the journal.

Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

empirical via ψ scans
 (*MolEN*; Fair, 1990)

$T_{\min} = 0.828$, $T_{\max} = 0.846$

3086 measured reflections

2913 independent reflections

2842 reflections with

$F > 0$

$R_{\text{int}} = 0.064$

$\theta_{\max} = 26.3^\circ$

$h = 0 \rightarrow 9$

$k = -11 \rightarrow 12$

$l = -12 \rightarrow 12$

3 standard reflections

every 250 reflections

frequency: 120 min

intensity decay: 1%

Refinement

Refinement on F

$R = 0.037$

$wR = 0.046$

$S = 1.03$

2842 reflections

205 parameters

H atoms riding

$w = 1/[\sigma(F^2) + (0.02F)^2 + 1]$

$(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 0.50 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Co—O1	2.136 (1)	O6—N3	1.199 (3)
Co—O3	2.091 (2)	N1—C1	1.323 (3)
Co—N2	2.134 (2)	N2—C3	1.337 (3)
O2—C1	1.234 (2)	N2—C4	1.335 (2)
O3—C7	1.254 (2)	N3—C11	1.475 (4)
O4—C7	1.251 (2)	C7—C8	1.512 (3)
O5—N3	1.195 (3)		
O1—Co—O3	92.67 (6)	O2—C1—N1	122.2 (2)
O1—Co—N2	92.88 (6)	O2—C1—C2	119.8 (2)
O3—Co—N2	90.19 (6)	N1—C1—C2	118.0 (2)
Co—O3—C7	126.8 (1)	N3—C11—C10	118.5 (2)
Co—N2—C3	119.1 (1)	N3—C11—C12	118.5 (2)
Co—N2—C4	123.0 (4)	N2—C3—C2	123.4 (2)
C3—N2—C4	118.0 (2)	N2—C4—C5	122.4 (2)
O5—N3—O6	122.9 (3)	O3—C7—O4	126.0 (2)
O5—N3—C11	118.8 (2)	O3—C7—C8	117.7 (2)
O6—N3—C11	118.2 (2)	O4—C7—C8	116.3 (2)
O1—Co—O3—C7	-18.3 (2)	O3—Co—N2—C3	34.7 (2)
N2—Co—O3—C7	74.6 (2)	O3—Co—N2—C4	-144.7 (2)
O1—Co—N2—C3	127.4 (2)	Co—O3—C7—O4	14.3 (3)
O1—Co—N2—C4	-52.0 (2)	Co—O3—C7—C8	-162.2 (1)

The title structure was solved by the Patterson method. The H-atom positions were calculated geometrically, with $U_{\text{eq}}(\text{H}) = 1.3U_{\text{eq}}$ of the parent non-H atom. A riding model was used in the refinement.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (John-

References

- Adiwidjaja, G., Rossmanith, E. & Kuppens, H. (1978). *Acta Cryst.* **B34**, 3079–3081.
- Amiraslanov, I. R., Mamedov, Kh. S., Movsumov, E. M., Musaev, F. N. & Nadzhafov, G. N. (1979). *Zh. Strukt. Khim.* **20**, 1075–1080.
- Antsyshkina, A. S., Chiragov, F. M. & Poray-Koshits, M. A. (1980). *Koord. Khim.* **15**, 1098–1103.
- Catterick, J., Hursthouse, M. B., New, D. B. & Thornton, P. (1974). *J. Chem. Soc. Chem. Commun.* pp. 843–844.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
- Hökelek, T. & Necefoglu, H. (1997). *Acta Cryst.* **C53**, 187–189.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Mikeshvili, Z. V. (1982). Dissertation, Tbilisi State University, Georgia.
- Nadzhafov, G. N., Shnulin, A. N. & Mamedov, Kh. S. (1981). *Zh. Strukt. Khim.* **22**, 124–128.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Shnulin, A. N., Nadzhafov, G. N., Amiraslanov, I. R., Usabaliev, B. T. & Mamedov, Kh. S. (1981). *Koord. Khim.* **7**, 1409–1416.

Acta Cryst. (1998). **C54**, 1244–1247

Bis[μ -methylenebis(dicyclohexylphosphine)-*P:P'*]bis[chloropalladium(I)](*Pd—Pd*) Diacetonitrile Solvate

MIHO HASHIOKA, KEN SAKAI AND TARO TSUBOMURA*

Department of Industrial Chemistry, Seikei University, Kichijoji-Kitamachi, Musashino, Tokyo 180, Japan. E-mail: tsubo@ch.seikei.ac.jp

(Received 28 November 1997; accepted 24 March 1998)

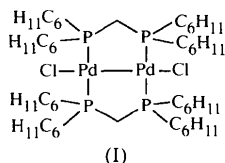
Abstract

A dinuclear palladium(I) complex bridged by two diphosphine ligands, bis[μ -methylenebis(dicyclohexylphosphine)-*P:P'*]bis[chloropalladium(I)](*Pd—Pd*) diacetonitrile solvate, [Pd₂Cl₂(C₂₅H₄₆P₂)₂]₂·2C₂H₃N, has been prepared, and the crystal structure determined.

The two approximately square-planar ligand arrays show twisting, and the torsion angles are interpreted in terms of the steric factors between the diphosphine ligands.

Comment

Phosphine-bridged Pd^I dimers have been known to contain a reactive metal-metal bond. In addition to the thermal reactivities, interesting photochemical and photophysical properties have recently been reported for dinuclear Pd^I and Pt^I complexes containing diphosphines as bridging ligands (Tsubomura *et al.*, 1994; Yip *et al.*, 1993). A diphosphine ligand, dppm [methylenebis(diphenylphosphine)], has frequently been used as a bridging ligand of monovalent palladium complexes. There have been two crystal structures reported of dinuclear Pd^I complexes containing dppm-type ligands, namely Pd₂(dmpm)₂Br₂ and Pd₂(dppm)₂Br₂, where dmpm is methylenebis(dimethylphosphine). In this paper, we report the crystal structure of a new Pd^I complex, (I), bridged by two dcpm ligands [dcpm is methylenebis(dicyclohexylphosphine)]. The molecule consists of two Pd^I atoms, bridged by two dcpm chelates and two terminal Cl atoms.



Figs. 1 and 2 show the structure of the complex. The Pd—Pd separation of 2.6461(7) Å is well within the range normally reported for single bonds between Pd^I atoms (2.53–2.70 Å; Cotton & Wilkinson, 1988). The Pd—Pd separation is longer than the value of 2.603(1) Å observed for the related dmpm complex, Pd₂(dmpm)₂Br₂ (Kullberg *et al.*, 1985), and shorter than the value of 2.699 Å in Pd₂(dppm)₂Br₂ (Holloway *et al.*, 1976). Both of the Pd atoms adopt almost square-planar geometry, with bond angles in the range 87.54(6)–93.46(6)°.

The eight-membered ring, made up of two Pd, four P and two methylene C atoms, shows twisting about the Pd—Pd axis, as reported previously for the two examples of dinuclear Pd^I complexes (Fig. 2). The torsion angles P1—Pd2—Pd1—P2 and P3—Pd2—Pd1—P4 are 36.92(6) and 34.78(5)°, respectively, and these are much smaller than the angles reported for the other two complexes. For diphosphine-bridged Pd^I—Pd^I complexes, an angle of 45° is suggested to be ideal, because of minimization of *dπ*-orbital overlap on the two Pd centres (Kullberg *et al.*, 1985). The twist angles of the three phosphine complexes mentioned above are in the following order: dcpm (35.8°) < dppm (39.0°) < dmpm (50.5°). The smallest twist angle, exhibited by

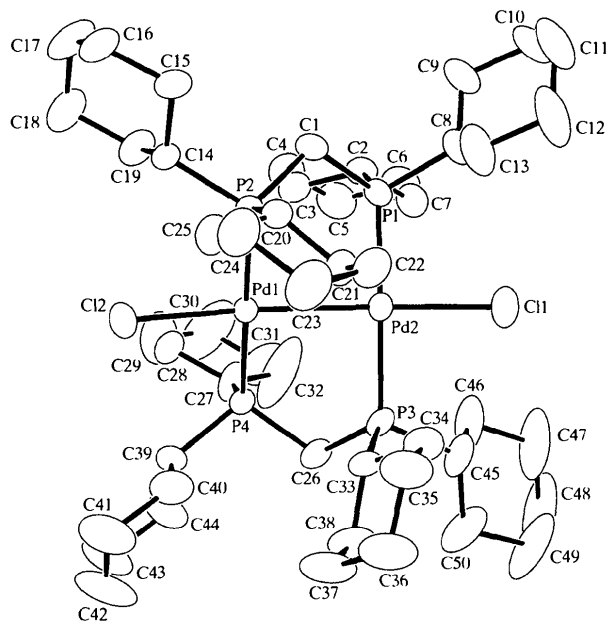


Fig. 1. The structure of the title palladium(I) complex. Ellipsoids are plotted at the 40% probability level and H atoms have been omitted for clarity.

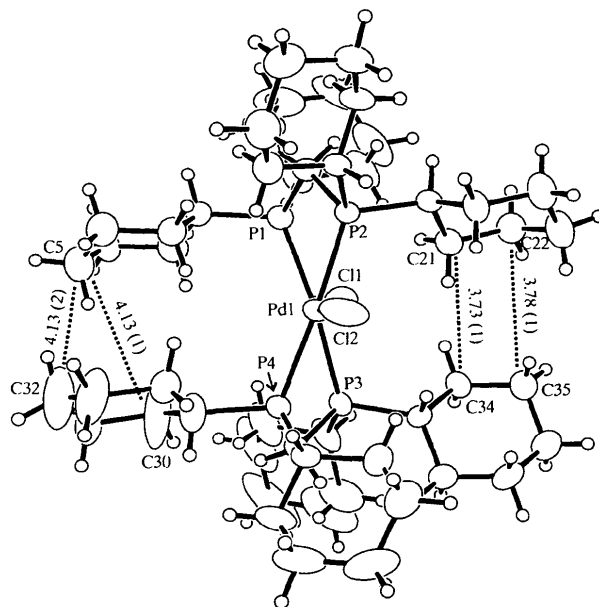


Fig. 2. A side view of the palladium(I) complex. Some interatomic distances between the cyclohexyl groups are also shown (Å).

the title dimer, can be interpreted in terms of the steric factors arising from the bulky cyclohexyl groups. Some short interligand C...C distances between the cyclohexyl groups are also shown in Fig. 2. The results clearly indicate that the bulky cyclohexyl rings are more effective in reducing the twist, in comparison with both the phenyl rings and the methyl groups.

The reactivity of the *M—M* bond of the diphosphine complexes may vary according to the alkyl group on the P atoms. For example, the reactivity of the dmpm complex is enhanced in comparison with the dppm complex (Kullberg & Kubiak, 1986). Furthermore, dcpm complexes of a zero-valent metal were reported to show unique reactivity, including C—H activation (Hackett & Whitesides, 1988). Although the reactions of the present dcpm—Pd^I complex have not been explored, the reactivity is expected to be different from that of other diphosphine complexes.

Experimental

Pd(PPh₃)₄ (Coulson, 1972) and PdCl₂(C₆H₅CN)₂ (Doyle *et al.*, 1960) were prepared as previously described. The diphosphine, dcpm, was used as received from Strem. The benzene used in the synthesis was distilled over calcium hydride under an Ar atmosphere. To a solution of Pd(PPh₃)₄ (0.06 mmol) in dry benzene (4 ml) under Ar was added a twofold excess of dcpm (0.12 mmol). The mixture was stirred for 5 min, then PdCl₂(C₆H₅CN)₂ (0.06 mmol) was added to the solution. This orange solution was stirred at 343 K for 2 h. The resulting red solution was cooled to room temperature and the precipitated solid was removed by filtration. The solution was concentrated to half its original volume and the red precipitate which formed was filtered. The product was dried under vacuum. Crystals suitable for X-ray diffraction were obtained by recrystallization from CH₃CN at 268 K.

Crystal data

[Pd ₂ Cl ₂ (C ₂₅ H ₄₆ P ₂) ₂].2C ₂ H ₃ N	Mo K α radiation
$M_r = 1183.0$	$\lambda = 0.71069 \text{ \AA}$
Monoclinic	Cell parameters from 25 reflections
$P2_1/n$	$\theta = 28.74\text{--}29.84^\circ$
$a = 28.021 (5) \text{ \AA}$	$\mu = 0.856 \text{ mm}^{-1}$
$b = 17.118 (4) \text{ \AA}$	$T = 295 (2) \text{ K}$
$c = 12.110 (2) \text{ \AA}$	Prism
$\beta = 90.44 (2)^\circ$	$0.5 \times 0.3 \times 0.2 \text{ mm}$
$V = 5809 (2) \text{ \AA}^3$	Red
$Z = 4$	
$D_x = 1.353 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Rigaku AFC-5S diffractometer	9124 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{\text{int}} = 0.04$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$\theta_{\text{max}} = 30^\circ$
$T_{\text{min}} = 0.70$, $T_{\text{max}} = 0.84$	$h = 0 \rightarrow 39$
17 784 measured reflections	$k = 0 \rightarrow 24$
16 930 independent reflections	$l = -17 \rightarrow 17$
	3 standard reflections every 150 reflections
	intensity decay: 3.8%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.029$
$R[F^2 > 2\sigma(F^2)] = 0.064$	$\Delta\rho_{\text{max}} = 1.154 \text{ e \AA}^{-3}$
$wR(F^2) = 0.184$	$\Delta\rho_{\text{min}} = -1.031 \text{ e \AA}^{-3}$

$S = 1.034$
 16 865 reflections
 552 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0410P)^2 + 15.4P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXL93* (Sheldrick, 1993)
 Extinction coefficient: 0.00047 (8)
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Pd1—P4	2.324 (2)	Pd2—Cl1	2.442 (2)
Pd1—P2	2.324 (2)	P1—C1	1.829 (6)
Pd1—Cl2	2.429 (2)	P2—C1	1.836 (6)
Pd1—Pd2	2.6461 (7)	P3—C26	1.829 (6)
Pd2—P1	2.315 (2)	P4—C26	1.839 (6)
Pd2—P3	2.323 (2)		
P4—Pd1—P2	176.05 (6)	P1—Pd2—Pd1	90.87 (4)
P4—Pd1—Cl2	93.46 (6)	P3—Pd2—Pd1	88.50 (4)
P2—Pd1—Cl2	87.54 (6)	Cl1—Pd2—Pd1	165.18 (5)
P4—Pd1—Pd2	91.42 (4)	C1—P1—Pd2	115.1 (2)
P2—Pd1—Pd2	88.44 (4)	C1—P2—Pd1	114.4 (2)
Cl2—Pd1—Pd2	166.64 (6)	C26—P3—Pd2	113.9 (2)
P1—Pd2—P3	173.88 (6)	C26—P4—Pd1	116.1 (2)
P1—Pd2—Cl1	91.88 (7)	P1—C1—P2	109.9 (3)
P3—Pd2—Cl1	90.28 (7)	P3—C26—P4	108.9 (3)

Metal-atom positions were determined by direct methods (*SAPI91*; Fan, 1991). The remaining non-H atoms were located using *DIRDIF* (Parthasarathi *et al.*, 1983) and difference Fourier techniques. H atoms in the complex molecule were all located at their calculated positions, and idealized before each refinement. Two acetonitrile molecules were found in the asymmetric unit. For one of the acetonitrile molecules, the C and N atoms were refined independently and anisotropically. The H atoms on the methyl group of the molecule were refined using the riding model. After several trials, the following disordered model was adopted for the other acetonitrile molecule: it was treated as two separate rigid linear groups, and the occupancies of the atoms in each group were set to 0.5. The positional and displacement parameters for the disordered solvent molecules were fixed in the final least-squares refinement. The magnitude of the largest difference Fourier peak is 1.15 e \AA^{-3} , only 0.66 \AA from atom C57 of the disordered acetonitrile molecule.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1994b). Program(s) used to solve structure: *SAPI91*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEX* (McArdle, 1995).

This work was partly supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1051). Services for accessing these data are described at the back of the journal.

References

- Cotton, F. A. & Wilkinson, G. (1988). *Advanced Inorganic Chemistry*, 4th ed., p. 932. New York: John Wiley & Sons.
 Coulson, D. R. (1972). *Inorg. Synth.* **13**, 121–124.

- Doyle, J. R., Slade, P. E. & Jonassen, H. B. (1960). *Inorg. Synth.* **6**, 216–219.
- Fan, H.-F. (1991). *SAPI91. Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.
- Hackett, M. & Whitesides, G. M. (1988). *J. Am. Chem. Soc.* **110**, 1449–1462.
- Holloway, R. G., Penfold, B. R., Colton, R. & McCormick, M. J. (1976). *J. Chem. Soc. Chem. Commun.* pp. 485–486.
- Kullberg, M. L. & Kubiak, C. P. (1986). *Inorg. Chem.* **25**, 26–30.
- Kullberg, M. L., Lemke, F. R., Powell, D. R. & Kubiak, C. P. (1985). *Inorg. Chem.* **24**, 3589–3593.
- McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
- Molecular Structure Corporation (1994a). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1994b). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6f. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Parthasarathi, V., Beurskens, P. T. & Slot, H. J. B. (1983). *Acta Cryst.* **A39**, 860–864.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Tsubomura, T., Itsuki, A., Homma, M. & Sakai, K. (1994). *Chem. Lett.* pp. 661–664.
- Yip, H.-K., Che, C.-M. & Peng, S.-M. (1993). *J. Chem. Soc. Dalton Trans.* pp. 179–187.

Acta Cryst. (1998). **C54**, 1247–1249

Organometallic Selenolates. IX.† (18-Crown-6)potassium (η^5 -Cyclopentadienyl)bis(1,4-tetraselenido- Se^1, Se^4 -tungstate(IV))

CARSTEN THÖNE, PETER G. JONES, JÖRG LAUBE AND STEFAN JÄGER

Institut für Analytische und Anorganische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: thoene@xray36.anchem.nat.tu-bs.de

(Received 10 February 1998; accepted 30 March 1998)

Abstract

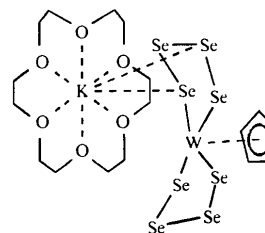
The title compound, [(18-crown-6)K]⁺[W(η^5 -C₅H₅)(η^2 -Se₄)₂]⁻ or [K(C₁₂H₂₄O₆)] [W(C₅H₅)(Se₄)₂], consists of the anion [CpW(Se₄)₂]⁻ (where Cp is cyclopentadienyl), which is linked to the [(18-crown-6)K]⁺ cation via two potassium–selenium contacts of 3.457 (5) and 3.527 (5) Å. One of the WSe₄ rings adopts an envelope conformation, whereas the other WSe₄ ring lies between the standard envelope and half-chair conformations.

† Part VIII: Jones *et al.* (1998).

The corresponding W–Se bond lengths lie in the range 2.441 (2)–2.570 (2) Å, indicating asymmetry in the chelation of both Se₄ ligands, which can also be seen from the Se–Se bond-length range of 2.300 (4)–2.447 (3) Å.

Comment

Transition-metal–selenido complexes exhibit interesting structural features associated with a variety of binding modes of the Se_n²⁻ ligands. Numerous crystal structures of (oligoselenido)metallate complexes have been reported, of which *M*(Se₄)_n²⁻ complexes are the most common (Cambridge Structural Database, Version of October 1997; Allen & Kennard, 1993; Wardle, Bhaduri *et al.*, 1988), because of the high stability of five-membered *M*Se₄ rings. However, examples of organometallic *RM*(Se₄)_x systems are rare. During our studies on new syntheses of transition-metal–selenido complexes, we described the formation of the tetraselenido complex [CpW(CO)₃]₂Se₄ (where Cp is cyclopentadienyl) via insertion of elemental selenium into the alkali-metal–tungsten bond of [LiW(CO)₃] in an appropriate ratio and subsequent oxidation with oxygen on SiO₂ (Jones & Thöne, 1996). A crystal structure analysis revealed a μ_2 - η^1 bonding pattern of the Se₄²⁻ ligand (Jones *et al.*, 1998). We present here the crystal structure of [(18-crown-6)K]⁺[CpW(Se₄)₂]⁻, (1).



(1)

Compound (1) consists of a cation–anion pair. The K⁺ cation lies 0.694 (8) Å out of the best plane through the O atoms of the crown ether [K–O 2.774 (14)–2.939 (14) Å] and is involved in weak interionic K···Se contacts of 3.457 (5) (K···Se1) and 3.527 (5) Å (K···Se3). The [CpW(Se₄)₂]⁻ anion consists of two WSe₄ rings with a common W atom. The coordination geometry at the W atom is slightly distorted tetragonal pyramidal, with W 0.999 (1) Å out of the basal plane (atoms Se1, Se4, Se5 and Se8; r.m.s. deviation 0.42 Å). The Se···Se contacts in this plane range from 2.937 (3) to 3.519 (3) Å, with Se···Se···Se angles between 82.73 (7) and 95.52 (7)°. The W–Cp(centre) vector makes an angle of 180 (1)° with the normal to the base of the pyramid.

The chelation of the Se₄²⁻ ligands is asymmetric in both WSe₄ rings; as seen from the W–Se bond