724. *The Preparation of Palladium Difluoride and Complex Fluorides of Palladium in Selenium Tetrafluoride.*

By NEIL BARTLETT and J. W. QUAIL.

Palladium trifluoride in selenium tetrafluoride is oxidised by bromine trifluoride to the quadripositive state; alone, selenium tetrafluoride reduces it to palladium difluoride. Selenium tetrafluoride has proved to be a good solvent in the preparation of fluoropalladates.

A trigonal modification of potassium hexafluoropalladate(IV) has been identified and its structure determined. Cæsium trifluoropalladate(II) has been prepared and evidence is presented for the existence of the potassium salt. It has not been possible to prepare complex fluorides of Pd^{3+} in selenium tetrafluoride.

ONLY two simple fluorides of palladium have been reported. The trifluoride, first prepared pure by Ruff and Ascher,[1] is the more easily made and is black and paramagnetic.[2] The difluoride, first obtained pure by Bartlett and Hepworth,[3] is pale violet and is the only paramagnetic bivalent palladium compound yet reported. Although palladium tetrafluoride is unknown, several complex fluoropalladates(IV) have been described.[4,5,6]

Apart from the 1 : 1 bromine trifluoride complex [7] no fluoro-complexes with terpositive palladium have been made. By employing the non-oxidising solvent, selenium tetrafluoride, we have attempted to make alkali-metal Pd^{3+} and Pd^{2+} fluoro-complexes, and have succeeded in preparing the latter. We have also found selenium tetrafluoride to be a suitable solvent for the preparation of hexafluoropalladates(IV).

Sharpe has shown that palladium bromide gives with bromine trifluoride a complex of terpositive palladium, BrF_3,PdF_3, which is easily decomposed to the trifluoride.[7] We find it has a magnetic moment $\mu_{eff} = 2{\cdot}2$ B.M. at 21°, close to Nyholm and Sharpe's [2] value for palladium trifluoride itself, $\mu_{eff} = 2{\cdot}0$ B.M., which they had interpreted as indicative of one unpaired spin. The palladium trifluoride, however, has a close-packed hexagonal fluorine atom arrangement with the palladium atoms in octahedral hole sites.[8] Their near-regular octahedral co-ordination suggests the electronic configuration of the Pd^{3+} is $4d^5_{\epsilon}4d^2_{\gamma}$, with three unpaired spins.[9] It is probable that the configuration in the bromine trifluoride adduct is the same. Since neither field-strength-dependence nor temperature-dependence data are available for these compounds, it is impossible to account reliably for the low values of the magnetic moments, although some spin pairing to give the configuration $4d^6_{\epsilon}4d^1_{\gamma}$ would be consistent with the observed moment.

When selenium tetrafluoride is added to the bromine trifluoride complex, bromine is immediately evolved and the solid fluoroselenonium hexafluoropalladate(IV) separates:

$$6BrF_3,PdF_3 + 12SeF_4 = 6(SeF_3)_2PdF_6 + Br_2 + 4BrF_3$$

Sharpe [5] reported a similar further oxidation of palladium, in bromine trifluoride solution in the presence of alkali-metal fluorides. Apparently selenium tetrafluoride, like the alkali fluorides, is a fluoride ion donor and in the presence of such bases the quadripositive state of palladium is stabilised by the formation of PdF_6 octahedra. Fluoroselenium

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[1] Ruff and Ascher, *Z. anorg. Chem.*, 1929, **183**, 204.
[2] Nyholm and Sharpe, *J.*, 1952, 3579.
[3] Bartlett and Hepworth, *Chem. and Ind.*, 1956, 1425.
[4] Cox, Sharp, and Sharpe, *J.*, 1956, 1242.
[5] Sharpe, *J.*, 1953, 197.
[6] Hoppe and Klemm, *Z. anorg. Chem.*, 1952, **268**, 364.
[7] Sharpe, *J.*, 1950, 3444.
[8] Hepworth, Jack, Peacock, and Westland, *Acta Cryst.*, 1957, **10**, 63.
[9] Sharpe, " Advances in Fluorine Chemistry," Butterworths Scientific Publications, London, 1958, Vol. I, p. 56.

hexafluoropalladate is isomorphous with its platinum tetrafluoride[10] and germanium tetrafluoride[11] analogues.

Pure potassium hexafluoropalladate(IV) is produced in the neutralisation

$$(SeF_3)_2PdF_6 + 2KSeF_5 = K_2PdF_6 + 4SeF_4$$

It gave an *X*-ray powder pattern which was wholly indexed on the basis of a trigonal unit cell. A specimen of the same compound was prepared with bromine trifluoride as solvent, but strong lines associated with another phase were also present. This accords with Sharpe's observation[5] that pure potassium hexafluoropalladate(IV) cannot be made in bromine trifluoride. The trigonal modification is commonly observed in A_2MF_6 compounds but this is the only reported example in the A_2PdF_6 series. Hoppe and Klemm[6] prepared a hexagonal modification, $a = 5{\cdot}75$, $c = 9{\cdot}51$ Å, of potassium hexafluoropalladate(IV) by a medium-temperature fluorination of the complex chloride. A third possible modification would have the energetically similar antifluorite structure, but this has not been observed although the cubic rubidium[6] and cæsium fluoropalladates[5,6] are known. For potassium fluoroplatinate the trigonal modification is the only one reported.[12] The structural data for this and the isomorphous fluorogermanate[13] are compared in Table 1 with our values for the fluoropalladate. Despite great similarity in structure, potassium hexafluoropalladate(IV) and potassium hexafluoroplatinate(IV) differ markedly in their behaviour with water; the fluoroplatinate may be recrystallised from water and the fluoropalladate is instantly hydrolysed with precipitation of brown palladium dioxide. The difference in lability is surprising in view of the presumed similarity of the electronic configurations in the Pt^{4+} and Pd^{4+} ions ($5d^6_\epsilon$ and $4d^6_\epsilon$ respectively).

TABLE 1.

	a (Å)	*c* (Å)	*c*/*a*	*x*F	*z*F	*z*K	M–F (Å)	Ref.
K_2GeF_6	5·62	4·65	0·827	0·148	0·220	0·700	1·77	13
K_2PdF_6	5·72	4·67	0·816	0·15	0·24	0·70	1·86	Present work
K_2PtF_6	5·76	4·64	0·806	0·15	0·25	0·74	1·91	12

Atomic positions of space group D_{3d}^3: Pd(Pt,Ge) in (*a*): 000; 2K in 2(*d*): $1/3,2/3,z$; $2/3,1/3,\bar{z}$; 6F in 6(i): $x,2x,z$; $x,\bar{x},z$, $2\bar{x},\bar{x},z$; $\bar{x},x,\bar{z}$; $\bar{x},2\bar{x},\bar{z}$; $2x,x,\bar{z}$.

The absence of a bromine trifluoride complex of quadripositive palladium must be assumed, since the displacement of selenium tetrafluoride gives the terpositive derivative:

$$2(SeF_3)_2PdF_6 + 3BrF_3 = 4SeF_4 + 2BrF_3,PdF_3 + BrF_5$$

Possibly the bromine trifluoride is linked to the palladium trifluoride by a fluorine bridge, and a similar co-ordination of quadripositive palladium would not suffice to stabilise this state.

When palladium trifluoride was treated with selenium tetrafluoride in an attempt to prepare a 1 : 1 adduct, the palladium trifluoride was reduced:

$$2PdF_3 + SeF_4 = 2PdF_2 + SeF_6$$

This reaction serves as a convenient preparative method for the difluoride. Fluoroselenonium hexafluoropalladate decomposes directly to the difluoride at 155° and there is no evidence that a palladium trifluoride–selenium tetrafluoride complex can exist. Bartlett and Hepworth[3] had conjectured that the selenium tetrafluoride derivative, from which they obtained palladium difluoride, was such a compound, but evidently their material was a mixture of the difluoride and fluoroselenonium hexafluoropalladate(IV).

Pure cæsium trifluoropalladate(II) can be made by mixing the components in selenium tetrafluoride. The *X*-ray powder pattern is complex and the compound is paramagnetic

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[10] Bartlett and Robinson, *J.*, 1961, 3417.

[11] Bartlett and Yu, *Canad. J. Chem.*, 1961, **39**, 81.

[12] Mellor and Stephenson, *Austral. J. Sci. Res.*, 1951, **4**, *A*, 406.

[13] Hoard and Vincent, *J. Amer. Chem. Soc.*, 1939, **61**, 2849.

although Gill and Nyholm have found a magnetic moment less than that expected for even one unpaired spin. Their temperature-susceptibility results are given in Table 2.

The rutile type structure of the difluoride [14] is consistent with the electronic configuration $4d^{6}_{\epsilon}4d^{2}_{\gamma}$, with two unpaired spins, although the room-temperature value for the magnetic moment (μ_{eff} 1·88 B.M.) is much smaller than the spin-only value ($\mu_{\text{calc.}}$ 2·83 B.M.). Antiferromagnetism or spin pairing or a combination of both may be responsible for this. A pairing of spins in this configuration would be expected to be accompanied by a large distortion of the co-ordination octahedron. This may account for the low symmetry of $CsPdF_3$ and its anomalous magnetic properties. Potassium fluoride will not combine with palladium difluoride in selenium tetrafluoride, probably because of the lower basisity of potassium fluoroselenate(IV) solution, potassium fluoride having markedly lower solubility than cæsium fluoride in selenium tetrafluoride.

A 1 : 1 mixture of potassium fluoride and palladium trifluoride in selenium tetrafluoride gives a mixture of palladium difluoride, potassium fluoroselenate(IV), and a complex fluoropalladate(II). A 2 : 1 mixture gives the same complex, some potassium hexafluoropalladate(IV), and potassium fluoroselenate(IV). This mixture has zero magnetic moment.

TABLE 2. *Cæsium trifluoropalladate*(II)*: Corrected molar susceptibilities.*

Temp. (°K)	286·5	260·6	234·8	210·8	185·5	182·9	157·0	146·4	118·3	82·3
$10^{6}\chi_{M}$	1043	1078	1132	1310	1335	1268	1318	1341	1416	1568
μ_{eff}	1·60	1·55	1·51	1·53	1·45	1·40	1·32	1·30	1·19	1·04

The measurements were made at 6411 oersteds, and the susceptibility is independent of the field strength.

Since potassium fluoride does not combine with palladium difluoride in selenium tetrafluoride, the complex fluoropalladate(II) must be derived from a hypothetical potassium fluoropalladate(III) by either reduction or disproportionation. Since two mols. of alkali fluoride are required to avoid the formation of palladium difluoride, the reactions producing the fluoropalladate(II) may be:

$$PdF_3 + 2KF = K_2PdF_5;\ 2K_2PdF_5 + 3SeF_4 = 2KPdF_3 + 2KSeF_5 + SeF_6;$$
$$2K_2PdF_5 + SeF_4 = K_2PdF_6 + KPdF_3 + KSeF_5$$

Both processes probably occur. The absence of paramagnetism of the bipositive palladium complex fluoride is unexpected in view of the paramagnetism of the simple fluoride and cæsium trifluoropalladate(II).

EXPERIMENTAL

Preparation of Palladium Trifluoride and its Adduct with Bromine Trifluoride.—The bromine trifluoride complex BrF_3,PdF_3 was prepared in a quartz bulb, as described by Sharpe [7] (Found: Br, 25·3; F, 39·0; Pd, 33·9. Calc. for BrF_3,PdF_3: Br, 26·5; F, 38·0; Pd, 35·5%). It was paramagnetic, $\mu_{\text{eff}} = 2{\cdot}24$ B.M. at 20°. The dark brown complex fluoride was decomposed at 220°, in a vacuum, to give black palladium trifluoride.

Preparation of Fluoroselenonium Hexafluoropalladate(IV).—The bromine trifluoride–palladium trifluoride adduct was refluxed, in a quartz bulb, with a large excess of selenium tetrafluoride. Bromine was evolved and the dark brown complex was converted into a yellow solid. Selenium tetrafluoride was removed under a vacuum at 100°, leaving a bulky yellow solid, *fluoroselenonium hexafluoropalladate*(IV) [Found: F, 45·6; Pd, 21·9; Se, 31·3. $(SeF_3)_2PdF_6$ requires F, 46·3; Pd, 21·6; Se, 32·1%]. It was diamagnetic, $\chi g = -0{\cdot}053 \times 10^{-6}$ c.g.s. units. The complex rapidly decomposed to palladium difluoride at 155° under atmospheric pressure. At 130°, however, the decomposition was incomplete after 30 min. and an *X*-ray powder photograph of the residue showed it to be a mixture of palladium difluoride and fluoroselenonium hexafluoropalladate(IV). The complex fluoride reacted rapidly with water, precipitating a brown solid containing palladium and selenium, probably palladous selenate. Hydrochloric acid dissolved the hexafluoropalladate and potassium chloride precipitated red potassium hexachloropalladate(IV) from the solution.

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[14] Bartlett and Maitland, *Acta Cryst.*, 1958, **11**, 747.

Reaction of Bromine Trifluoride with Fluoroselenonium Hexafluoropalladate(IV).—The yellow complex fluoride dissolved in warm bromine trifluoride to give a red solution. From this, bromine trifluoride was removed under a vacuum at room temperature; this left a dark brown paramagnetic residue. An *X*-ray powder photograph showed it to be BrF_3,PdF_3.

Preparation of Potassium Hexafluoropalladate(IV) *in Selenium Tetrafluoride.*—" AnalaR " potassium bromide (1·688 g.) and palladium dibromide (1·892 g.) were converted respectively into potassium tetrafluorobromite and the 1 : 1 bromine trifluoride–palladium trifluoride adduct by bromine trifluoride. The reactions were carried out in separate quartz bulbs and, when the volatile products had been removed, selenium tetrafluoride was distilled on to each residue and the mixtures were refluxed to give, in one bulb, a solution of potassium fluoroselenate(IV) and, in the other, a suspension of fluoroselenonium hexafluoropalladate(IV). The solution was added to the suspension, and the mixture refluxed for 1 hr. The bright yellow suspended potassium hexafluoropalladate(IV) (2·166 g.) was recovered by distilling off the selenium tetrafluoride at 100° under a vacuum (Found: F, 37·9; Pd, 34·6. Calc. for K_2PdF_6: F, 38·1; Pd, 35·7%). It was diamagnetic.

Structure Determination of K_2PdF_6.—Thin-walled Pyrex glass capillaries (0·5 mm. in diameter) were charged in a dry-box with finely powdered samples and sealed. Photographs were taken on a 14·32 cm. camera with Cu-K_α radiation from a nickel filter. The photographs were indexed on a trigonal unit cell with $a = 5{\cdot}717 \pm 0{\cdot}003$, $c = 4{\cdot}667 \pm 0{\cdot}003$ Å, the Nelson–Riley extrapolation function [15] being employed. The calculated and found values of $1/d^2$ are in Table 3.

TABLE 3. *Structure determination of potassium hexafluoropalladate*(IV).

hkl	$1/d^2$ Calc.	$1/d^2$ Obs.	*hkl*	$1/d^2$ Calc.	$1/d^2$ Obs.	*hkl*	$1/d^2$ Calc.	$1/d^2$ Obs.	*hkl*	$1/d^2$ Calc.	$1/d^2$ Obs.	*hkl*	$1/d^2$ Calc.	$1/d^2$ Obs.
100	0·0408	0·0424	103	0·4539	0·4567	321	0·8213	0·8245	331	1·1475	1·1493	503	1·4331	1·4338
001	0·0459	0·0476	212	0·4693	0·4716	402	0·8364	0·8379	005	1·1478		215	1·4333	
101	0·0867	0·0888	220	0·4896	0·4916	410	0·8568	0·8595	421	1·1884	1·1895	600	1·4688	1·4698
110	0·1223	0·1250	310	0·5304	0·5343	223	0·9027	0·9056	323	1·1884		430	1·5095	1·5105
111	0·1683	0·1704	113	0·5355	0·5381	411	0·9027		105	1·1885		324	1·5097	
201	0·2091	0·2115	221	0·5355		313	0·9435	0·9439	502	1·2036	1·2055	305	1·5150	1·5150
102	0·2244	0·2267	302	0·5509	0·5534	322	0·9589	0·9607	224	1·2242	1·2254	333	1·5147	
210	0·2856	0·2886	203	0·5764	0·5777	500	1·0200	1·0215	510	1·2648	1·2670	423	1·5556	1·5560
112	0·3060	0·3086	311	0·5763		214	1·0202		314	1·2650		431	1·5555	
211	0·3315	0·3338	401	0·6987	0·7005	412	1·0404	1·0415	115	1·2701	1·2715	520	1·5912	1·5914
202	0·3469	0·3494	213	0·6987		501	1·0659	1·0687	413	1·2699		225	1·6374	1·6376
300	0·3672	0·3696	312	0·7140	0·7158	403	1·0659		511	1·3106	1·3116			
301	0·4131	0·4158	004	0·7345	0·7372	330	1·1016	1·1029	205	1·3110				
003	0·4132		320	0·7752	0·7779				422	1·3260	1·3270			

TABLE 4. *Observed and calculated intensities for* K_2PdF_6(trig.).

hkl	Intensity Calc. × 10^{-3}	Intensity Obs.	*hkl*	Intensity Calc. × 10^{-3}	Intensity Obs.	*hkl*	Intensity Calc. × 10^{-3}	Intensity Obs.	*hkl*	Intensity Calc. × 10^{-3}	Intensity Obs.
100	721	s	201	794	v.s.	301	47	w	113	107	m
001	244	m	102	210	m	003	22		221	30	
101	949	v.s.	210	42	w	103	15	v.v.w.	302	23	v.w.
110	427	s	112	57	w	212	259	m.s.	203	62	m.s.
200	0·5	Nil	211	275	m.s.	220	145	m	311	127	
111	153	m.w.	202	346	s	310	31	v.w.	400	2	Nil
002	8	Nil	300	81	w						

Good agreement between observed and calculated intensities was obtained by placing the atoms in the following positions of space group $C\bar{3}m - D_{3d}^3$: Pd in (0,0,0); 2K in $\pm$ (2/3, 1/3, z_K) with $z_K = 0{\cdot}70 \pm 0{\cdot}02$; 6F in $\pm$ $(x_F, \bar{x}_F, z_F)(x_F, 2x_F, z_F)(2\bar{x}_F, \bar{x}_F, z_F)$ with $x_F = 0{\cdot}15 \pm 0{\cdot}01$ and $z_F = 0{\cdot}24 \pm 0{\cdot}02$.

Table 4 shows a comparison of observed and calculated intensities. The latter were calculated with the formula

$$I \alpha F_{hkl}^2 \,.\, P \,.\, \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

where the symbols have their usual meaning. Values of the scattering factors were taken

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[15] Azaroff and Buerger, " The Powder Method," McGraw-Hill Book Co., Toronto, 1958, p. 238.

from Sagel's book.[16] Some difficulty was encountered in the assessment of the relative intensities because of preferred orientation of the crystallites in some samples. In photographs showing this effect the intensities of *hk*0 reflexions were enhanced and of 001 reflexions diminished.

Cæsium Hexafluoropalladate(IV).—This was prepared similarly to the potassium salt but gave a clear orange-red solution in the selenium tetrafluoride. The product was the yellow diamagnetic solid described by Sharpe.[5]

Preparation of Palladium Difluoride.—Palladium trifluoride, when refluxed with selenium tetrafluoride at atmospheric pressure, became brown. The lilac-tinted solid left when the selenium fluoride had been removed was palladium difluoride (Found: F, 26·1; Pd, 73·1. Calc. for PdF_2: F, 26·3; Pd, 73·7%). An *X*-ray powder photograph showed only the lines of palladium difluoride.

Reactions between Palladium Trifluoride and Potassium Fluoride in Selenium Tetrafluoride.—An equimolar mixture of potassium fluoride and palladium trifluoride was refluxed for 3 hr. in selenium tetrafluoride. An *X*-ray powder photograph showed the lilac-tinted product to be a mixture of palladium difluoride, potassium fluoroselenate(IV), and a third phase which gave rise to a more diffuse pattern. When a 2 : 1 molar ratio of potassium fluoride to palladium trifluoride was used, a magenta suspension appeared which settled, and as the selenium tetrafluoride was removed a white solid crystallised on its surface. An *X*-ray powder photograph of the magenta material showed, weakly, a pattern of more diffuse lines which corresponded to those of the unknown phase in the 1 : 1 mixture and a weak pattern of lines corresponding to the K_2PdF_6 pattern. The white solid gave the *X*-ray powder pattern of potassium fluoroselenate(IV). Palladium difluoride was not produced in the reaction. The magenta solid had zero magnetic moment. Yellow potassium tetrachloropalladate(II) was formed when dilute hydrochloric acid was added to the solid.

Cæsium Trifluoropalladate(II).—An equimolar mixture of cæsium fluoride and palladium difluoride was refluxed for 3 hr. at atmospheric pressure, the pale lilac suspension becoming brown. The selenium tetrafluoride was removed under a vacuum and left pinkish-brown *cæsium trifluoropalladate*(II) (Found: F, 19·2; Pd, 36·1. $CsPdF_3$ requires F, 19·2; Pd, 36·0%). The *X*-ray powder pattern was diffuse and complex, but the lines characteristic of palladium difluoride were absent.

Attempted Preparation of Potassium Trifluoropalladate(II).—When potassium fluoride was substituted for cæsium fluoride in the procedure just described there was no reaction, the *X*-ray powder photograph of the residue, after four hours' refluxing showing a mixture of palladium difluoride and potassium fluoroselenate(IV).

Analyses.—Palladium and bromine were determined as metal and silver bromide respectively in the 1 : 1 bromine trifluoride–palladium trifluoride adduct, and the palladium in potassium hexafluoropalladate(IV) as metal, by Sharpe's methods.[7] Otherwise, palladium was precipitated as the dimethylglyoxime complex. Selenium was reduced to the element, by sulphurous acid, in the filtrate from the palladium precipitate. Fluoride was determined as lead chloride fluoride in the hydrofluoric acid–fluorosilicic acid distillate from perchloric acid solution.[17]

Chemicals and Reagents.—" Pure Palladium Sponge " as supplied by Platinum Chemicals, Asbury Park, N.J., was used. The bromine trifluoride was as supplied by the Matheson Co. Inc., Illinois. Selenium tetrafluoride was prepared according to Aynsley, Peacock, and Robinson's directions.[18]

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THE CHEMISTRY DEPARTMENT, THE UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER 8, B.C., CANADA.
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[16] Sagel, " Tabellen zur Rontgenstrukturanalyse," Springer-Verlag, Berlin, 1958, p. 106—119.

[17] Willard and Winter, *Ind. Eng. Chem.*, *Analyt.*, 1933, **5**, 7.

[18] Aynsley, Peacock, and Robinson, *J.*, 1952, 1231.