

not proceed as written. On the other hand, a similar reaction has been reported¹⁰ to occur. There was no trimethylsilyl chloride produced in an ampule holding the reactants at 100 °C for 20 h.

Characterization. Temperature programmed thermal decomposition (TPTD) examination of the amide imide revealed (Figure 1) two well-defined events with maxima at 125 and 420 °C. The profiles of the TPTD of three independent samples, containing different levels of impurities, were essentially the same. This is an indication that the KBr and KNH₂ are dispersed in the amide with little or no chemical interaction. The maxima in the TPTD corresponded with the evolution of ammonia and nitrogen, respectively, and served to establish the conditions for the preparation of the nitride which was conducted subsequently at 300 °C. The final residue in the TPTD was metallic tin. The volatile evolution is well-defined, and at 300 °C, prior to any significant evolution of nitrogen, the ammonia loss is almost complete with very little hydrogen left as evidenced by the absence of any NH vibration in the IR spectrum of the nitride. The IR spectrum of the nitride is very simple. It contains a single prominent band at 620 cm⁻¹, in agreement with previous observations³ on material obtained in a glow-discharge system. It is interesting to note the difference in thermal behavior between bulk powder nitride, which decomposes significantly at 420 °C, and glow-discharge films, which decompose only at >720 °C.³ Evidently the activation energy for decomposition is greatly enhanced in the film.

The nitride was subjected to XPS analysis for qualitative purposes. Binding energies, referenced to C(1s) at 284.6 eV, were 396.2 and 485.1 eV for N(1s) and Sn(3d_{5/2}) respectively. The intensity ratio expressed as atomic concentrations (N/Sn) is 0.92, a figure which differs from the idealized value of 1.33. This situation is not unusual considering the empirical sensitivity factors used to convert intensities to concentrations and the fact that the technique analyzes the surface of the material, which may have a composition that departs from that of the bulk. In agreement with the bulk chemical analysis, the XPS analysis detected potassium but no bromide. The values for the N and Sn binding energies are in accordance with those of other nitrides^{11,12} although the nitrogen value is at the low end of the range, more in line with the interstitial nitrides than the covalent ones. This suggests considerable electron density shift from the metal to the nitrogen. A moderate shift in the tin value to a higher energy (compared with tin metal) is observed here as in the case of titanium nitride.¹³

The tin nitride powder prepared in the course of this study was found to be amorphous by X-ray diffraction. The nitride is brick red while the amide is pale yellow.

Attempts were made to determine the electrical resistivity of the nitride. A portion of the material was compressed into a pellet at room temperature under 550 MPa. The apparent density of the pellet at that stage was 3.16 g/cm³, which is about 62% of the value determined by Janeff² with a pycnometer. The void space in the pellet is approximately correct for the packing of spheres. The pellet was subjected to a thermal treatment of 8 h at 500 °C with the expectation of promoting sintering and additional densification. The treatment was conducted in an autoclave at 10 MPa nitrogen to prevent nitrogen loss from the nitride. The pellet had a marginal weight loss of 1.2%, but densification proceeded only slightly to 3.29 g/cm³. The electrical resistivity of the pellet at this stage was excessive, apparently due to poor contact among the particles of the material. A purer specimen, appropriate for resistivity measurements, was prepared as a film by CVD at atmospheric pressure under anaerobic conditions according to ref 6. Briefly, a stream of argon was used

to sweep a source containing (Et₂N)₄Sn, held at 150 °C, into a reaction zone, held at 300 °C, which contained the specimens to be coated. A side stream of anhydrous ammonia was also introduced to the hot reaction zone. The thickness of the coating on a quartz plate, used for the resistivity measurements, was derived from the gain in weight and assuming a density of 5.1 g/cm³. The coating on quartz was light brown in color. Those on silicon were iridescent because of interference with visible light. The resistivity at room temperature was 0.15 Ω cm, compared with 1.4 × 10⁻⁴ Ω given in ref 2 and 66-5.6 Ω cm on crude films that decreased to 6.3-1.4 Ω cm after annealing as reported in ref 3b. It is seen that the result found in the present work would support those given in ref 3b. It is possible that the specimen examined by Janeff² might have been contaminated with metallic tin, which would explain the higher conductivity. It is not uncommon to sputter free metal in a glow-discharge system. The IR spectrum of the material obtained in the CVD setup was identical with that of bulk powder from the amide imide intermediate. It did not show evidence of oxide species such as bands at 660 or 510 cm⁻¹ due to SnO₂ and SnO or a band that develops at 545 cm⁻¹ upon long exposure of bulk nitride to air. Furthermore, thermal decomposition at 800 °C of the film left a bright metallic coating, suggesting little or no oxygen on the initial film.

Experimental Section

All manipulations were conducted in a vacuum line and in an inert-gas glovebox (H₂O and O₂ <1 ppm). Ammonia was further dried by contact with metallic sodium. Liquid-ammonia reactions and product washing were conducted in sealed heavy-walled ampules provided with a side arm separated from the body of the ampule by a glass frit. In a typical reaction, about 2 mmol of tin(IV) bromide and a slight excess over the stoichiometric amount of potassium amide were loaded into an ampule together with about 15 mL of liquid ammonia. Washing of solids was done with ammonia recovered by a thermal gradient from the side arm that collected the soluble fraction being filtered. The TPTD analysis was conducted in a system containing a furnace, ramped at 10 °C/min. The volatiles evolved were continuously swept by high-purity helium into a Model 5970 Hewlett-Packard mass selective detector. The XPS analysis was conducted with a McPherson Model 36 electron spectrometer using Al Kα radiation at 250 W. Sample preparation for XPS was conducted in an inert-gas glovebox. Electrical resistivities were measured by the four-probe method. Infrared spectra were obtained with a Digilab FTIR 60 spectrophotometer.

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Bond Lengths in Covalent Fluorides. A New Value for the Covalent Radius of Fluorine

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From a consideration of observed bond lengths, we propose a new value of 54 pm for the covalent radius of fluorine. Pauling¹ originally gave a value of 64 pm, but after the determination of the bond length in the F₂ molecule,² the value of 72 pm, half the F-F bond length, was generally adopted. However, the observed bond lengths in many covalent fluorides are considerably shorter than those calculated from either of these values. More recently

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Table I. Normal X-F Single Bond Lengths for Species in Which the Central Atom Has a Filled Valence Shell and No Lone Pairs

species	d_{X-F} , pm	r_X cov, ^a pm	$d_{X-F}(\text{pred})$, pm			Δ , ^b pm			ref
			c	d	e	c	d	e	
BF ₄ ⁻	141	86	158	150	140	+17	+9	-1	f
CF ₄	132	77	149	141	131	+17	+9	-1	g
NF ₄ ^{+p}	130	70	142	134	124	+12	+4	-6	h
AlF ₆ ³⁻	181	126	198	190	180	+17	+9	-1	i
SiF ₆ ²⁻	171	117	189	181	171	+18	+10	0	j
PF ₆ ⁻	164	110	182	174	164	+18	+10	0	k
SF ₆	156	104	176	168	158	+20	+12	+2	l
GeF ₆ ²⁻	176	122	194	186	176	+18	+10	0	m
AsF ₆ ⁻	175	122	194	186	176	+19	+11	+1	n
SeF ₆	168	116	188	180	170	+19	+11	+2	o

^a r_X = covalent radius of X. ^bDifference between $d_{X-F}(\text{predicted})$ and $d_{X-F}(\text{observed})$. ^c r_F (covalent radius of F) = 72 pm. ^d r_F = 64 pm. ^e r_F = 54 pm. ^fWells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: London, 1984. ^gSutton, L. *Tables of Interatomic Distances*; Chemical Society Special Publications 11 and 18; Royal Society of Chemistry: London. ^hChriste, K. O.; Lund, M. D.; Thorup, N.; Russell, D. R.; Fawcett, J.; Bau, R. *Inorg. Chem.* **1988**, *27*, 2450. ⁱNaray Szabo, S.; Susvari, K. Z. *Kristallogr.* **1938**, *99*, 27. Nohr, R. S.; Kuznesof, P. M.; Wynne, K. J.; Kenney, M. E.; Siebenman, P. G. *J. Am. Chem. Soc.* **1981**, *103*, 4371. ^jKetelaar, J. Z. *Kristallogr.* **1935**, *92*, 155. ^kBode, H.; Teufer, G. *Acta Crystallogr.* **1956**, *9*, 825. ^lKelly, H.; Fink, M. *J. Chem. Phys.* **1982**, *77*, 1813. ^mVincent, W. B.; Hoard, J. L. *J. Am. Chem. Soc.* **1942**, *64*, 1233. Kodashova, T. S. *Krystallografiya* **1957**, *2*, 609. ⁿIbers, J. A. *Acta Crystallogr.* **1956**, *9*, 967. Gafner, G.; Kruger, G. *J. Acta Crystallogr.* **1974**, *B30*, 458. Minkwitz, R.; Bernstein, D.; Bent, H.; Sartore, P. *Inorg. Chem.* **1991**, *30*, 2157. Mootz, D.; Wiebeke, M. *Inorg. Chem.* **1986**, *25*, 3095. ^oBartell, L.; Jin, A. *J. Mol. Struct.* **1984**, *118*, 47. ^pFour electron pairs on the valence shell of N may be crowded.

Jolly,³ in his textbook, suggested a value of 58 pm which, although it gives better agreement with observed bond lengths in a number of cases, has not been widely adopted.

Various explanations have been given to account for the many significant discrepancies between the sum of the covalent radii and observed bond lengths. For example, the Schomaker-Stevenson equation⁴ proposed in 1941 and still widely used applies an empirical correction based on the difference in the electronegativities of the bonded atoms. The equation assumes that polar bonds are shorter than nonpolar bonds, although there seems to be little experimental evidence to support this assumption. Moreover, although the equation often reduces the difference between observed and calculated bond lengths, it rarely eliminates the discrepancy.⁵

The N-N, O-O, and F-F bonds in hydrazine, hydrogen peroxide and fluorine, have unusually small bond enthalpies and are abnormally long, and the lengths and weakness of these bonds have been attributed to inter- and intraatomic interactions between the lone pairs in the valence shells of the nitrogen, oxygen, and fluorine atoms.⁶ Thus for N, O, and F it is inappropriate to take half of their single bond lengths as the standard covalent radii of these elements.

We propose that the most appropriate and useful value for the covalent radius of fluorine, r_F , is 54 pm. By addition to other standard radii,⁷ this radius gives bond lengths for the species in Table I that are within a few percent of their observed bond lengths. Species with X-F bonds that are not included in Table I fall into two obvious classes; they have either long bonds or short bonds.

Long Bonds: Complete Valence Shells with Lone Pairs

Long bonds are due to lone-pair-lone-pair repulsions as we have mentioned above for the F-F, O-O, and N-N bonds. Thus, we also expect most N-F and O-F bonds to be abnormally long (Table II). In general for an XF_n molecule the bonds will be longer than predicted using a covalent radius of 54 pm for fluorine whenever there are one or more lone pairs in a filled valence shell. On the basis of the highest observed coordination numbers, it

Table II. Long X-F Bonds for Species in Which the Central Atom Has a Complete Valence Shell with One or More Lone Pairs

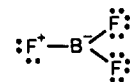
species	$d_{X-F}(\text{obs})$, ^a pm	d_1 , ^b pm	VSC ^c	ref
NF ₃	137.1	124	4	d
OF ₂	140.9	116	4	d
F ₂	143	108	4	2
SF ₅ ⁻	155.9 (ax)	158	4	e
	171.8 (eq)			
ClF ₅	157 (ax)	153	6	e
	167 (eq)	153		
BrF ₅	169.7 (ax)	168	6	e
	176.8 (eq)	168		

^aax = axial bond; eq = equatorial bond. ^bSingle X-F bond length from sum of covalent radii (r_F = 54 pm). ^cVSC = valence shell capacity for electron pairs (octet rule, duodecet rule, etc.). ^dWells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: London, 1984. ^eGillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, MA, 1991.

appears that the maximum number of electron pairs that can occupy a valence shell increases from period 1 to period 5 as follows: period 1, one pair (duet rule); period 2, four pairs (octet rule); periods 3 and 4, six pairs (duodecet rule);⁸ and period 5, more than six pairs and probably eight. Thus in any fluoride in which there are the maximum number of electron pairs on the central atom, of which one or more are lone pairs, the bonds adjacent to the lone pair will be long. An example is BrF₅, where the bonds in the base of the square pyramid have a length of 177 pm while the apical bond has a normal length of 170 pm. Further examples are given in Table II.

Short Bonds: Incomplete Valence Shells without Lone Pairs

In molecules in which the central atom has an incomplete valence shell with less than the maximum number of electron pairs, lone-pair repulsions can be relieved by delocalization of electron density from fluorine into the incomplete valence shell of the central atom, giving rise to partial double bond character and correspondingly bonds shorter than predicted from 54 pm for the covalent radius of fluorine. Some examples are given in Table III. For example, the B-F bond in BF₃ has a length of 131 pm whereas in BF₄⁻ it has a length of 141 pm, which is nearly the predicted B-F single bond distance ($86 \pm 54 = 140$ pm). The short bond in BF₃ can be ascribed to delocalization of the fluorine lone pairs into the incomplete valence shell of boron as expressed by three resonance structures such as



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- (6) Jolly, W. L. *Acc. Chem. Res.* **1983**, *16*, 370.
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Table III. Short X-F Bonds for Species in Which the Central Atom Has an Incomplete Valence Shell and No Lone Pairs

species	$d_{X-F}(\text{obs})^a$, pm	d_1^b , pm	VSC ^c	ref
BF ₃	130.7	140	4	<i>d</i>
Al ₂ F ₆	160 (br)	180	6	<i>e</i>
	172	180		
AlF ₃	163	180	6	<i>f</i>
SiF ₄	155.5	171	6	<i>g</i>
(F ₃ Si) ₂ O	155.6	171	6	<i>h</i>
F ₃ SiOMe	156.1	171	6	<i>i</i>
F ₃ SiNMe ₂	156.1	171	6	<i>j</i>
PF ₅	153.4 (eq)	164	6	<i>k</i>
	157.7 (ax)	164		
F ₃ PO	152.4	164	6	<i>l</i>
(F ₂ PN) ₃	154.8	164	6	<i>m</i>
AsF ₅	165.6 (eq)	176	6	<i>n</i>
	171.1 (ax)	176		
LiSbF ₆	187.7	195	8	<i>o</i>
Cs ₂ [(F ₃ Sb) ₂ O]	187	195	8	<i>p</i>
TeF ₆	181.5	190	8	<i>q</i>
(F ₃ Te) ₂ O	182.0 (eq)	190	8	<i>r</i>
	179.9 (ax)	190		
R ⁺ TeOF ₅ ⁻	185	190	8	<i>s</i>
IF ₇	185.8 (eq)	187	8	<i>t</i>
	178.6 (ax)	187		
IOF ₅	181.7 (eq)	187	8	<i>u</i>
	186.3 (ax)	187		

^abr = bridge bond; eq = equatorial bond; ax = axial bond. ^bSingle X-F bond length from sum of covalent radii ($r_F = 54$ pm). ^cVSC = valence shell capacity for electron pairs (octet rule, duodecet rule, etc.). ^dYamamoto, S.; Kuwabara, R.; Takami, M.; Kuchitsu, K. *J. Mol. Spectrosc.* **1986**, *115*, 333. ^eGillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, MA, 1991; p 105. ^fWells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: London, 1984; p 444. ^gBeagley, B.; Brown, D. P.; Freeman, J. M. *J. Mol. Struct.* **1973**, *18*, 335. ^hAirey, W.; Glidewell, G.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M.; Cruickshank, D. W. J. *Trans. Faraday Soc.* **1970**, *66*, 551. ⁱAirey, W.; Glidewell, G.; Robiette, A. G.; Sheldrick, G. M. *J. Mol. Struct.* **1971**, *8*, 413. ^jAirey, W.; Glidewell, G.; Robiette, A. G.; Sheldrick, G. M.; Freeman, J. M. *J. Mol. Struct.* **1971**, *8*, 423. ^kHansen, K. W.; Bartell, L. *Inorg. Chem.* **1965**, *4*, 1775. ^lMoritani, T.; Kuchitsu, K.; Morino, Y. *Inorg. Chem.* **1971**, *10*, 344. ^mDavis, M. I.; Paul, J. W., Jr. *J. Mol. Struct.* **1971**, *9*, 478. ⁿClippard, F. B., Jr.; Bartell, L. S. *Inorg. Chem.* **1970**, *9*, 805. ^oBurns, J. H. *Acta Crystallogr.* **1962**, *15*, 1098. ^pHaase, W. *Chem. Ber.* **1973**, *106*, 41. ^qGundersen, G.; Hedberg, K.; Strand, T. *G. J. Chem. Phys.* **1978**, *68*, 3548. ^rOberhammer, H.; Seppelt, K. *Inorg. Chem.* **1978**, *17*, 1435. ^sMiller, P. K.; Abney, K. D.; Rappe, A. K.; Anderson, O. P.; Strauss, H. *Inorg. Chem.* **1988**, *27*, 2255. ^tAdams, W. J.; Thompson, H. R.; Bartell, L. *J. Chem. Phys.* **1970**, *53*, 4040. ^uBartell, L. S.; Clippard, F. B.; Jacob, E. J. *Inorg. Chem.* **1976**, *15*, 3009.

corresponding to a bond order of $1\frac{1}{3}$. Similarly, the Si-F bonds in SiF₄ (155 pm) and in (F₃Si)₂O (156 pm) are shorter than that in SiF₆²⁻ which has an observed bond length of 171 pm, equal to the single bond value calculated from $r_F = 54$ pm. The P-F bonds in PF₃ (average 155 pm), and POF₃ (152 pm), are shorter than the predicted single bond length of 164 pm and the observed value of 164 pm in PF₆⁻.

Incomplete Valence Shells with Lone Pairs

Unlike the elements of the second period, the elements of the third and subsequent periods may have unshared pairs in a valence shell that has less than the maximum number of electron pairs for that shell, as for example in PF₃ and BrF. It is a basic assumption of the VSEPR model that a lone pair takes up more space in the valence shell than a bonding pair,⁹ which raises the question of when a valence shell should be considered to be complete and not able to accommodate any more electron pairs, even though the total number of electron pairs is less than capacity of the valence shell for bonded pairs. We have found that it is a useful empirical rule to assume that for period 3 and 4 elements

Table IV. X-F Bonds in Molecules with a Central Atom with an Incomplete Valence Shell Containing One or More Lone Pairs

species	$d_{X-F}(\text{obs})^a$, pm	d_1^b , pm	type ^c	VSC ^d	$\sum \text{ON}^e$	ref
PF ₃	157.0	164	s	6	5	<i>f</i>
SF ₂	159	158	n	6	6	<i>g</i>
SF ₄	154.3 (eq)	158	n	6	6	<i>h</i>
	164.6 (ax)	158	l			
ClF	162.8	153	l	6	7	<i>i</i>
ClF ₂ ⁺	157	153	n	6	6	<i>j</i>
ClF ₃	158 (eq)	153	n	6	7	<i>k</i>
	170 (ax)	153	l			
AsF ₃	170.6	174	s?	6	5	<i>l</i>
SeF ₄	168.2 (eq)	170	n	6	6	<i>m</i>
	177 (ax)	170	l			
BrF	175.6	168	l	6	7	<i>n</i>
BrF ₂ ⁺	169	168	n	6	6	<i>o</i>
BrF ₃	173 (eq)	168	l	6	7	<i>p</i>
	181 (ax)	168	l			
BrF ₄ ⁻	181	168	l	6	8	<i>q</i>
KrF ₂	187	165	l	6	8	<i>l</i>
SbF ₄ ⁻	192 (eq)	194	n	8	7	<i>r</i>
	207 (ax)	194	l			
TeF ₅ ⁻	196 (eq)	190	n	8	8	<i>s</i>
	185 (ax)					
IF ₄ ⁺	177 (eq)	187	s	8	7	<i>r</i>
	184 (ax)	187	n			
IF ₅	187.1 (eq)	187	n	8	8	<i>r</i>
	181.4 (ax)	187	s?			
XeF ₂	197.7	184	l	8	11	<i>r</i>
XeF ₃ ⁺	184 (eq)	184	n	8	9	<i>r</i>
	191 (ax)	184	l			
XeF ₄	194	184	l	8	10	<i>r</i>
XeF ₅ ⁺	184.3 (eq)	184	n	8	8	<i>r</i>
	181 (ax)	184	n			
XeF ₅ ⁻	201	184	l	8	11	<i>s</i>
XeF ₆	189	184	l	8	9	<i>l</i>
XeF ₈ ²⁻	196	184	l	8	11	<i>k</i>
	208	184	l			

^aax = axial bond; eq = equatorial bond. ^bSingle X-F bond length from sum of covalent radii ($r_F = 54$ pm). ^cl = long, n = normal, s = short. ^dVCR = valence shell capacity for electron pairs (octet rule, duodecet rule, etc.). ^e $\sum \text{ON}$ = total occupancy number $x + ny$, where x = number of bond pairs and y = number of lone pairs for a given species, with $n = 2$ for periods 3 and 4 and $n = 3$ for period 5 (see text). ^fMorino, Y.; Kuchitsu, K.; Moritani, T. *Inorg. Chem.* **1969**, *8*, 867. ^gJohnson, D. R.; Powell, F. X. *Science* **1969**, *164*, 950. ^hTolles, M. W.; Gwinn, W. D. *J. Chem. Phys.* **1962**, *36*, 1119. ⁱGilbert, D. A.; Roberts, A.; Griswold, P. A. *Phys. Rev.* **1949**, *75*, 1723. ^jEdwards, A. J.; Christie, K. O. *J. Chem. Soc., Dalton Trans.* **1976**, 175. Bougon, R.; Cicha, W. V.; Lance, M.; Nierlich, M. *Inorg. Chem.* **1991**, *30*, 102. ^kSmith, D. F. *J. Chem. Phys.* **1953**, *21*, 609. ^lWells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: London, 1984. ^mBowater, I. C.; Brown, R. D.; Burden, F. R. *J. Mol. Spectrosc.* **1968**, *28*, 454. ⁿSmith, D. F.; Tidwell, M.; Thomas, D. V. *Phys. Rev.* **1950**, *77*, 420. ^oEdwards, A. J.; Christie, K. O. *J. Chem. Soc., Dalton Trans.* **1976**, 139. ^pMagnusson, D. W. *J. Chem. Phys.* **1957**, *27*, 223. ^qSly, W. O.; Marsh, R. E. *Acta Crystallogr.* **1957**, *10*, 378. ^rGillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, MA, 1991. ^sChristie, K. O.; Curtis, E. C.; Dixon, D. A.; Mercier, H. P.; Saunders, J. C. P.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 3351.

a lone pair has a domain that is approximately twice as large as the domain of a bonding pair, while for a period 5 element it is approximately three times as large. This rule is based on the observations (i) that related S(IV) and S(VI) compounds such as SO₂ and SO₃, and SOF₂ and SO₂F₂, have very similar bond lengths and bond angles¹⁰ and (ii) that XeO₃ has smaller bond angles than XeO₄.¹¹ We therefore give a lone pair an occupancy number of 2 for a period 3 or 4 element and an occupancy number of 3 for a period 5 element and a bonding pair an occupancy number of 1.

If the sum of the occupancy numbers of the electron pairs in a valence shell ($\sum \text{ON}$) is equal to, or greater than, the maximum

(9) Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, MA, 1991; p 48.

(10) Reference 9, p 133.

(11) Reference 9, p 154.

number of electron pairs for that shell (the valence shell capacity, VSC) then the shell is considered to be filled and cannot accept electron density from fluorine atoms to relieve lone-pair-lone-pair repulsions. Instead repulsions between the lone pairs on the central atom and the fluorine lone pairs will produce long bonds. Thus, the observed bond length in PF_3 (157 pm) in which the valence shell of phosphorus (VSC = 6) has three bonding pairs and one lone pair (total occupancy number, $\sum\text{ON} = 5$, <6) is shorter than the calculated value ($110 + 54 = 165$ pm) because the fluorine lone pairs can delocalize into the incomplete valence shell of phosphorus. In contrast in SF_2 ($\sum\text{ON} = 6$) the bond length of 159 pm is close to the calculated value of $104 + 54 = 158$ pm. Similarly in BrF_2^+ ($\sum\text{ON} = 6$) the bonds are of normal length (169 pm), while in BrF ($\sum\text{ON} = 7$, >6) the bond is long (176 pm), as are the basal bonds (177 pm) in BrF_5 ($\sum\text{ON} = 7$). In BrF_4^- ($\sum\text{ON} = 8$) the bonds are still longer (181 pm). Examples are shown in Table IV.

Conclusions

A covalent radius for fluorine of 54 pm gives calculated bond lengths in agreement with experiment for those species in which the bonds are expected to be "normal", that is, in which the central atom has a filled valence shell and no lone pairs. In species in which the central atom has an incomplete valence shell, electron delocalization from fluorine gives short bonds. In species in which there are lone pairs in a filled valence shell on the central atom, lone-pair repulsions give long bonds. In species in which there are lone pairs in an incomplete valence shell, an empirical rule for the effective size of the domain of a lone pair enables us to decide if the capacity of the valence shell is, or is not, exceeded and, therefore, if the bonds are expected to be long, normal, or short.

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A Dinuclear Vanadyl(IV) Complex of 3,5-Dicarboxypyrazole: Synthesis, Crystal Structure, and Electron Spin Resonance Spectra

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Introduction

Our previous work with 3,5-dicarboxypyrazole (H_3Dcp) as a dinucleating ligand has shown that the ligand readily accommodates a number of transition metals ions in square-planar configuration.¹ This report shows that the ligand will also bind VO^{2+} in a dinuclear fashion. The only metal previously reported to chelate with Dcp, which possesses unpaired electrons, is copper. The copper centers, whose unpaired electrons lie in the $d_{x^2-y^2}$ orbital, were found to couple antiferromagnetically ($2J = -200.2$ cm^{-1}) via superexchange through the pyrazole bridge. The vanadyl ion similarly has a single unpaired electron. However, the electronic coupling of the vanadyl ions is through the d_{xy} orbital in the ground state.

There has been some previous work on vanadyl dimers and their electronic interactions.² These dimers show a tendency toward spin exchange when their orbitals are able to interact. Direct d_{xy} - d_{xy} overlap generally results in antiferromagnetic coupling. Their tendency toward superexchange is limited, as the ground-

Table I. Crystal Data and Structure Determination Summary

compd	$(\text{Bu}_4\text{N})_2[(\text{VO})_2(\text{Dcp})_2]$
empirical formula	$\text{C}_{42}\text{H}_{74}\text{N}_6\text{O}_{10}\text{V}_2$
fw	924.97 ₅
cryst color and habit	purple prisms
cryst dimens	$0.15 \times 0.12 \times 0.06$ mm ³
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
Z	2
a	12.809 (6) Å
b	12.515 (8) Å
c	18.050 (8) Å
α	81.32 (4)°
β	91.16 (4)°
γ	118.13 (4)°
V	2518 (2) Å ³
d(calc)	1.220 g cm ⁻³
F(000)	9.98 electrons
linear abs coeff (μ)	4.1 cm ⁻¹
radiation type	Mo K α , $\lambda = 0.71073$ Å, Lp corrected, graphite monochromator
temp	ambient
R^a	0.0837
R_w^b	0.0640

$$^a R = \sum(|F_o| - |F_c|) / \sum|F_o| \quad ^b R_w = [\sum(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

state unpaired electron typically lies in the d_{xy} orbital in a vanadyl complex of C_{4v} symmetry. However, other mechanisms for exchange exist and several vanadyl dimers have shown weakly coupled exchange to give a low-lying triplet state, as evidenced by ESR spectroscopy.³

The best characterized of these triplets are the vanadyl tartrates, most notably the sodium salt of vanadyl(IV) *d,l*-tartrate.^{3a} The vanadyl *d,l*-tartrate forms a bis chelate containing two vanadyl ions in an anionic complex, similar to our system. The vanadyl *d,l*-tartrate anion also crystallizes in a roughly coplanar fashion with a metal-metal distance of 4.082 Å.⁴ The main difference lies in the lower symmetry of the tartrates and the relative arrangement of the vanadyl oxygen atoms. Relative to the vanadium-vanadium vector, they are trans in the tartrates while they are cis in our complex.

Experimental Section

$(\text{Bu}_4\text{N})_2[(\text{VO})_2(\text{Dcp})_2]$ was prepared by dissolving 3,5-dicarboxypyrazole hydrate (0.250 g, 1.44 mmol) in 25 mL of hot water. To this was added a solution of vanadyl sulfate hydrate (0.235 g, 1.44 mmol) in 5 mL of water. Addition of a 4.3-mL aliquot of tetrabutylammonium hydroxide (1 M in MeOH) caused the solution to turn purple. Evaporation to dryness and trituration of the residue with *tert*-butyl alcohol followed by filtration gave the purple crystalline complex. Recrystallization is done by dissolving the complex in acetone and layering it with *tert*-butyl alcohol. Yield: 0.4667 g (70%). IR (KBr pellet): $\nu(\text{COO})$ 1681 cm^{-1} , $\nu(\text{VO})$ 1012 cm^{-1} . Anal. Calc for $\text{C}_{42}\text{H}_{74}\text{N}_6\text{O}_{10}\text{V}_2$: C, 54.54; H, 8.06; N, 9.09. Found: C, 54.77; H, 7.91; N, 8.97. Mp: 256–258 °C.

Physical Measurements. UV-visible spectroscopy was performed on a Shimadzu UV-160 spectrophotometer. Cyclic voltammetry was performed on a Princeton Applied Research (PAR) potentiostat/galvanostat, Model 173, a PAR universal programmer, Model 175, and a PAR digital coulometer, Model 179. Working and reference electrodes were platinum wire with a silver wire counter electrode. ESR spectroscopy was performed on a Bruker ER 200E-SRC spectrometer equipped with a low-temperature cavity and controller. X-ray diffraction data were gathered on a Syntex P2, diffractometer. The structure solutions were routine with procedures previously described.⁵ The parameters used

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