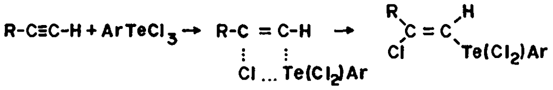
Te may be estimated to be 1·79 Å; a value of 1·78 Å is found in $TeCl_2(C_7H_7O)(C_7H_{11}O_2)$ (Castellano, Zukerman-Schpector, Ferreira & Comasseto, 1986).

The fact that the title compound is in a *Z* configuration is consistent with a four-member transition state (II) and not with a telluronium intermediate which should lead to the *E* isomer.



(II)

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Structure of Wolffram's Salt Analogues [M(−chxn)$_2$Br]Br$_2$ [M = Pd, Pt; −chxn = (−)-1,2-cyclohexanediamine]

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Abstract. *trans*-Dibromobis[(−)-1(*R*),2(*R*)-cyclohexanediamine]palladium(IV)–bis[(−)-1(*R*),2(*R*)-cyclohexanediamine]palladium(II) tetrabromide, $[Pd(C_6H_{14}N_2)_2Br_2][Pd(C_6H_{14}N_2)_2]Br_4$, $M_r = 936·2$, MDO1: monoclinic, $a = 24·464\,(3)$, $b = 7·073\,(1)$, $c = 10·586\,(2)$ Å, $\beta = 102·504\,(6)°$, $V = 1788·4\,(4)$ Å^3, $Z = 2$; superposition structure: orthorhombic, $I222$, $a = 23·884\,(3)$, $b = 7·073\,(1)$, $c = 5·293\,(1)$ Å, $V = 894·2\,(2)$ Å^3, $Z = 1$, $D_x = 1·783$ g cm^{-3}, $F(000) = 558$, Ag $K\alpha$ ($\lambda = 0·56087$ Å), $\mu = 36·3$ cm^{-1}, $T = 295$ K, $R(F) = 0·032$ for 1390 observed unique reflexions [$I > 3\sigma(I)$]. *trans*-Dibromobis[(−)-1(*R*),2(*R*)-cyclohexanediamine]platinum(IV)–bis[(−)-1(*R*),2(*R*)-cyclohexanediamine]platinum(II) tetrabromide, $[Pt(C_6H_{14}N_2)_2Br_2][Pt(C_6H_{14}N_2)_2]Br_4$, $M_r = 1326·4$, MDO1: monoclinic, $a = 24·478\,(3)$, $b = 7·022\,(1)$, $c = 10·747\,(1)$ Å, $\beta = 102·668\,(7)°$, $V = 1802·4\,(3)$ Å^3, $Z = 2$; superposition structure: orthorhombic, $I222$, $a = 23·884\,(3)$, $b = 7·022\,(1)$, $c = 5·374\,(1)$ Å, $V = 901·3\,(2)$ Å^3, $Z = 1$, $D_x = 2·443$ g cm^{-3}, $F(000) = 622$, Mo $K\alpha$ ($\lambda = 0·71073$ Å), $\mu = 144·5$ cm^{-1}, $T = 295$ K, $R(F) = 0·036$ for 2697 reflexions [$I > 3\sigma(I)$]. $[Pt(C_6H_{14}N_2)_2Cl_2][Pt(C_6H_{14}N_2)_2]Cl_4$, $M_r = 1059·6$, MDO1: monoclinic, $a = 24·810\,(4)$, $b = 6·820\,(1)$, $c = 10·316\,(2)$ Å, $\beta = 101·999\,(3)°$, $V = 853·7\,(3)$ Å^3, $Z = 2$. The superposition structures are isomorphous with the platinum chloride compound [Larsen & Toftlund (1977). *Acta Chem. Scand. Ser. A*, **31**, 182–186]. They are built up of M^{IV}—X···M^{II} chains parallel to the *c* axis, but with two half-weight halide ions indicating disorder. Pd^{IV}—Br = 2·521 (4), Pd^{II}—Br = 2·782 (4) and Pd—N = 2·058 (3) Å. PdN_4 is tetrahedrally distorted with N—Pd—N = 177·6 (8)°. Pt^{IV}—Br =

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2·498 (1), Pt^{II}—Br = 2·884 (1), Pt—N = 2·064 (3) Å and N—Pt—N = 177·7 (4)°. Diffuse reflexions could be indexed in terms of a twinned monoclinic cell with $a_m = (a_o^2 + c_o^2)^{1/2}$, $b_m = b_o$, $c_m = 2c_o$, $\beta = 90 + \arctan(c_o/a_o)$°. The complexes crystallize with a disordered structure of OD (order–disorder) type, the orthorhombic cell corresponds to the superposition structure and the monoclinic to the MDO (maximum degree of order) structure. Diffuse scattering was also observed for the Pt–Cl complex.

Introduction. Craven & Hall (1961) confirmed Reihlen & Flohr's (1934) suggestion that Wolffram's red salt (Wolffram, 1990) should be formulated as a mixed Pt^{II},Pt^{IV} compound, $[Pt(ea)_4][Pt(ea)_4Cl_2]Cl_4.4H_2O$ (ea = ethylamine). Since then many of the related diamine compounds known as Wolffram's salt analogues have been studied because of the interest in one-dimensional conductors. The salts are typically very deeply coloured, strongly pleochroic and have metallic appearance. They contain chains of alternating metal and halogen atoms, the structures being disordered and often give rise to diffuse scattering. The platinum and palladium cyclohexanediamine complexes are shown to be OD (order–disorder) structures: the superposition structures of the bromine derivatives have been determined.

Experimental. $[Pd(C_6H_{14}N_2)_2Br_2][Pd(C_6H_{14}N_2)_2]Br_4$, superposition structure. A crystal, 0·275 × 0·188 × 0·025 mm, was mounted on a Huber diffractometer. Cell dimensions were determined from the setting angles of 40 reflexions with $10 < 2\theta < 21°$ measured with Mo $K\alpha$ radiation ($\lambda = 0·71073$ Å) at $\pm 2\theta$. Intensities were measured out to $(\sin\theta/\lambda)_{\max} = 0·89$ Å^{-1} using an ω–2θ scan and Pd filtered Ag $K\alpha$ radiation ($\lambda = 0·56087$ Å), 2θ scan width $(0·8 + 0·692\tan\theta)$°, divided into 50 steps, 2 s/step. Reflexions with $-42 \le h \le 42$, $0 \le k \le 12$, $-9 \le l \le 9$ were measured giving 2810 independent reflexions of which 1390 had $I > 3\sigma(I)$, $R_{\rm int} = 0·079$. Reflexions 002 and 020 were monitored every 50 reflexions, the overall fall-off in intensity was 1·0%. The data were corrected for absorption, transmission factors ranging from 0·487 to 0·902.

Least-squares refinement (on F), all non-H atoms refined anisotropically, H atoms were kept fixed in calculated positions with a common $U_{\rm iso}$. The starting coordinates were those of the platinum chloride analogue except for Br(1). Since Br(1) is close to $z = 0·5$ there is a very large correlation, 0·981, between z and U_{33}. z for Br(1) was given a starting value of 0·48 and refined using data with $\sin\theta/\lambda > 0·5$ Å^{-1}, this gave a value close enough to the correct value that refinement could proceed normally using all the data. The occupation factor for Br(1) was 0·5. Anomalous-dispersion factors were included for Pd and Br with f'' multiplied by a factor η (Rogers, 1981) which was refined giving $\eta = -1·11$ (6), and an isotropic extinction parameter was refined giving $g = 0·86\ (6) \times 10^{-4}$ corresponding to a minimum value of $I/I_{\rm corr}$ of 0·814. The weighting scheme was $w = 1/\sigma(F)$, where $\sigma(F) = [\sigma_{\rm cs}(F^2) + 1·02F^2]^{1/2} - |F|$ and $\sigma_{\rm cs}(F^2)$ is the standard deviation of F^2. The final cycle of refinement with 53 variable parameters gave $R = 0·032$, $wR = 0·029$, $S = 0·85$, $(\Delta/\sigma)_{\max} = 0·03$, $\Delta\rho = 0·6$ (1) to $-0·6$ (1) e Å^{-3}. Fractional coordinates are listed in Table 1,* bond distances and angles in Table 2.

$[Pt(C_6H_{14}N_2)_2Br_2][Pt(C_6H_{14}N_2)_2]Br_4$, superposition structure. A crystal, 0·400 × 0·212 × 0·038 mm. was mounted on a Huber diffractometer. Cell dimensions were determined from the setting angles of 25 reflexions with $19 < 2\theta < 28°$ measured with Mo $K\alpha$ radiation ($\lambda = 0·71073$ Å) at $2\theta,\omega,\chi,\varphi$; $-2\theta,-\omega,\chi,\varphi$; $2\theta,\omega,180+\chi,\varphi$ and $-2\theta,-\omega,180+\chi,\varphi$. Intensities were measured out to $(\sin\theta/\lambda)_{\max} = 0·905$ Å^{-1} using an ω–2θ scan and Nb filtered Mo $K\alpha$ radaition, 2θ scan width $(0·8 + 0·692\tan\theta)$°, divided into 50 steps, 1 s/step. Reflexions with $-42 \le h \le 42$, $-12 \le k \le 12$, $0 \le l \le 9$ were measured giving 2803 independent reflexions of which 2697 had $I > 3\sigma(I)$, $R_{\rm int} = 0·097$. Reflexions 601, 042 and 003 were monitored every 50 reflexions, the overall fall off in intensity was 14·0%. The data were corrected for absorption, transmission factors ranging from 0·102 to 0·563.

Least-squares refinement (on F), all non-H atoms refined anisotropically, H atoms were kept fixed in calculated positions with a common $U_{\rm iso}$. The starting coordinates were those of the palladium bromide analogue. Anomalous-dispersion factors were included for Pt and Br, η refined to $-1·19$ (4), and an isotropic extinction parameter was refined giving $g = 0·71\ (7) \times 10^{-4}$ corresponding to a minimum value of $I/I_{\rm corr}$ of 0·601. The weighting scheme was $w = 1/\sigma(F)$, where $\sigma(F) = [\sigma_{\rm cs}(F^2) + 1·02F^2]^{1/2} - |F|$ and $\sigma_{\rm cs}(F^2)$ is the standard deviation of F^2. The final cycle of refinement with 53 variable parameters gave $R = 0·036$, $wR = 0·040$, $S = 1·20$, $(\Delta/\sigma)_{\max} = 0·04$, $\Delta\rho = 1·7$ (1) to $-1·8$ (1) e Å^{-3}. Fractional coordinates are listed in Table 1,* bond distances and angles in Table 2.

Diffuse scattering. The palladium bromide and platinum bromide complexes gave diffraction patterns with sharp reflexions corresponding to the orthorhombic cell but rotation photographs about **c** showed diffuse streaks between the layer lines indicating a doubling of the c axis, and Weissenberg

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53732 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^5$ *for* Pd, Pt *and* Br, $\times 10^4$ *for* C *and* N) *and* U_{eq} (Å^2) ($\times 10^4$ *for* Pd, Pt *and* Br, $\times 10^3$ *for* N *and* C)

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

	x	y	z	U_{eq}
[Pd($C_6H_{14}N_2$)$_2$Br$_2$][Pd($C_6H_{14}N_2$)$_2$]Br$_4$				
Pd	0	0	0	123 (2)
Br(1)	0	0	47531 (83)	199 (8)
Br(2)	58740 (2)	0	0	346 (3)
N	640 (1)	1949 (4)	81 (25)	19 (1)
C(1)	1171 (1)	926 (5)	719 (6)	19 (1)
C(2)	1692 (1)	2089 (6)	235 (21)	26 (2)
C(3)	2214 (2)	906 (7)	749 (8)	33 (2)
[Pt($C_6H_{14}N_2$)$_2$Br$_2$][Pt($C_6H_{14}N_2$)$_2$]Br$_4$				
Pt	0	0	0	151 (1)
Br(1)	0	0	46405 (19)	234 (5)
Br(2)	58806 (3)	0	0	367 (3)
N	643 (1)	1963 (4)	76 (14)	21 (1)
C(1)	1174 (2)	937 (5)	701 (7)	21 (1)
C(2)	1696 (2)	2109 (6)	179 (20)	32 (2)
C(3)	2221 (2)	909 (8)	727 (11)	36 (2)

Table 2. *Bond lengths* (Å), *angles* (°) *and torsion angles* (°)

	M = Pd	M = Pt
M—Br(1)	2·516 (4)	2·494 (1)
M—Br(1^{iv})	2·777 (4)	2·880 (1)
M—Br(1)	2·521 (4)*	2·498 (1)*
M—Br(1^{iv})	2·782 (4)*	2·884 (1)*
M—N	2·058 (3)	2·064 (3)
N—C(1)	1·500 (5)	1·497 (5)
C(1)—C(1^{i})	1·515 (7)	1·516 (8)
C(1)—C(2)	1·513 (5)	1·520 (6)
C(2)—C(3)	1·526 (6)	1·539 (7)
C(3)—C(3^{i})	1·507 (9)	1·496 (12)
N—M—N^{i}	84·2 (1)	83·9 (2)
N—M—N^{ii}	177·6 (7)	177·7 (4)
N^{i}—M—N^{iii}	95·9 (1)	96·2 (2)
Br(1)—M—N	88·8 (4)	88·9 (4)
Br(1)—M—N^{i}	91·2 (4)	91·1 (2)
M—N—C(1)	108·0 (2)	108·3 (2)
N—C(1)—C(2)	113·3 (3)	113·1 (3)
N—C(1)—C(1^{i})	107·7 (4)	107·8 (3)
C(2)—C(1)—C(1^{i})	112·6 (3)	112·2 (4)
C(1)—C(2)—C(3)	110·1 (4)	109·7 (4)
C(2)—C(3)—C(3^{i})	111·9 (4)	111·5 (4)
M—N—C(1)—C(1^{i})	41·0 (8)	40·7 (5)
M—N—C(1)—C(2)	166·3 (6)	165·4 (5)
N—C(1)—C(1^{i})—N^{i}	−54·7 (10)	−54·2 (7)
C(2^{i})—C(1^{i})—C(1)—C(2)	54·1 (8)	55·3 (9)
N—C(1)—C(2)—C(3)	−176·0 (8)	−176·7 (5)
C(1^{i})—C(1)—C(2)—C(3)	−53·4 (8)	−54·4 (8)
C(1)—C(2)—C(3)—C(3^{i})	54·9 (8)	56·1 (9)
C(2)—C(3)—C(3^{i})—C(2^{i})	−56·6 (9)	−57·7 (10)

Symmetry code: (i) $-x, -y, z$; (ii) $x, -y, -z$; (iii) $-x, y, -z$; (iv) $1+x, y, z$.

* Corrected for riding motion.

photographs of these intermediate layers showed streaks in the **a** direction, and for the Pd complex there were also diffuse spots on the streaks which could be indexed in terms of a twinned monoclinic cell with: $a_m = (a_o^2 + c_o^2)^{1/2}$; $b_m = b_o$; $c_m = 2c_o$, $\beta = 90 + \arctan(c_o/a_o)°$. The complexes crystallize with a disordered structure of OD type (Dornberger-Schiff, 1966), the orthorhombic cell corresponds to the superposition structure and the monoclinic to the MDO (maximum degree of order) structure. A 36 h oscillation photograph of the Pt–Cl–cyclohexanediamine complex about the *c* axis also showed very faint diffuse scattering indicating that here also the *c* axis should be doubled. Toftlund, Waage Jensen & Jacobsen (1987) have also observed similar weak reflexions on Laue photographs taken with monochromatic radiation.

Computations were carried out on a VAX 6210 computer with the following programs: *INTEG* – based on the Nelmes (1975) algorithm for integration of intensities; *DATAP* and *DSORT* (State University of New York) for data processing; modified *ORFLS* (Busing, Martin & Levy, 1962) for least-squares refinement; *ORFFE* (Busing, Martin & Levy, 1964) for geometry; *ORTEP* (Johnson, 1965) for drawings. Scattering curves those of Cromer & Mann (1968) for Pt, Pd, Br, N and C atoms, and Stewart, Davidson & Simpson (1965) for H atoms; anomalous-dispersion corrections for Pt, Pd and Br atoms from Cromer & Liberman (1970).

Discussion. The structures are built up of chains of alternating M^{IV} and M^{II} atoms, *i.e.* Br—M^{IV}—Br···M^{II}···Br—M^{IV}—Br··· as shown in Fig. 1, which represents one of the MDO structures. The superposition structure based on the family of reflexions (h_o, k_o, l_o) is shown in Fig. 2. It was not possible to measure the diffuse reflexions on account of their weakness and the discussion is based on values derived from the superposition structure. Toftlund, Waage Jensen & Jacobsen (1987) have shown by ESR (electron-spin resonance) spectra, resonance Raman spectra and conductivity measurements that the Pd—Br complex has Pd^{III} defects within the chains; such defects would have little or no effect on the bulk structure as determined by X-ray diffraction.

Pd^{IV}—Br = 2·521 (4), Pd^{II}—Br = 2·782 (4) and Pd—N = 2·058 (3) Å. PdN$_4$ is tetrahedrally distorted with N—Pd—N = 177·6 (8)°. Pt^{IV}—Br = 2·498 (1), Pt^{II}—Br = 2·884 (1), Pt—N = 2·064 (3) Å and N—Pt—N is 177·7 (4)°. The M—Br distances are corrected for riding motion (Busing & Levy, 1964), the correction was 0·004 Å in each case. The ligand has the expected geometry. The covalent radii of Pt and Pd are both close to 1·32 Å regardless of the oxidation state being II or IV, the M—Cl distances are 2·310 (1) Å in K_2PtCl_4 (Obha, Sato & Saito, 1983), 2·314 (1) Å in K_2PtCl_6 (Obha & Saito, 1984), 2·3066 (2) Å in K_2PdCl_4 and 2·3094 (3) Å in K_2PdCl_6 (Takazawa, Obha & Saito, 1988) giving the following radii: Pd^{II} 1·317, Pd^{IV} 1·319, Pt^{II} 1·320, and Pt^{IV} 1·324 Å. This means that one would expect the same

M^{IV}—Br distances in both compounds and also that there should be no disorder of the ligands since M—N will not be affected by the oxidation number of M. In fact Pd^{IV}—Br is slightly longer than Pt^{IV}—Br and both are longer than the expected value of 2·46 Å (1·32 + 1·14). Metal—halogen distances in Wolffram's salt analogues are listed in Table 3, the covalent radii, r, for each pair of metal atoms (obtained from M—X by subtracting 0·99 Å for Cl, 1·14 Å for Br and 1·33 Å for I) are plotted against each other in Fig. 3. This shows (*a*) that long M^{IV}—X bonds are associated with relatively short M^{II}—X distances, (*b*) that there is a forbidden range bounded by $r_b = r_a \pm 0{\cdot}18$, and (*c*) chlorides give very close to the expected value of 1·32 Å, bromides give a wider range of r although over half are in the range 1·30 to 1·34 Å, iodides give r from 1·36 to 1·50 Å. The apparent exception to (*b*) is the orthorhombic form of $[Pten_2][Pten_2Br_2](ClO_4)_4$ (Endres, Keller, Martin, Traeger & Novotny, 1980) which was later refined in another space group (Keller, Müller, Ledezma & Martin, 1985) giving the unreasonably small value of 1·24 Å for $r_{M^{IV}}$. There seems to be a general trend that the charge transfer along the chain, as shown by the increase in $r_{M^{II}}$ and the decrease in $r_{M^{IV}}$, increases with the atomic number of the halogen.

I am indebted to Professor H. Toftlund of the University of Odense for the crystals, and to the Carlsberg Foundation and the Danish Science Research Council for the diffractometer.

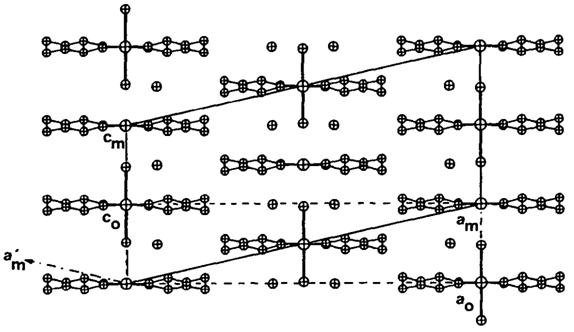

Fig. 1. The MDO structure projected down the b axis, showing the relation between the monoclinic MDO cell (a_m and c_m) and the orthorhombic superposition cell (a_o and c_o); a_o' is the a axis of the other MDO twin.

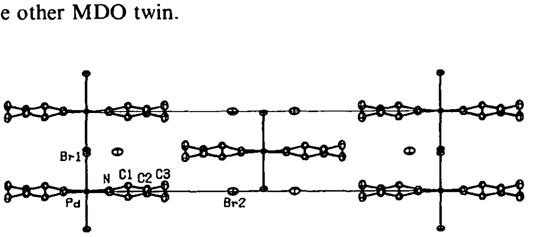

Fig. 2. The superposition cell showing the atom numbering.

Table 3. *Geometry of* $[ML_2][ML_2X_2]Y_4$ *and related compounds*

L*	M	X	Y	M^{IV}—X	M^{II}—X	Ref.†
en	Pd	Cl	ClO_4	2·324 (3)	3·033 (3)	ASBSDK 38 1158
chxn	Pd	Br	Br	2·521 (4)	2·782 (4)	This work
en	Pd	Br	ClO_4	2·472 (2)	2·914 (2)	ZNAB2 40 57
en	Pd	Br	ClO_4	2·496 (1)	2·911 (1)	ACSCEE 41 876
chxn	Pt	Cl	Cl	2·324 (2)	2·834 (2)	ACAPCT 31 182
dapn	Pt	Cl	ClO_4	2·299^a 2·339^a	3·213^a 3·173^a	MFKCAL 11 209
ea	Pt	Cl	Cl	2·339 (5) 2·326 (7)	3·054^a 3·069^a	ACSCEE 43 1863^b
en	Pt	Cl	ClO_4	2·318^a	3·085^a	MFKCAL 11 209
mn	Pt	Cl	ClO_4	2·334 (12)	3·203 (18)	JCDTBI 1986 403
tacd	Pt	Cl	PF_6	2·309 (3)	3·514 (3)	ACSCEE 42 963
tacd	Pt	Cl	ClO_4	2·319 (3)	3·219 (3)	ACSCEE 42 963
tn	Pt	Cl	BF_4	2·299 (6)	3·096 (6)	BCSJA8 51 3514
tn	Pt	Cl	BF_4	2·31 (1)	3·09 (1)	ACSCEE 39 1514^c
chxn	Pt	Br	Br	2·498 (1)	2·884 (1)	This work
dapn	Pt	Br	$(Cu_3Br_5)/2$	2·55 (2)	3·07 (2)	ZNAB2 33 1263
ea	Pt	Br	Br	2·447 (5) 2·479 (6)	3·139 (5) 3·107 (6)	ASBSDK 32 279^b
ea	Pt	Br	Br	2·284 (7) 2·684 (6)	3·811 (7) 3·411 (6)	ASBSDK 36 760^g
en	Pt	Br	ClO_4	2·71 (2)	2·76 (2)	ASBSDK 36 35^k
en	Pt	Br	ClO_4	2·555 (14) 2·471 (8)	2·935 (14) 3·019 (8)	ACSCEE 41 16^d
en	Pt	Br	ClO_4	2·377 (8)	3·080 (8)	ACSCEE 41 16^{e,l}
en	Pt	Br	ClO_4	2·442 (7)	3·018 (7)	INOCAJ 29 981^m
mn	Pt	Br	ClO_4	2·468 (3)	3·219 (4)	JCDTBI 403
tn	Pt	Br	ClO_4	2·546 (7)	2·955 (7)	BCSJA8 51 3514
tn	Pt	Br	ClO_4	2·47 (1)	3·03 (1)	ACSCEE 39 1514^c
tn	Pt	Br	BF_4	2·541 (5)	2·921 (5)	BCSJA8 51 3514
tn	Pt	Br	BF_4	2·47 (1)	2·99 (1)	ACSCEE 39 1514^c
dapn	Pt	I	I	2·815 (2)	2·995 (2)	ASBSDK 36 35
dapn	Pt	I	ClO_4	2·704 (11) 2·726 (9)	3·115 (11) 3·039 (9)	ASBSDK 35 1468^d
dapn	Pt	I	ClO_4	2·791 (8)	3·036 (8)	ASBSDK 35 1885^f
dapn	Pt	I	ClO_4	2·770 (9)	2·956 (9)	ASBSDK 34 2295^e
dapn	Pt	I	ClO_4	2·750^c	2·930^c	ZNAB2 39 197
en	Pt	I	ClO_4	2·773	3·085	INOCAJ 29 981^m

Notes: (*a*) calculated from authors's coordinates, (*b*) tetrahydrate, (*c*) data from BCSJA8 51 3514 re-refined in $A2_122$, (*d*) monoclinic, (*e*) orthorhombic, (*f*) as ASBSDK 35 1468 refined in centrosymmetric space group, (*g*) omitted from plot as Pt—Br is shorter than a Pt—Cl bond, (*k*) refined in $I222$, (*l*) refined in $Ic2a$, (*m*) monoclinic, grown at 7 kbar.

* chxn = cyclohexanediamine, dapn = diaminopropane, ea = ethylamine, en = ethylenediamine, mn = methylamine, tacd = tetraazacyclotetradecane, tn = trimethylenediamine.

† See *Notes for Authors* (1985) for a description of the journal Codens, note MFKCAL is *Mem. Fac. Sci. Kyushu Univ. Ser. C.*

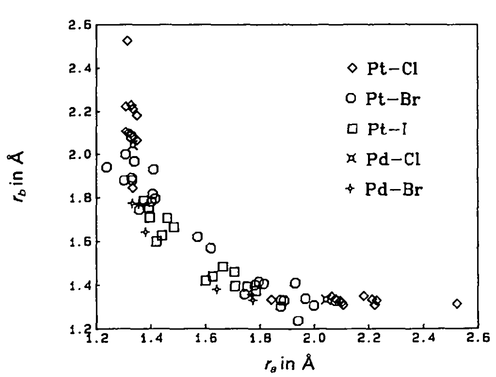

Fig. 3. Correlation plot of the metal atom radii, r_a and r_b, in $M_a..X..M_b$.

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Cyclopalladated Complexes. Synthesis and Crystal Structure of Di-μ-chloro-bis[(2′,6′-dimethylazobenzenato-C^2,N^2)palladium(II)]

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Abstract. $C_{28}H_{26}Cl_2N_4Pd_2$, $M_r = 702{\cdot}25$, monoclinic, $P2_1/n$, $a = 12{\cdot}993\,(3)$, $b = 11{\cdot}739\,(3)$, $c = 27{\cdot}592\,(7)$ Å, $\beta = 99{\cdot}29\,(2)°$, $V = 4153\,(2)$ Å^3, $Z = 6$, $D_x = 1{\cdot}69$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 15{\cdot}0$ cm^{-1}, $F(000) = 2088$, $T = 298$ K, $R = 0{\cdot}053$ and $wR = 0{\cdot}045$ for 4341 reflections with $I > 3\sigma(I)$. The complex has a dimeric structure with the 2′,6′-dimethylazobenzene ligands, H*L*, mutually *trans* with respect to the Pd–Pd axis, and bonded to Pd^{II} atoms which have a square-planar geometry. The two [(*L*)Pd] moieties are connected by two bridging Cl atoms. The Pd_2Cl_2 core is planar.

Introduction. The bis(chloro)-bridged cyclopalladated compounds are the expected product which forms when species such as azobenzenes are reacted with palladium(II) chloride derivatives (Omae, 1979; Constable, 1984). Nevertheless, in spite of the large number of synthetized complexes, to the best of our knowledge, no X-ray structural data are available for this group of compounds. In this paper we report on the synthesis and crystal structure of the cyclometallated μ-Cl dimer obtained from 2′,6′-dimethylazobenzene.

Experimental. All the starting reagents were used as received without further purification. The 2′,6′-dimethylazobenzene, H*L*, was prepared by reacting nitrosobenzene (1 mmol) and 2,6-dimethylaniline (1:1 molecular ratio) in acetic acid (6 ml). The mixture was stirred overnight at room temperature; thereafter water (20 ml) and diethyl ether (20 ml) were added. The H*L* product (red, oily) was separated from the organic layer by chromatography (SiO_2/petroleum ether 313–333 K) and characterized by IR and NMR spectroscopies.

The complex $[(L)PdCl]_2$, was prepared treating an ethanolic solution (10 ml) containing 1 mmol of H*L* with $(PhCN)_2PdCl_2$ (1:1 molecular ratio). The mixture was stirred at room temperature for 12 h. The orange solid which forms was filtered, washed with pentane and dried under vacuum (yield 70%). Anal. calc. for $C_{28}H_{26}Cl_2N_4Pd_2$: C, 47·89; H, 3·73; N, 7·98. Found: C, 48·03; H, 3·77; N, 8·06.

Crystals suitable for X-ray analysis have been obtained from ethanol. An orange crystal 0·12 × 0·14 × 0·22 mm was used for intensity data collection. X-ray diffraction measurements were performed with a Siemens *R*3*m*/*V* four-circle diffractometer, ω-scan technique, graphite-monochromated Mo $K\alpha$ radiation, scan range $2\theta = 1$–$50°$ (-1

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