The three-rings are the most interesting ones. Most of these have the expected 2–1 configuration, but one of eight has all three metals displaced in the same direction. If this one were the same as the others, the two halves of the asymmetric unit would have the same type of puckering and be related by a twofold screw axis parallel to **a**. This could increase the symmetry but would then give rise, for instance, to four-rings of the type $++++$ and six-rings with $+--+--$ configuration. It would require a thorough topological investigation to find whether the present puckering pattern gives rise to the highest possible number of opposite neighbours.

It is quite obvious that twinning is very likely to occur in a structure of this kind. With the pseudosymmetry described above, it requires very few mistakes in the puckering for the *a* and *b* axes to become interchanged. The degree of twinning and the size of the coherently scattering regions seem related to the conditions of formation. The crystals of binary Mo_5O_{14}, which gave very diffuse superlattice reflexions, had been prepared by relatively short (~1 d) heat treatment at low temperature (520°C) and were evidently much more densely twinned than the crystals studied here, which grew very slowly from the melt. Schröder (1972) reported that Mo_5O_{14} crystals prepared by reducing MoO_3 in a stream of HCl gas gave no superstructure reflexions at all. Considering that the crystal growth was very rapid in that case (completed in the order of 10 min) it seems likely that the coherent regions were so small that the superstructure spots completely disappeared in the background.

This investigation forms part of a research program supported by the Swedish Natural Science Research Council. N.Y. acknowledges a scholarship from the Japan–Sweden Foundation, Tokyo.

References

BUERGER, M. J. (1956). *Proc. Nat. Acad. Sci.* **42**, 776.
CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
EKSTRÖM, T. (1972*a*). *Acta Chem. Scand.* **26**, 1843–1846.
EKSTRÖM, T. (1972*b*). *Mater. Res. Bull.* **7**, 19–26.
EKSTRÖM, T. & NYGREN, M. (1972*a*). *Acta Chem. Scand.* **26**, 1827–1835.
EKSTRÖM, T. & NYGREN, M. (1972*b*). *Acta Chem. Scand.* **26**, 1836–1842.
International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.
JAHNBERG, L. (1971). *Chem. Commun. Univ. Stockholm*, No. XIII.
KIHLBORG, L. (1959). *Acta Chem. Scand.* **13**, 954–962.
KIHLBORG, L. (1963*a*). *Ark. Kem.* **21**, 427–437.
KIHLBORG, L. (1963*b*). *Ark. Kem.* **21**, 471–495.
KIHLBORG, L. (1969). *Acta Chem. Scand.* **23**, 1834.
SCHRÖDER, F. A. (1972). *Z. Naturforsch.* **27*b***, 498–500.
TAKEUCHI, Y. (1972). *Z. Kristallogr.* **135**, 120–136.
YAMAZOE, N., EKSTRÖM, T. & KIHLBORG, L. (1975). *Acta Chem. Scand.* In the press.

Acta Cryst. (1975). B**31**, 1672

The Crystal and Molecular Structures of *cis*-Dichloroethylenediamineplatinum(II) *and* Palladium(II)

BY JOHN IBALL, MARY MACDOUGALL AND SHEELAGH SCRIMGEOUR
*Chemistry Department, University of Dundee, Dundee, DD*1 4*HN, Scotland*

(*Received* 13 *December* 1974; *accepted* 3 *February* 1975)

The structures of *cis*-M(en)Cl_2 (M = Pt, Pd) have been determined from diffractometer data and refined by least-squares calculations: $R = 0{\cdot}073$ for Pt(en)Cl_2 (437 reflexions) and 0·057 for Pd(en)Cl_2 (416 reflexions). The compounds are isomorphous, space group $C222_1$ with $Z = 4$. The metal atoms have a square-planar configuration and the ethylenediamine rings are puckered. Intermolecular Pt···Pt and Pd···Pd distances are 3·381 and 3·369 Å respectively.

Introduction

It has been shown that certain complexes of the Pt group metals exhibit interesting biological effects (Rosenberg, Van Camp & Krigas, 1965). At low concentrations some are effective bactericides while others stop cell division and force bacteria to grow into long filaments. Some of these complexes are also very potent broad-spectrum antitumour agents. Of the complexes tested on animals the following were the most potent: (1) *cis*-$Pt^{IV}(NH_3)_2Cl_4$, (2) *cis*-$Pt^{II}(NH_3)_2Cl_2$, (3) *cis*-$Pt^{II}enCl_2$, (4) *cis*-$Pt^{IV}enCl_4$. We report the structure of

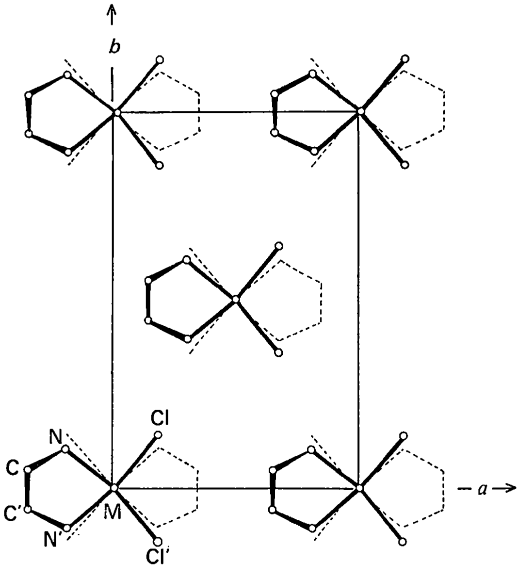
(3) and the corresponding Pd compound. Preliminary crystal data for Pt(en)Cl_2 have been published by Martin, Jacobson, Hunter & Benson (1970).

Experimental

Both compounds crystallize as thick yellow needles. Cell dimensions and space group were determined from photographs (Cu $K\alpha$) and confirmed by measurements made on a Wooster four-circle diffractometer. Intensities were collected on the diffractometer (Cu $K\alpha$). Crystals used for data collection were of roughly spherical shape and spherical absorption corrections were applied. The intensities were placed on a common scale and converted to structure factors in the usual way [Pt(en)Cl_2, 437 reflexions; Pd(en)Cl_2, 416 reflexions.]

Crystal data

(i) *cis*-Dichloroethylenediamineplatinum(II); $PtCl_2C_2N_2H_8$, $M=326{\cdot}08$, orthorhombic, $a=8{\cdot}100$ (4), $b=12{\cdot}411$ (6), $c=6{\cdot}761$ (3) Å, $U=679$ Å^3, $Z=4$, $D_x=3{\cdot}18$ g cm^{-3}, $F(000)=584$, μ(Cu $K\alpha$) $=458$ cm^{-1}. Space group $C222_1$. (ii) *cis*-Dichloroethylenediaminepalladium(II); $PdCl_2C_2N_2H_8$, $M=237{\cdot}38$, orthorhombic, $a=8{\cdot}116$ (4), $b=12{\cdot}416$ (6), $c=6{\cdot}736$ (3) Å, $U=679$ Å^3, $Z=4$, $D_x=2{\cdot}22$ g cm^{-3}, $F(000)=456$, μ(Cu $K\alpha$) $=291$ cm^{-1}. Space group $C222_1$.



[M= Pd or Pt]

Fig. 1. A projection of the structure of M(en)Cl_2 (M = Pd or Pt) on the (001) plane. The dotted lines indicate molecules at $c/2$.

Structure determination

Pt(en)Cl_2

The structure was determined by the heavy-atom technique. A Patterson synthesis revealed a Pt atom at the origin and four other peaks in the plane xy. These were clearly Pt–Cl vectors and the duplication was due to false symmetry introduced because the intensities of hkl reflexions with $l=2n+1$ were very weak. The molecule had to have a twofold axis of symmetry, and structure factor calculations, with calculated atomic positions, indicated that this symmetry axis had to be parallel to **a**. Two of the Pt–Cl vector peaks were chosen as indicating the position of the Cl atoms and structure-factor calculations followed by Fourier syntheses gave more accurate coordinates for the Pt and Cl atoms. Scattering factors were from *International Tables for X-ray Crystallography* (1962). The curve for Pt was corrected for anomalous dispersion. Isotropic temperature factors of 1·75 and 3·5 Å^2 were used for Pt and Cl atoms respectively. R at this stage was 0·190. The positions of the N and C atoms were found from difference maps. A structure factor calculation gave an R of 0·098.

Refinement

Refinement was by block-diagonal least-squares calculations. The C and N atoms were refined isotropic-

Table 1. *Atomic coordinates and thermal parameters*

(*a*) Atomic coordinates ($\times 10^4$) for (i) Pt(en)Cl_2, (ii) Pd(en)Cl_2 (estimated standard deviations in parentheses), and temperature parameters for C, N and H atoms. (The same H coordinates were used for both compounds.)

	x/a	y/b	z/c	B (Å^2)
N(i)	−2032 (35)	996 (21)	−85 (111)	4·53 (50)
N(ii)	−1870 (15)	1057 (10)	−87 (41)	3·91 (22)
C(i)	−3456 (57)	460 (35)	621 (67)	4·88 (83)
C(ii)	−3474 (21)	530 (14)	507 (25)	3·91 (35)
Cl(i)	1911 (10)	1374 (6)	24 (31)	
Cl(ii)	1871 (4)	1374 (3)	21 (14)	
Pt	27 (3)	0	0	
Pd	−45 (1)	0	0	
H(1)	−1619	1665	833	6·0
H(2)	−1966	1351	−1465	6·0
H(3)	−3490	419	1977	6·0
H(4)	−4415	973	7	6·0

Table 1 (*cont.*)

(*b*) Anisotropic temperature factors for Pt and Pd ($\times 10^5$) and for Cl ($\times 10^4$) (estimated standard deviations in parentheses). (i) Pt(en)Cl_2, (ii) Pd(en)Cl_2. $T=\exp[-(h^2b_{11}+k^2b_{22}+l^2b_{33}+hkb_{12}+hlb_{13}+klb_{23})]$.

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Pt	717 (11)	0	0	312 (5)	−51 (76)	1258 (18)
Pd	564 (11)	0	0	263 (5)	−140 (45)	1461 (20)
Cl(i)	178 (11)	−87 (12)	−94 (84)	68 (4)	94 (34)	239 (15)
Cl(ii)	137 (4)	−121 (5)	136 (26)	59 (2)	−18 (18)	254 (8)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with estimated standard deviations in parentheses*

Length	M=Pt	M=Pd	Angle	M=Pt	M=Pd
N–C	1·42 (6)	1·511 (22)	C–N–M	111 (2)	110 (1)
N–M	2·08 (3)	1·978 (12)	N–M–Cl	95·3 (7)	90·8 (3)
M-Cl	2·288 (8)	2·309 (3)	Cl-M-Cl	96·4 (6)	95·3 (3)
C–C	1·42 (9)	1·482 (34)	N–M–N′	73 (2)	83 (1)
			N–C–C′	100 (6)	105 (3)

ally, Pt and Cl anisotropically. H atom positions were calculated and included in the structure-factor calculations in the later stages but not refined. The Pt atom was allowed to refine along **a** only. The weighting scheme was

$$\sqrt{w}=1/\{1+[(|F_o|-F^*)/G^*]^2\}^{1/2}$$
$$(F^*=90{\cdot}0,\ G^*=30{\cdot}0)\,.$$

After several cycles R was reduced to 0·073.† (Three reflexions with large values of $|F_o-F_c|$ were excluded from the refinement.)

$Pd(en)Cl_2$

The Pd and Pt compounds are isomorphous. The coordinates of the Pt complex were used as the starting point for the refinement. Several cycles of least-squares refinement, along the same lines as those for $Pt(en)Cl_2$, reduced R to 0·057.† The scattering factor for Pd was corrected for anomalous dispersion.

Results

Atomic parameters are given in Table 1 (*a*) and (*b*), and bond lengths and angles in Table 2. Least-squares mean planes calculated for both compounds showed that the plane of the metal, Cl and N atoms is in each molecule within experimental error parallel to (001). The deviations of the Cl and N atoms (Pt: 0·046, 0·033; Pd: 0·044, 0·034 Å) from these mean planes are not significant, but those of C (Pt: 0·43; Pd: 0·35 Å) are.

In both molecules the metal atom is close to the origin and is surrounded by two Cl and two N atoms in a *cis* square-planar arrangement. The C atoms are twisted out of this plane, one above and the other below.

The distances Pt–Cl [2·288 (8) Å] and Pt–N [2·08 (3) Å] are similar to those reported for *cis*-dichlorodiamineplatinum(II) (Milburn & Truter, 1966) and dichloro-2,2′-bipyridylplatinum(II) (Osborn & Rogers, 1974). The Pt···Pt distance is 3·381 Å, which compares well with 3·39 Å in *cis*-dichloroethylenediamineplatinum(II) (Martin *et al.* 1970) and with 3·45 Å in dichloro-2,2′-bipyridylplatinum(II). The arrangement of molecules is illustrated in Fig. 1.

Pd···Pd, Pd–Cl and Pd–N distances are 3·369, 2·309 (3) and 1·978 (12) Å respectively. These compare well with values in, for example, *cis*-dichloro-(*meso*-2,3-diaminobutane)palladium(II) (Ito, Marumo & Saito, 1971), the corresponding distances being 3·34, 2·317 and 2·03 Å; the chelate rings are also puckered. Similarly values reported for bis(ethylenediamine)palladium(II) chloride are Pd–N (2·03, 2·04), C–N (1·484, 1·469) and C–C (1·518 Å) (Wiesner & Lingafelter, 1966).

We are grateful to Professor Ross of the Chester Beatty Research Institute, London, for crystals of the Pt and to Dr D. R. Williams, St Andrews University, for a sample of the Pd compound. We thank the S.R.C. and Cancer Research Campaign for financial support.

References

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Ito, T., Marumo, F. & Saito, Y. (1971). *Acta Cryst.* B**27**, 1695–1701.

Martin, D. S. Jr, Jacobson, R. A., Hunter, L. D. & Benson, J. E. (1970). *Inorg. Chem.* **9**, 1276–1278.

Milburn, G. H. W. & Truter, M. R. (1966). *J. Chem. Soc.* (*A*), pp. 1609–1616.

Osborn, R. S. & Rogers, D. (1974). *J. Chem. Soc. Dalton*, pp. 1002–1004.

Rosenberg, B., Van Camp, L. & Krigas, T. (1965). *Nature, Lond.* **205**, 698–699.

Wiesner, J. R. & Lingafelter, E. C. (1966). *Inorg. Chem.* **5**, 1770–1775.

---

† Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30911 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.