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March 1984

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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For Synthetic Metals

Intercalation of Graphite by Silicon Tetrafluoride and Fluorine to Yield a Second-Stage Salt $C_{24}SiF_5$.

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Summary

Powdered graphite (either finely broken HOPG or Union Carbide SP1) interacts with 1:1 SiF_4/F_2 mixture ($\sim$ 50 atmospheres) at 40°, to yield a second stage compound (a_o = 2.46(1), c_o = 11.29(1) Å) of composition $C_{\sim 24}SiF_5$. This product interacts with excess PF_5 with quantitative displacement of SiF_4 to yield a first-stage fluorophosphate (a_o = 2.46(1); C_o = 7.65(1) Å) according to the equation: $C_{24}SiF_5 + 2\ PF_5 \rightarrow C_{24}PF_6.PF_5 + SiF_4$. The first-stage fluorophosphate falls to a second stage salt (a_o = 2.46(1); c_o = 10.87 Å) under vacuum: $C_{24}PF_6.PF_5 \xrightarrow{20°} C_{24}PF_6 + PF_5$. This is identical to that prepared directly: $24C + PF_5 + \frac{1}{2}F_2 \rightarrow C_{24}PF_6$. Extensive reduction of $C_{24}PF_6$, at $\sim$ 20°: $2\ C_{24}PF_6 + PF_3 \rightarrow 48C + 3\ PF_5$ to graphite of crystallinity comparable to that of the starting graphite establishes that the initial $C_{24}SiF_5$ does not involve extensive fluorination of the graphite. The ease of displacement of SiF_4 by superior fluoroacids indicates that $C_{24}SiF_5$ can be a valuable precursor for other graphite salts. Ready formation of a first-stage fluoroborate, C_7BF_4, I_c = 7.70(1) Å contrasts with the failure to similarly prepare a first-stage SiF_5^- salt.

This work was supported in part by the Committee on Research of the University of California, Berkeley, and by the Director, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

Introduction

The pattern of graphite intercalation by hexafluorides of the third transition series[1] had indicated that the intercalation of such molecules, to form $C_x^+MF_6^-$ salts, requires a minimum electron affinity of approximately 120 kcal mole^{-1}. Such a threshold electron affinity also accounts[2,3] for the spontaneous intercalation of graphite by arsenic pentafluoride and for the failure of the physically similar pentafluoride of phosphorus to do likewise. For the half reaction:

$$3\ EF_5 + 2\ e^- \rightarrow 2\ EF_6^- + EF_3$$

the values for $-\Delta H^\circ_{298}$ (per mole of electrons) are[4,5]: for $AsF_5 \geqslant 123$ kcal mole^{-1} and for $PF_5 = 87(8)$ kcal mole^{-1}. Recently Rosenthal and Bartlett have shown[6] that gaseous PF_3 reduces the second-stage salt, $C_{24}PF_6$, at 20°:

$$2\ C_{24}PF_6 + PF_3 \rightarrow 48C + 3\ PF_5$$

the recovered graphite possessing crystallinity comparable with that of the starting graphite. The threshold energy for MF_6^- intercalation therefore appears to be thermodynamic.

Intercalation of graphite by BF_4^- formed from BF_3 and F_2 was first claimed by Cohen.[7] A second-stage fluoroborate $C_{16}BF_4$ has been reported[8] by Ebert and Selig as a product of the interaction of graphite with BF_3 and $C\ell F$. Graphite fluoroborates have also been prepared by Vogel and Herold and their coworkers[9] by using nitryl fluoroborate as the oxidizing agent, but those syntheses have also resulted in the incorporation of solvent molecules (nitromethane) as well as fluoroborate. First-stage fluoroborate devoid of such

dielectric spacers had not been reported hitherto. A first-stage salt C_7BF_4 has been prepared as part of this study. Ready intercalation of graphite by BF_4 is in accord with the very favorable fluoride-ion affinity[10] of BF_3, from which[11] $-\Delta H^\circ_{298}(BF_{3(g)} + \frac{1}{2}F_{2(g)} + e^- \rightarrow BF_{4(g)}^-) =$ 154 kcal mole^{-1}.

Beauchamp and Murphy[12] have concluded that the fluoride-ion affinity of SiF_4 is only slightly inferior to that of BF_3. Since the SiF_5^-, although roughly 5/4th the volume of BF_4^-, requires no further separation of the carbon-atom sheets[13] than does BF_4^-, the energy expended for salts of comparable charge, $C_y^+EF_x^-$, should be similar. It seemed therefore that graphite salts $C_y^+SiF_5^-$ should exist.[14]

Intercalation of graphite by SiF_4 in the presence of F_2 has been achieved and a vacuum stable second-stage salt of composition $C_{24}SiF_5$ appears to represent the intercalation limit. This paper describes its preparation and some of its properties.

Experimental

Materials: The graphite used was of two forms: HOPG chips (kindly provided by A. W. Moore, Carbon Products Division, Union Carbide) were filed by hand into powder; SP-1 graphite (Union Carbide) was used as supplied. Although the SP-1 crystallites were of considerably smaller particle size, they interacted somewhat more slowly than the fragmented HOPG in all cases. All graphite samples were baked at 500° under vacuum and were pretreated with F_2 (300 torr) for four hours. Silicon tetrafluoride and fluorine were used as obtained from The Matheson Company, East Rutherford, N. J. Phosphorus pentafluoride (also from The Matheson Company) was purified by trap-to-trap distillation and checked for purity by infrared spectroscopy.

Instrumentation: Infrared spectra of the reactant gases and gaseous products were recorded using a Perkin-Elmer 597 spectrophotometer. The gas cell was of stainless stell provided with AgCl windows cut from 1 mm. thick sheet, the path length being 10 cm. Debye-Scherrer X-ray powder photographs were taken on a General Electric Precision camera (nominal circumference 45 cm.) using Ni-filtered Cu K_α radiation. Samples were packed in thin-walled quartz capillaries (usually 0.7 mm. diameter), as supplied by Charles Supper & Co. Analyses were performed by the microanalysis Laboratory of the Department of Chemistry, University of California, Berkeley.

Apparatus and Sample Handling: The reaction vessel in all cases was a three-inch length of 3/8" diameter stainless steel rod, drilled to an inner

diameter of ¼" and connected to a stainless steel Whitey valve by Swagelock compression fittings. Its capacity was ∿ 2.5 ml. Gas transfers were performed in a stainless steel vacuum system and all manipulations of solid materials were carried out in a dry nitrogen atmosphere of a Vacuum Atmospheres Corp. Dri-Lab. Gases to be transferred to the reaction vessel were measured out in a section of the vacuum line of ∿ 70 ml capacity. This included the volume of a Monel Helicoid Bourdon gauge measuring 0 to 1000 mm. Hg. abs., as supplied by American Chain and Cable Co. Inc., Bridgeport, Connecticut. Typically gases measured out in the 70 ml. volume were condensed sequentially in the reaction vessel (which was not part of the fixed volume) by cooling that vessel to -196°.

Preparation of $C_{24}SiF_5$. Silicon tetrafluoride (500 torr) and F_2 (500 torr) were each transferred from the line to graphite contained in the reaction vessel which was then closed and warmed to ∿ 20° for 8 hours. SiF_4 (1000 torr) and F_2 (1000 torr) were added again from the line and the vessel was warmed to 40° in a water bath for ∿ 12 hrs. Remaining gases were removed in a dynamic vacuum at ∿ 20°. Results for four preparations are listed in Table 1. They indicate an approximate composition $C_{24}SiF_5$. X-ray powder data (given in Table 2) established $C_{24}SiF_5$ to be a second-stage compound with a_o = 2.46(1); c_o = 11.30(2)Å. That the Si : F ratio was 1:5 and not 1:6 was indicated by the stoichiometry of the interaction with PF_5.

Interaction of $C_{24}SiF_5$ with PF_5. A large molar excess of PF_5 has condensed on to $C_{24}SiF_5$ in the small-volume reaction vessel and the reactants were left for

20 hours at 20°. The gases were vented to a closed volume of the vacuum line which incorporated the infrared cell. Infrared spectroscopy showed that the vented volatiles (including the excess PF_5) were rich in SiF_4. The solid product was a first-stage compound which fell to a second-stage compound $C_{24}PF_6$ (see below). The first stage compound had the composition $C_{24}PF_6.PF_5$ (see Table 3). It was handled in the Dri-Lab at ∿ 20° without severe loss of PF_5 and the X-ray powder samples prepared under these conditions provided the data given under $C_{24}PF_6.PF_5$ in Table 2. When $C_{24}PF_6.PF_5$, derived from $C_{24}SiF_5$, was subjected to a dynamic vacuum it lost only PF_5 (as established by infrared spectroscopy) and yielded the second-stage material $C_{24}PF_6$ (see Table 4). This material was indistinguishable, in its X-ray powder diffraction pattern, from that prepared directly from graphite, PF_5 and F_2 (see below). The second-stage compound $C_{24}PF_6$ consumed approximately an equimolar quantity of PF_5 when exposed to it, at 20°, to again yield $C_{24}PF_6.PF_5$.

Preparation of $C_{24}PF_6.PF_5$ and $C_{24}PF_5$ from graphite, PF_5 and F_2. A large molar excess of PF_5 and just sufficient F_2 to meet the requirements of the $C_{24}PF_6.PF_5$ synthesis were condensed onto the graphite in the reaction vessel which was warmed to ∿ 20° for 24 hours. Remaining gases were vented to the Dri-Lab atmosphere and the solid was examined by X-ray powder photography. If the product was not a homogeneous first-stage compound it was again treated with PF_5, containing a small concentration of F_2, for a further 8 hours at 20°. The first-stage compound prepared in this way was indistinguishable from that derived from $C_{24}SiF_5$. As illustrated in Table 4 such samples of $C_{24}PF_6.PF_5$ fall to $C_{24}PF_6$ in a dynamic vacuum.

Preparation of $C_{11}PF_6$. A vacuum stable first-stage hexafluorophosphate of approximate composition $C_{11}PF_6$ was prepared by treating graphite (typically 10.5 mm. mole) with PF_5 and F_2 (400 and 300 torr respectively as measured in the line) at ∿ 20° for 12 hours. Volatiles were removed in a dynamic vacuum. The vacuum-stable residual solid (PF_6^- uptake 0.95 mm. moles) proved to be a first stage compound, with a_o = 2.46(1), c_o = 7.79(3) Å, carbon analysis of which gave C = 47.3%; required for $C_{11}PF_6$: C = 47.7%.

Preparation of a first-stage graphite fluoroborate. Graphite (12.1 mm. mole) was treated with BF_3 and F_2 (700 and 600 torr respectively in the fixed volume of the vacuum line) at ∿ 20° for 24 hours in the small volume reactor. Volatiles were removed in a dynamic vacuum at ∿ 20°. Gravimetry indicated uptake of 1.68 mm. mole BF_4 and a composition $C_{7.2}BF_4$, with which carbon analysis is in good agreement: C, required: 49.9%; C, found: 49.8%. X-ray powder photographs yielded the following 00ℓ d spacings (Å): (001) 7.64, s; (002) 3.83_2 vs; (003) 2.56_6 mm., indicating an I_c of 7.69(2) Å. The salt is deep blue and vacuum stable at 20°.

Discussion

Although it was quickly apparent that the product at the maximum intercalation limit of graphite by $SiF_4|F_2$ mixtures was a second-stage compound of approximate composition $C_{24}SiF_x$ the determination of x posed difficulties. It was known from previous work in these laboratories[15] and from the work of Ebert and Selig,[8] that graphite is intercalated by PF_6^- to form first-stage salts, but that PF_5 alone is not intercalated by graphite. Since PF_5 does not add

more than one F^-, it appeared that the displacement of SiF_4, confidently predicted on thermodynamic grounds,[16] would provide for the counting of the number of F^- coordinated to the SiF_4 in $C_{24}SiF_x$ i.e. for the determination of y in the scheme:

$$C_xSiF_{4+y} + y\ PF_5 \rightarrow C_x(PF_6)_y$$

The first stage compound of composition $C_{24}PF_6.PF_5$, the stoichiometry of which is suggestive of salt of a μ-fluoro-bridged anion $F_5P\text{-}F\text{-}PF_5$, had not been anticipated. Species such as $F_5P\text{-}F\text{-}PF_5^-$ have been considered by Ebert et al[17]. The ready fall of $C_{24}PF_6.PF_5$ to the second-stage compound $C_{24}PF_6$ according to the equation:

$$C_{24}PF_6.PF_5 \rightarrow C_{24}PF_6 + PF_5$$

established however that the stoichiometry of the fluorosilicate precursor must have been $C_{24}SiF_5$. The first-stage compound $C_{24}PF_6.PF_5$ proved to be preparable directly from graphite PF_5 and F_2. The last species was regulated to just meet the stoichiometric requirements:

$$24\ C + 2\ PF_5 + \tfrac{1}{2}F_2 \rightarrow C_{24}PF_6.PF_5$$

More fluorine generates the vacuum stable first-stage compound $C_{11}PF_6$.

Attempts to prepare the second-stage material, $C_{24}SiF_5$, using HOPG chips, suitable for conductivity studies, have not been successful, not even a pure third-stage being preparable. Both in these efforts and the unsuccessful attempts to prepare a first-stage compound using finely powdered graphite, pressures of SiF_4 and F_2 up to 20 atmospheres were employed but temperatures in excess of 40° were avoided because of the concern to avoid fluorination of the graphite. Thus SiF_4 is clearly seen to be inferior, both to PF_5 and GeF_4,

as a fluorine-sponsored intercalator. Each of the latter fluoroacids readily yields first stage salts in the presence of fluorine, and even large HOPG chips are so intercalated. This is compatible with the high exothermicity of the process $EF_{x(g)} + \frac{1}{2}F_{2(g)} + e^- \rightarrow EF_{x+1(g)}$ which is -163 kcal $mole^{-1}$ for each of these molecules.[5] Of course it is the high value of the fluoride ion affinity of GeF_4 and PF_5 (101 kcal $mole^{-1}$ for each) which makes a major contribution to this oxidizing power and also provides for the ready displacement of SiF_4. From the observations of Murphy and Beauchamp[12] we can assume that the fluoride ion affinity of SiF_4 is less (less exothermic measured as an enthalpy change) than 92 kcal $mole^{-1}$. It may well be much less.

The ease with which graphite has proved able to intercalate BF_3 in the presence of fluorine to form C_7BF_4 a first-stage salt, indicates that the fluoride ion affinity of BF_3 may be apppreciably superior to that of SiF_4. Evidently, of the fluoroacids considered here, SiF_4 is the poorest promotor of graphite oxidation. The weak fluoroacid properties of SiF_4 mean however that SiF_4 can be readily displaced by stronger and less volatile acids. Thus SiF_4 is displaced from $C_{24}SiF_5$ not only by PF_5 but also by BF_3 and this provides a convenient route to lower-stage salts. Perhaps a more important application, however, is in the intercalation of fluoride ion acceptors which are themselves unstable to elemental fluorine. An instance of this is the displacement[18] of SiF_4 by $C_6F_5PF_4$. This fluorophosphorane is fluorinated (yielding PF_5 and fluorobenzene) when exposed to F_2 but when added to $C_{24}SiF_5$ only SiF_4 is observed as a volatile and the fluorophosphorane is intercalated:

$$SiF_5^- + C_6F_5PF_4 \rightarrow C_6F_5PF_5^- + SiF_4$$

Table 1. Gravimetric data and carbon analyses for $C_{24}SiF_5$ preparations*

millimoles of carbon	millimoles of SiF_5 taken up	$C:SiF_5$ molar ratio	% C found ($C_{24}SiF_5$ requires C = 70.1%)
17.0	0.71	24	69.6
18.8	0.86	22	70.5
17.0	0.71	24	-
18.4	0.79	23	-

* X-ray powder photographs of all preparations were alike and indicative of a pure second stage material. Samples analyzed for carbon were also analyzed for H and N each of which proved to be insignificant.

Table 2. d Spacings (Å) and relative intensities from X-ray powder data* for first-stage $C_{11}PF_6$ and $C_{12}PF_{5.5}$, and second-stage $C_{24}PF_6$ and $C_{24}SiF_5$

	$C_{11}PF_6$			$C_{12}PF_{5.5}$			$C_{24}PF_6$			$C_{24}SiF_5$		
hkℓ	I/I_o	d_{obs}	d_{calc}	I/I_o	d_{obs}	d_{calc}	I/I_o	d_{obs}	d_{calc}	I/I_o	d_{obs}	d_{calc}
001	m	7.639	7.789	s	7.603	7.621	m	11.19	10.87			
002	vs	3.867	3.894	vs	3.809	3.810						
003	m	2.599	2.596	m	2.541	2.540	vs	3.631	3.624	vs	3.760	3.768
004				-	-		m	2.721	2.718	m	2.833	2.826
100	m	2.124	2.126	m	2.111	2.126	m	2.127	2.127	s	2.125	2.128
005				-	-		-	-				
006							mw	1.808	1.812			
007				-	-		w	1.554	1.553	w	1.614	1.615
110	w	1.227	1.227	m	1.227	1.227	m	1.228	1.228	s	1.228	1.228
111				w	1.212	1.212						
112				w	1.167	1.168						
a_o(Å)		2.45(1)			2.45(1)			2.46(1)			2.46(1)	
c_o(Å)		7.79(2)			7.62(2)			10.87(6)			11.30(2)	

* Powdered samples were contained in thin walled quartz capillaries of 0.7 mm. diameter. A General Electric 'Precision' camera of 45 cm. nominal circumference was used with Ni filtered CuK_α radiation.

Table 3. Stoichiometry of the interaction of $C_{24}SiF_5$ with PF_5*

millimoles $C_{24}SiF_5$	millimoles PF_5 taken up	molar ratio $PF_5/C_{24}SiF_5$
0.28	0.56	2.0
0.38	0.77	2.0
0.26	0.50	1.9

* X-ray powder photographs of all solid products $C_{24}PF_6.PF_5$ showed only a first stage pattern (Table 2).

Table 4. Conversion of $C_{24}PF_6.PF_5$ to $C_{24}PF_6$

Origin of the $C_{24}PF_6.PF_5$	millimoles $C_{24}PF_6.PF_5$	millimoles PF_5 removed under vacuum at 20°	% C in residue ($C_{24}PF_6$ requires 66.5%)
1. via $C_{24}SiF_5$	0.31	0.27	65.6
2. $24C + \frac{1}{2}F_2 + 2PF_5$	0.42	0.41	69.4

Acknowledgements

This work was supported in part by the Committee on Research of the University of California, Berkeley, and by the Director, Chemical Sciences Division of the U. S. Department of Energy under Contract Number DE-AC03-76SF00098.

The authors also thank Dr. A. Moore of Parma Technical Center, Union Carbide Corporation for generously supplying the HOPG graphite, and Professor Dr. Reinhardt Schmutzer and his coworkers of Technische Universität, Braunschweig for the sample of $C_6F_5PF_4$.

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2. B. W. McQuillan, Ph.D. Thesis, University of California, Berkeley, April 1981, LBL Report 12228.

3. N. Bartlett and B. W. McQuillan, in "Intercalation Chemistry", S. M. Whittingham and A. Jacobson, eds., Academic Press, Inc. N.Y., London, 1982, pp. 19-53.

4. The value of $\Delta H^\circ_f(AsF_{5(g)}) = -296$ kcal mole^{-1} is from A. Woolf, J. Fluorine Chem., 15 (1980) 533-537. The fluoride ion affinity of $AsF_{5(g)}$, $-\Delta H^\circ_{298}$ $(AsF_{5(g)} + F^-_{(g)} \rightarrow AsF^-_{6(g)})$, has been evaluated (T. E. Mallouk, G. L. Rosenthal and N. Bartlett, to be published) to be ≥ 110 kcal mole^{-1} from which $\Delta H^\circ_{f,298}(AsF^-_{6(g)}) \leq -468$ kcal mole^{-1}. The value of $\Delta H^\circ_{f,298}(AsF_{3(g)}) = -198$ kcal mole^{-1} is that cited by Woolf.

5. Hubbard, et al., J. Chem. Thermodynamics, 2 (1970) 221-225, have established $\Delta H^\circ_{298}(PF_{3(g)} + F_{2(g)} \rightarrow PF_{5(g)}) = -152(1)$ kcal mole. For the fluoride ion affinity, $-\Delta H^\circ_{298}(PF_{5(g)} + F^-_{(g)} \rightarrow PF^-_{6(g)}) =$ 100(6) kcal mole^{-1} (T. E. Mallouk, G. L. Rosenthal and N. Bartlett, to be published).

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6. G. L. Rosenthal and N. Bartlett, to be published.

7. A. D. Cohen, French Patent 2, 291, 151 (1975).

8. C. B. Ebert and H. Selig, Mater. Sci. Eng. 31 (1977) 177. and Synthetic Metals, 3 (1981) 53.

9. D. Billaud, A. Pron, F. L. Vogel, and A. Herold, Mater. Res. Bull., 15 (1980) 1627-34.

10. J. Haartz and K. McDaniel, J. Am. Chem. Soc., 95 (1972) 8562 and J. L. Beauchamp, J. Chem. Phys., 64 (1976) 929, have used Altshuller (J. Am. Chem. Soc., 77 (1955) 6187) value for ΔH°_{298} ($BF_{3(g)} + F^{-}_{(g)} \rightarrow BF^{-}_{4(g)}$) = -71 kcal mole^{-1}, rather than the value of -91 kcal mole^{-1} given by Bills and Cotton (J. Phys. Chem., 64 (1960) 1477). Recent thermodynamic evaluation of $C\ell O_2^{+}BF_4^{-}$ in these laboratories indicate that the value of Bills and Cotton is the correct one.

11. In all evaluations, $\Delta H_{f,298}(F^{-}_{(g)})$ = -62(2) kcal mole^{-1}, which is based upon $\Delta H_{f,298}(F_{(g)})$ = 18.86 kcal mole^{-1} from the JANAF Tables (Dow Chemical Company, Midland, Michigan, 1960 to 1977) and the electron affinity recommended by A. C. Sharpe (in "Halogen Chemistry", V. Gutman, ed., Academic Press, London 1967, Vol. 1, pp. 1-40.) for $F_{(g)}$ = 81(2) kcal mole^{-1}.

12. M. K. Murphy, and J. L. Beauchamp, J. Am. Chem. Soc., 99 (1977) 4992.

13. SiF_5^{-} as a D_{3h} molecule with its threefold axis tilted with respect to $\underline{c}_0$ or as a square based pyramid (an octahedral MF_6 less one F ligand) would not pack very differently from MF_6 species. The latter fit with least separation of the carbon-atom sheets when a threefold axis is perpendicular to the sheets.

14. A. D. Cohen, unknown to us, had claimed graphite SiF_5^- salts in a patent (A. D. Cohen, U.S. Patent 4, 128, 499 (1979)). Reaction conditions and stoichiometries are not specified. The patent claims: "Typically, the conversion is completed in as little as two hours." The meaning of "completed" is not evident, since neither stoichiometries nor stages are specified. It is our finding that first-stage products are not formed, thus the graphite intercalation is never complete, in the sense of the galleries having been fully occupied. The patent gives no evidence to support SiF_5^- salt formation as opposed to SiF_6^{2-}.

15. E. M. McCarron, Y. J. Grannec, and N. Bartlett, J. Chem. Soc., Chem. Commun., (1980) 890.

16. Even though PF_6^- is larger than SiF_5^- and the lattice energies of salts of the former are smaller than those of the latter, silicon tetrafluoride is conspicuously less able to form stable salts with fluoride ion donors than is PF_5. Thus $SF_3^+PF_6^-$ and $C\ell O_2^+PF_6^-$ are in equilibrium with $SF_4|PF_5$ and $C\ell O_2F|PF_5$ at room temperature and ordinary pressures whereas there is no evidence for the existence of the corresponding SiF_5^- salts even at low temperatures. From a study of the PF_6^- salts mentioned, G. L. Rosenthal has determined $\Delta H^\circ_{298}(PF_{5(g)} + F^-_{(g)} \rightarrow PF_6^-{}_{(g)})$ to be -101 kcal mole^{-1}.

17. L. B. Ebert, D. R. Mills, J. C. Scanlon, and H. Selig, Mat. Res. Bull., 16 (7), 831 (1981).

18. The $C_6F_5PF_4$ was supplied by Professor Dr. R. Schmutzler and his co-workers for the purpose of making $C_x^+C_6F_5PF_6^-$ salts. The failure to prepare large HOPG samples of $C_{24}SiF_5$ has impeded the physical characterization of these derivatives, however.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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