Within the Cu	(1) polyhedro	on	Within the Cu(2) polyhedron									
Cu(1)-O(4) -O(5) -O(6) -O(6') -O(7) -O(7')	(F) 1·983 1·963 2·365 2·479 1·943 2·044	(G) 1·92 2·08 2·42 2·51 1·96 2·01	Cu(2)-O(1) -O(2) -O(3) -O(4) -O(5) -O(7)	(F) 1·946 2·795 1·958 2·397 1·989 2·008	(G) 1·99 2·74 1·97 2·47 1·92 2·01							
$\begin{array}{l} O(4) -Cu(1) -O(6)\\ O(4) -Cu(1) -O(6')\\ O(4) -Cu(1) -O(7')\\ O(4) -Cu(1) -O(7')\\ O(5) -Cu(1) -O(6')\\ O(5) -Cu(1) -O(6')\\ O(5) -Cu(1) -O(7')\\ O(6) -Cu(1) -O(7')\\ O(6) -Cu(1) -O(7')\\ O(6) -Cu(1) -O(7')\\ O(6) -Cu(1) -O(7)\\ O(6) -Cu(1) -O(6')\\ O(6) $	89.5° 93.1 86.2 97.1 86.9 90.3 95.5 81.6 95.0 89.8 89.0 176.2 175.3	90° 93 88 96 88 89 96 80 95 90 89 89 	$\begin{array}{c} O(1)-Cu(2)-O(2)\\ O(1)-Cu(2)-O(3)\\ O(1)-Cu(2)-O(4)\\ O(1)-Cu(2)-O(5)\\ O(2)-Cu(2)-O(3)\\ O(2)-Cu(2)-O(5)\\ O(2)-Cu(2)-O(7)\\ O(3)-Cu(2)-O(7)\\ O(3)-Cu(2)-O(7)\\ O(4)-Cu(2)-O(7)\\ O(5)-Cu(2)-O(7)\\ O(1)-Cu(2)-O(7)\\ O(2)-Cu(2)-O(7)\\ O(2)-Cu(2)-O(7)\\ O(1)-Cu(2)-O(7)\\ O(2)-Cu(2)-O(4)\\ O(2)-Cu(2)-O(4)\\$	84.5° 93.9 98.6 92.1 87.1 82.4 102.6 92.2 93.6 74.4 81.8 170.0 176.9	86° 93 98 90 87 79 102 94 95 73 84 —							
O(7) - Cu(1) - O(7')	1/4·2	_	O(3) - Cu(2) - O(5)	167.3								
	V	vithin the ars	senate tetrahedron									
As-U(3) -O(4) -O(5) -O(8)	1.680 1.664 1.773 1.615	1.68 1.65 1.73 1.61	O(3)-As-O(4) O(3)-As-O(5) O(3)-As-O(8) O(4)-As-O(5) O(4)-As-O(8)	104·8° 109·3 110·1 109·9 114·4	103° 111 112 109 116							
Hydrogen be	ond distances	5	O(5)-As-O(8)	108.3	105							
$\begin{array}{l} O(1) -O(6) \\ O(1) -O(8) \\ O(1') -O(8) \\ O(2) -O(6) \\ O(2') -O(6) \\ O(7) -O(8) \\ O(2) -O(5) \end{array}$	3.052 2.583 2.834 2.753 2.882 2.585 2.918	2·95 2·61 2·77 2·94 2·70 2·63 2·96										

Table 2. Interatomic distances and angles for euchroite

The average standard deviations of the bond lengths for this refinement are: Cu-O 0.012; As-O 0.012. That of the angles is  $0.50^{\circ}$ .

molecules. The difference in birefringence may be partly caused by the rotation of the structural unit into a plane parallel to (010) in euchroite.

It has been stated (Palache, Berman & Frondel, 1951) that euchroite possesses a  $\{110\}$  and  $\{101\}$  cleavage in traces. Fig. 1 shows the hypothesized  $\{110\}$  cleavage developed by breaking hydrogen bonds between O(1) and O(8) and between O(7) and O(8). Also one stronger bond need be broken between Cu(2) and O(3). The  $\{101\}$  cleavage cannot be accounted for in any simple manner.

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# The similarity of atomic radius of palladium (II) and palladium (IV). By J.D.Bell, D.Hall and T.N.WATERS, Chemistry Department, University of Auckland, New Zealand

#### (Received 28 February 1966)

A number of apparently trivalent complexes of palladium and platinum have been investigated crystallographically (Brosset, 1948; Cohen & Hughes, 1954; Hall & Williams, 1958; Craven & Hall, 1961, 1966; Ryan & Rundle, 1961; Wallen, Brosset & Vannerberg, 1962), and invariably the structures have proved to be based on chains in which divalent and tetravalent atoms alternate, *e.g.*  $Pd(NH_3)_2Cl_3$ is in fact  $Pd^{II}(NH_3)_2Cl_2$ .  $Pd^{IV}(NH_3)_2Cl_4$ , with structure



In practice, however, the diffraction patterns show evidence of disorder, the stacking of chains being susceptible to mistakes which involve their translation by one half the repeat distance in the chain direction. It has been supposed that this is possible because the dimensions of the complex ions are essentially the same, irrespective of the valence state of the central metal, and this view is supported by the atomic radii listed by Pauling (1960). Nonetheless there does not appear to be any instance in which bond lengths have been measured in comparable compounds with sufficient precision to make such an assertion, and for this reason the well established structures of ammonium chloropalladate-(II) and ammonium chloropalladate(IV) have been re-examined.

#### Ammonium chloropalladate (II)

Crystals of  $(NH_4)_2$ PdCl<sub>4</sub> were grown as fine bronze tetragonal needles which were strongly pleochroic. Cell dimensions were determined from Weissenberg photographs by the method of Main & Woolfson (1963) as  $a=7\cdot205\pm$  $0\cdot006$ ,  $c=4\cdot26\pm0\cdot02$  Å, in agreement with the values previously reported by Dickinson (1922). The density was measured by flotation as 2·1 g.cm<sup>-3</sup>, and the calculated value for one molecule per unit cell is 2·14. Intensities were measured visually from Weissenberg photographs, taken with Cu Ka radiation, for the layers hk0 - hk3. The crystals used were of square section, and cylindrical absorption corrections were applied. The h0l layer was also photographed, using a crystal which had been cut to an approximate cube. It did not, however, prove possible to obtain such a crystal that was not multiple, and the h0l data were used to correlate the layers about **a**, but were otherwise excluded from the refinement.

The structure was confirmed as that previously described (Dickinson, 1922) i.e. as in P4/mmm, with palladium in (a). 0,0,0; nitrogen in (e),  $0, \frac{1}{2}, \frac{1}{2}$ ; and chlorine in (j), x, x, 0, with  $x \sim 0.23$ . The chlorine parameter x, anisotropic thermal parameters for palladium and chlorine, and an isotropic thermal parameter for nitrogen, were then refined by a block-diagonal least-squares procedure. Scattering curves assumed were those of Thomas & Umeda (1957) for palladium and those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for chlorine and nitrogen. Real corrections for dispersion were made to the palladium and chlorine values. The weighting system was similar to the Hughes scheme except that terms for very small  $F_{obs}$  were further downweighted. Thirteen terms which appeared to be affected by extinction were removed from the data. The final R index for the 118 independent terms included was 0.073. The final values for the parameters are listed in Table 1 and observed and calculated

#### Table 1. Atomic parameters

Amm	onium chloro	palladate(II)					
Pd Cl N	x 0 0·2257 0	$\begin{array}{ccc} y & z \\ 0 & 0 \\ 0.2257 & 0 \\ \frac{1}{2} & \frac{1}{2} \end{array}$		$b_{11}$ 0.00523 0.01212	$\begin{array}{c} b_{12} \\ -0.00543 \end{array}$	<i>b</i> <sub>33</sub> 0·02868 0·06072	B 4·28
Amm	onium chloro	palladate(IV)					
Pd	0	0	0				0.413
Cl	0.2337	0	0	0.00254		0.00516	
Ν	1 <u>4</u>	*	4				2.47

# Table 2. Observed and calculated structure factors ( $\times 2.5$ )

Values marked with an asterisk were assumed to be affected by extinction. The table gives, reading from left to right,  $h, k, l, F_o, F_c$ .

## Ammonium chloropalladate (II)

12223333444+4555555566666	10120123012340123450123	000000000000000000000000000000000000000	963 148 1096 1811* 620 982* 1135 1945* 1262 354 5955 1416* 1620 256 5552 1119 975 441 1264 945	1238 -115 13248 599 9660 1158 2491 1349 598 1612 364 579 951 955 1229 951 955 13555 1229 955 13555	6667778888889911222333	456123012340101012012	0000000000011111111	421 357 839 611 1101 919 942 542 4865 894 545 894 545 10787 1025 1275 1539	481 3555 7255 599 124,6 84,3 666 483 448 633 920 550 1873 1924 -690 11245 598 1400 1740	3444455555556666666677778	3013401234501235612350	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1370 1660* 1254 665 1211 1600 1174 316 764 1174 339 748 1274 329 748 1203 988 329 7734 1203 985 821	1413 1923 1253 577 1328 1636 1145 306 727 1224 1605 266 725 1005 266 725 1136 725 1136 727 1347 633 678 1176 864 335 731	8888991122233334444455	1234010101201230123001	1 1 1 1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	700 397 485 548 714 4549 898 2545 758 765 1250 578 7578 7578 7578 7578 7578 7578 757	636 401 433 556 870 969 961 935 2226 810 1392 810 1392 810 334 518 1256 91 791	555566666666777788888112	2345012345612350123011	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	261 495 980 406 663 1352 433 2255 558 2555 2558 10522 755 740 888 323 866 9 834 834	299 502 1029 391 633 : 069 420 324 596 675 266 691 557 266 691 557 389 1003 1001 719	2 3 3 3 3 4 4 4 4 5 5 5 5 5 5 6 6 6 6 7 7 7	201230113401234511234123	333333333333333333333333333	1415 551 1069 914 1096 821 1096 821 1096 821 1096 821 1096 821 1096 821 1096 821 1096 821 1056 775 559 775 559 777 660 5570 6125 4536 492	1337 479 828 1023 866 1123 8466 1100 435 847 1004 733 285 508 784 662 509 737 644 509 737 643 478 7578
										Ar	nn	nc	niu	m ch	loro	p۵	all	adat	e (IV	)									
0244466	2202402	0000000	3461 1905 5691 3127 5463 2538 1512	4954 1842 8803 3735 6850 3398 1603	668885 5	460246	000000	3015 1525 3427 2274 4350 2582	2967 1420 4929 2470 4370 2164	6 10 10 10 10 10	802460	000000	3684 2313 1299 2345 1221 2820	3141 2462 1334 2234 1241 2806	12 12 1 3 5	2 4 1 3 1	0 1 1 1	1609 2447 2666 2269 1649 2415	1528 2541 4178 2797 1872 3620	5 5 7 7 7 7	351357	1 1 1 1 1	2756 3465 1203 1118 2037 819	2806 3392 1564 1094 1774 672	1		1 1 5 1 5 1 7 1 1 1 5 1	2194 2312 2945 1780 887 922	2787 2342 2718 1666 808 1073

structure factors are listed in Table 2. The palladiumchlorine bond length is 2.299 Å, with  $\sigma = 0.004$  Å. This estimate of error allows for uncertainty in both atomic parameter and cell dimension.

# Ammonium chloropalladate(IV)

Crystals of  $(NH_4)_2PdCl_6$  were obtained, following Sharpe (1953), as small wine-red octahedra. The axial length of the cubic cell was determined from a calibrated rotation photograph as  $9.84 \pm 0.01$  Å, in agreement with Sharpe (1953). The density has been measured as 2.48 g.cm<sup>-3</sup> (Ketelaar & von Walsem, 1938), and the calculated volume for 4 molecules per cell is 2.476. All crystals comprised several individuals giving rise to multiple spots, and the most suitable that could be found was one for which the separate reflexions coincided over half of the Weissenberg film, at least when the equi-inclination angle was very small. Intensities were measured visually from such spots for the layers *hk*0 and *hk*1. Spherical absorption corrections were applied.

This structure was also confirmed as previously described (Ketelaar & von Walsem, 1938), *i.e.* as in *Fm3m* with palladium in (a), 0,0,0; nitrogen in (c),  $\frac{1}{4}$ ,  $\frac{1}{4}$ ; and chlorine in (e), x,0,0, with  $x \sim 0.23$ . Refinement was then as before, except that only the chlorine could adopt anisotropic thermal parameters, and separate scale factors were used for the *hk*0 and *hk*1 data. Eight terms appeared to suffer from extinction and were removed. The *R* index for the 29 terms included was 0.071. The final parameters are listed in Table 1, and observed and calculated structure factors in Table 2.

The palladium-chlorine bond length is 2.300 Å, with  $\sigma = 0.007$  Å.

The assumption that Pd(II) and Pd(IV) have effectively the same atomic radius has thus been confirmed.

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Further refinement of the crystal structure of acetanilide. By C. J. BROWN, The Sir William Ramsay and Ralph Forster Laboratories, University College, Gower Street, London, W.C.1, England

## (Received 29 March 1966)

As a result of a number of requests the crystal structure of acetanilide (Brown & Corbridge, 1954) has been further refined. The original X-ray intensity data were used and Cruickshank's (1961) program was used for refining the positional and anisotropic thermal parameters on a Pegasus computer. Seven cycles of structure factors and least squares reduced R from  $11\cdot2\%$  to  $5\cdot9\%$  taken over the 1125 observed F(hkl). The structure amplitude agreement is given in Table 1, the new atomic parameters in Table 2, and the bond lengths and inter-bond angles in Table 3.

The equation of the mean plane through the benzene

ring is 
$$0.2049X - 0.5482Y - 0.8108Z = 0.4229$$

from which the atoms are displaced by C(1) - 0.014; C(2) + 0.009; C(3) + 0.001; C(4) - 0.010; C(5)0; C(6) + 0.013 Å. The nitrogen atom is -0.046 Å out of this plane so that the C-N bond makes an angle of  $1.9^{\circ}$  with the plane of the ring.

The equation of the mean plane containing C(7), C(8), N and O is

0.3689X - 0.2990Y - 0.8801Z = 1.8978

from which the atoms are displaced by C(7) + 0.002; C(8) 0; N -0.001; and O -0.001 Å. The normals to these two planes are inclined at 17.6°; the value of 37°54′ given in the previous paper was wrong.

The hydrogen bond, assumed to be linear, makes angles of  $110\cdot2^{\circ}$  with the N-C(1) bond,  $121\cdot9^{\circ}$  with N-C(7), and  $139\cdot1^{\circ}$  with O'-C(7').

The results of this further refinement seem to indicate an improvement in overall regularity of the molecule; the benzene ring is more nearly regular and more planar; the acetyl group is now planar, and the mean standard deviation of a bond has been reduced from 0.0056 to 0.0034 Å. There is no change in the conformation of the molecule; the mean change in non-hydrogen positional coordinates is only 0.012 Å. This is of interest since in the structure of *N*methylacetanilide (Pedersen & Pedersen, 1965) the C(8) and O atoms have changed places, together with other differences in molecular geometry. Presumably this *exo* configuration is the more stable one when the oxygen atom does not have to be forced into the *endo* configuration to accept a hydrogen bond.