from DNA, but there are differences in the reaction properties and product ratios. The similar reactivity of peroxide with Mn(II)- and Fe(III)-bleomycin is also seen with the mechanistically similar enzyme cytochrome P-450,[6] which has been prepared with Mn(II) substituted for Fe(III). The Mn(II)-substituted protein is active, but with altered substrate specificity and kinetic properties. Mn(II)-substituted cytochrome P-450, while active with peroxide, is no longer active with O$_2$, just like Mn(II)-bleomycin. Both the coordination of iron ligands[7,19] and activation pathways for cytochrome P-450[20] and bleomycin[3] are quite similar, notwithstanding bleomycin's lack of either a thiol or an aromatic macrocyclic moiety, like a porphyrin.[1] Activated bleomycin appears to initially execute a 4′-deoxyribose hydrogen abstraction,[21] such as cytochrome P-450 does with other substrates.[20] Since there is spectral evidence that a monooxygenated species of Mn(II)-substituted cytochrome P-450 may be relatively long-lived,[6] we are hopeful that an analogous oxygen complex, if produced, may be evident with Mn(II)-bleomycin as well. The form of oxygen ligated by Mn(II)-bleomycin, however, need not be the same as that bound to Fe(III)-bleomycin.

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(19) Burger, R. M.; Kent, T. A.; Horwitz, S. B.; Münck, E.; Peisach, J. *J. Biol. Chem.* **1983**, *258*, 1559-1564.
(20) White, R. E.; Coon, M. J. *Annu. Rev. Biochem.* **1980**, *49*, 315-356.
(21) Wu, J. C.; Kozarich, J. W.; Stubbe, J. A. *J. Biol. Chem.* **1983**, *258*, 4694-4697.

Articles

Contribution from the Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, 1000 Berlin 33, West Germany, and Department of Chemistry, Clemson University, Clemson, South Carolina 29631

Pentafluoroselenium Isocyanate and Pentafluorotellurium Isocyanate, F$_5$Se—N=C=O and F$_5$Te—N=C=O

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The previously unknown F$_5$Se—N=C=O is prepared from Xe(OSeF$_5$)$_2$ and HCN; F$_5$Te—N=C=O can be prepared similarly but also by more straightforward routes.[2] Compared with that of F$_5$S—N=C=O, the isocyanate reactivity is reduced in F$_5$Te—N=C=O and even more so in F$_5$Se—N=C=O.

Introduction

F$_5$S—N=C=O has been known for many years.[3,4] It exhibits a chemistry of a typical isocyanate, so it adds to protic substrates to form urethanes or to carbonyls to form azomethines.[5] Quite in contrast to this, the tellurium-nitrogen chemistry of this type was rather underdeveloped and the selenium-nitrogen chemistry was nonexistent. TeF$_5$—N=C=O has recently been prepared from F$_5$Te—NH—Si(CH$_3$)$_3$;[2] the latter, from TeF$_6$.[6] Since SeF$_6$ does not undergo any controlled substitution reactions, no direct key for the preparation of F$_5$SeN< systems was available. We thus prepared F$_5$Se—N=C=O from Xe(OSeF$_5$)$_5$ and HCN. This reaction was suggested by an earlier reaction of Xe(OTeF$_5$)$_2$ with HCN, which resulted in TeF$_5$NCO, in an attempt to prepare a xenon-carbon bond. As discussion will show, it was not at all clear from the beginning that we obtained an isocyanate rather than a cyanate. This problem has now been solved by an electron-diffraction study of F$_5$S—N=C=O, F$_5$Se—N=C=O, and F$_5$Te—N=C=O, which proved all materials to be isocyanates.[7]

Experimental Section

General Data. ^{1}H and ^{19}F NMR spectra were recorded on a Varian EM 360 instrument. IR spectra were taken on a Beckman IR 12; Raman spectra, on a Cary 82 with Ar-laser excitation. Mass spectra were recorded on a Varian MAT CH 5 or Varian MAT 711. Moisture-sensitive materials were handled in a Braun glovebox with a water level of about 1 ppm.

Reagents. Xe(OTeF$_5$)$_2$, Hg(OSeF$_5$)$_2$, Hg(OTeF$_5$)$_2$,[8] and XeF$_2$[10] were prepared by literature methods. SeOF$_2$ was obtained from SeO$_2$ and SF$_4$.[9]

Xenon Bis(pentafluoroselenate), Xe(OSeF$_5$)$_2$.[8] In the glovebox, a 100-mL stainless-steel vessel was filled with 30 g of XeF$_2$. An open Teflon-FEP tube containing 16 g of SeOF$_2$ was then placed carefully upright in the stainless steel vessel on top of the XeF$_2$. The vessel was closed and cooled to −30 °C for 1 h. Then the vessel was shaken for 2 days at room temperature. The gas contents of the vessel were mainly xenon, which is blown out, purified by washing and drying, and used again for the preparation of XeF$_2$.

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(2) Hartl, H.; Huppman, P.; Lentz, D.; Seppelt, K. *Inorg. Chem.* **1983**, *22*, 2183.
(3) Tullock, W. C.; Coffman, D. D.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 357.
(4) Duncan, L. C.; Rhyne, T. C.; Clifford, A. F.; Shaddix, R. E.; Thompson, J. W. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 133.
(5) (a) Thrasher, J.; Howell, J. L; Clifford, A. F. *J. Fluorine Chem.* **1984**, *24*, 431. (b) Thrasher, J. S.; Howell, J. L.; Clifford, A. F. *Inorg. Chem.* **1982**, *21*, 1616. (c) Thrasher, J. S. Ph.D. Dissertation, Virginia Polytechnic Institute and State University, 1981. (d) Howell, J. L. Ph.D. Dissertation, Virginia Polytechnic Institute and State University, 1978.
(6) Seppelt, K. *Inorg. Chem.* **1973**, *12*, 2837.
(7) Oberhammer, H.; Seppelt, K.; Mews, R. *J. Mol. Struct.* **1983**, *101*, 325.
(8) Seppelt, K.; Nothe, D. *Inorg. Chem.* **1973**, *12*, 2727.
(9) Lentz, D.; Seppelt, K. *Inorg. Synth.*, in press.
(10) Malm, J. G.; Selig, H.; Jortner, J.; Rice, S. A. *Chem. Rev.* **1965**, *65*, 199.

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The remaining solid in the vessel was impure $Xe(OSeF_5)_2$ contaminated with some $SeOF_2$. The solid sublimed at 10^{-2} mbar onto a 0 °C cold finger; yield 20.3 g of $Xe(OSeF_5)_2$, 67.2%.

Pentafluoroselenium Isocyanate, $F_5Se{-}N{=}C{=}O$. *Caution*! $F_5Se{-}N{=}C{=}O$ has exploded several times, especially if pure.

In the glovebox, 7 g of $Xe(OSeF_5)_2$ was added to a 100-mL stainless-steel vessel; 0.8 g of HCN was then condensed onto it by vacuum transfer after first cooling the reactor to −196 °C and evacuating it. The reactor was held overnight at −6 to −8 °C. The contents of the vessel were than pumped through −110 and −196 °C traps.

The −110 °C trap contained impure $F_5Se{-}N{=}C{=}O$, which was condensed on dry, powdered KF to bind $HOSeF_5$. After this, the volatile materials were condensed on 4-Å molecular sieves, that previously had been dried under high vacuum at 250 °C. The molecular sieve/product mixture was held overnight at −6 °C. Then all volatiles were quickly pumped through −110 and −196 °C traps. The −110 °C trap contained almost pure $F_5Se{-}N{=}C{=}O$, with only a little HCN impurity; yield 1.4 g, 47%. A second reaction with molecular sieves gave an HCN-free product, but only with considerable loss of the isocyanate.

Mp: −79 °C. Bp: +39 °C. IR (gas): 2290 (m), 1104 (s), 788 (vs), 767 (s), 729 (w), 661 (w), 491 (w, sh), 470 (s), 429 (s) cm^{-1}. Raman (liquid): 2262 (s), 1095 (m), 770 (w), 743 (w), 673 (vs), 650 (vs), 516 (w), 457 (s), 412 (m), 364 (m), 254 (m), 147 (w, sh), 139 (m) cm^{-1}. Mass spectrum (70 eV): m/z 217 (M^+), 175 (SeF_5^+), 137 (SeF_3^+), 99 (SeF^+), 42 (NCO^+); a very small peak at m/z 237 indicating $F_5Se{-}NH{-}COF^+$. The mass numbers are given for ^{80}Se. ^{19}F NMR (AB_4 pattern): δ_A 53.9, δ_B 83.3 ppm; $J_{AB} = 222.4$ Hz, $J_{^{77}Se-A} = 1417$ Hz, $J_{^{77}Se-B} = 1429$ Hz.

Anal. Calcd for CNF_5SeO: C, 5.55; N, 4.99; F, 43.99; Se, 36.56. Found: C, 5.55; N, 6.08; F, 42.90; Se, 35.44.

Preparation of TeF_5NCO. Method A. $TeF_5{-}NH{-}Si(CH_3)_3$ was reacted with COF_2 according to ref 2. This is by far the best method, except for the difficult separation of $(CH_3)_3SiF$ and $TeF_5{-}N{=}C{=}O$.

Method B. The mercurial $Hg(OTeF_5)_2$ (17.4 g, 25.7 mmol) was loaded into a 200-mL stainless-steel cylinder in the inert-atmosphere box. The vessel was then degassed and frozen to −196 °C before condensing in ClCN (3.07 g, 50.0 mmol). The reaction mixture was allowed to warm slowly overnight to room temperature from −78 °C. After 10 days the volatile products were distilled under vacuum through −105 and −196 °C traps. The −105 °C trap held the product TeF_5NCO (12.21 g) in 92% yield, while the −196 °C trap contained a small quantity of both CO_2 and TeF_5NCO. The infrared and NMR spectra of the TeF_5NCO produced by these methods were identical with those previously reported.[2] Mass spectral data not initially reported (80 eV): m/z 267 (M^+, 49%), 260 (Te_2^+, 3%), 248 ($M - F^+$, 71%), 225 (TeF_5^+, 48%), 206 (TeF_4^+, 3%), 187 (TeF_3^+, 100%), 168 (TeF_2^+, 21%), 149 (TeF^+, 15%), 130 (Te^+, 12%). The mass numbers are given for ^{130}Te; the intensities include all isotopes.

Method C. $Xe(OTeF_5)_2$ (1.15 g, 1.9 mmol) was added to a 20-mL FEP reactor in the inert-atmosphere box. The vessel was then cooled to −196 °C and evacuated. Hydrogen cyanide (1.9 mmol) was then added by vacuum transfer. The mixture was warmed to 0 °C, where the reaction formed a yellow solution that slowly evolved xenon. After 3 days, the reactor was cooled to −196 °C and a small amount of noncondensible gas was pumped away. Xenon (1.8 mmol) was then removed at −114 °C and shown to be essentially pure by the lack of an infrared spectrum. The material remaining in the reactor was then removed at 0 °C, and the infrared spectra showed it to be a mixture of $HOTeF_5$ and TeF_5NCO with a small amount of TeF_6 and HCN. The total amount of volatiles removed at 0 °C corresponded to 3.8 mmol. No attempt was made to separate the latter mixture, and it was assumed to be essentially a 1:1 mixture of $HOTeF_5$ and TeF_5NCO.

Preparation of $TeF_5NHC(O)CH_3$. The isocyanate TeF_5NCO (1.13 g, 4.3 mmol) was condensed onto freshly distilled CH_3COOH (0.24 g, 4.0 mmol) in a 300-mL glass reaction cylinder. The mixture was warmed to room temperature and allowed to stand for 1 week with stirring at that temperature. At this time the volatile products, consisting primarily of CO_2, unreacted TeF_5NCO, and some SiF_4, were removed. The resulting solid residue was sublimed under vacuum at 50 °C to yield $TeF_5NHC(O)CH_3$ (0.79 g, 2.8 mmol) in 70% yield.

Mp: 102–102.5 °C. IR (mull): 3030 (m, b), 2840 (m, b), 2685 (w, b), 1703 (s, b), ν_{CONH}), 1455 (m, b, δ_{NH}), 1235 (s, δ_{CH}), 1047 (w), 1005 (m), 960 (w, sh), 947 (w), 772 (m, sh), 710 (vs, b, ν_{TeF}), 648 (m), 583 (m) cm^{-1}. Raman (solid): 3035 (11), 3000 (10), 2939 (38), 2823 (4), 1711 (5, sh), 1678 (24), 999 (6), 958 (12), 766 (9), 691 (86), 642 (100), 574 (32), 355 (13), 337 (10), 323 (7), 303 (21), 265 (7), 255 (7), 200 (2), 140 (6), 124 (8) cm^{-1}. Mass spectrum (70 eV): m/z 283 (M^+, 3%), 268 ($M - CH_3^+$, 9%), 264 ($M - F^+$, 2%), 263 ($M - HF^+$, 4%), 260 (Te_2^+, 8%), 248 (TeF_4NCO^+, 22%), 225 (TeF_5^+, 17%), 206 (TeF_4^+, 4%), 187 (TeF_3^+, 100%), 168 (TeF_2^+, 26%), 149 (TeF^+, 11%), 130 (Te^+, 7%), 57 ($CH_3C(O)N^+$, 11%), 56 ($CH_2C(O)N^+$, 6%), 43 (CH_3CO^+, $NHCO^+$, 38%), 42 (CH_2CO^+, NCO^+, 4%). The mass numbers are given for ^{130}Te; the intensities include all isotopes. ^1H NMR (acetone-d_6): δ 8.23 (b s, NH), 1.73 (s, CH_3). ^{19}F NMR (AB_4 pattern, acetone-d_6): δ_A −36.1, δ_B −41.5; $J_{AB} = 173.1$ Hz, $J_{^{125}Te-B} = 3595$ Hz.

Anal. Calcd for $C_2H_4NTeF_5O$: C, 8.55; H, 1.43; N, 4.99; Te, 45.47; F, 33.86. Found: C, 8.84; H, 1.54; N, 5.08; Te, 45.31; F, 33.6.

Preparation of $TeF_5N{=}C(Cl)CH_3$. The amide $TeF_5NHC(O)CH_3$ (0.25 g, 0.89 mmol) and PCl_5 (0.41 g, 2.0 mmol) were placed into a 300-mL glass reaction cylinder in an inert-atmosphere box. Carbon tetrachloride (~3 mL) was added to the reaction cylinder, which was then chilled to −196 °C and degassed. The reaction mixture was then warmed to room temperature and allowed to stand at that temperature with stirring for 48 h. Repeated trap-to-trap distillations and placement on $AlCl_3$ to remove any remaining $POCl_3$ yielded $TeF_5N{=}C(Cl)CH_3$ (0.23 mmol, 26% yield), a colorless liquid with ~2–3 torr vapor pressure at room temperature.

IR (gas): 1650 (s, $\nu_{N=C}$), 1137 (w), 720 (s, ν_{TeF}), 700 (w, sh) cm^{-1}. Mass spectrum (80 eV): m/z 286 ($M - CH_3^+$, 4%), 266 ($M - Cl^+$, 88%), 241 (TeF_4Cl^+, 6%), 228 ($TeF_3NCCH_3^+$, 4%), 225 (TeF_5^+, 100%), 206 (TeF_4^+, 2%), 187 (TeF_3^+, 63%), 168 (TeF_2^+, 26%), 149 (TeF, 15%), 130 (Te^+, 11%), 76 ($NCClCH_3^+$, 41%), 41 ($NCCH_3^+$, 32%), 40 ($NCCH_2^+$, 32%). The mass numbers are given for ^{130}Te and ^{35}Cl; the intensities include all isotopes. ^1H NMR: δ 3.03 (s, CH_3). ^{19}F NMR (AB_4 pattern): δ_A −39.7, δ_B −47.3; $J_{AB} = 169.3$ Hz, $J_{^{125}Te-A} = 3265$ Hz, $J_{^{125}Te-B} = 4045$ Hz.

Anal. Calcd for $C_2H_3NTeF_5Cl$: C, 8.03; H, 1.00; N, 4.68. Found: C, 8.22; H, 1.05; N, 4.70.

Preparation of $TeF_5N{=}C(H)(CH_3)_2$. Freshly distilled *N*,*N*-dimethylformamide (4.1 mmol) was transferred to a 100-mL glass reaction cylinder, frozen to −196 °C, and degassed prior to the addition of TeF_5NCO (1.23 g, 4.65 mmol). The resulting mixture was warmed to room temperature and allowed to react for 10 days. The volatile products, consisting primarily of CO_2 and unreacted TeF_5NCO, were then removed under dynamic vacuum. The remaining residue was washed with CH_2Cl_2 and filtered through a frit under vacuum to yield 0.41 g of a pale yellow oil. Further attempts to purify the product by either distillation or column chromatography were unsuccessful.

IR (capillary film): 2980 (w), 2940 (w), 1650 (vs, $\nu_{N=C}$), 1420 (m), 1350 (m), 1235 (w), 1130 (m), 1060 (w), 953 (m), 787 (m), 675 (vs, ν_{TeF}) cm^{-1}. Mass spectrum (80 eV): m/z 296 (M^+, 5%), 277 ($M - F^+$, 2%), 260 (Te_2^+, 23%), 225 (TeF_5^+, 3%), 187 (TeF_3^+, 13%), 168 (TeF_2^+, 5%), 149 (TeF^+, 2%), 130 (Te^+, 5%), 71 ($M - TeF_5^+$, 42%), 70 ($NCN(CH_3)_2^+$, 8%), 69 ($NCN(CH_3)CH_2^+$, 16%), 44 ($N(CH_3)_2^+$, 100%), 43 ($N(CH_3)CH_2^+$, 12%), 42 ($NC_2H_4^+$, 28%). The mass numbers are given for ^{130}Te; the intensities include all isotopes. ^1H NMR (acetone): δ 8.12 (s, N=CH), 3.03 and 2.96 (s, NCH_3). ^{19}F NMR (AB_4 pattern, acetone): δ_A −26.3, δ_B −31.1; $J_{AB} = 177.2$ Hz, $J_{^{125}Te-B} = 3613$ Hz, $J_{^{123}Te-B} = 3030$ Hz.

Preparation of $TeF_5N{=}C(H)C_6H_5$. Benzaldehyde and TeF_5NCO were reacted in the same manner as in the preceding reaction. Again all attempts to purify the straw-colored oil resulted only in further decomposition. Mass spectral analysis gave a strong ion cluster for Te_2^+, probably resulting from thermal degradation. Infrared and NMR spectra also gave evidence for $TeF_5N{=}C(H)C_6H_5$. IR (capillary film): 1640 (s, b, $\nu_{N=C}$), 680 (vs, b, ν_{TeF}) cm^{-1}. ^1H NMR (CH_2Cl_2): δ 8.3–7.5 (b m, C_6H_5 and N=CH). ^{19}F NMR (AB_4 pattern, acetone): δ_A −25.2, δ_B −30.1; $J_{AB} = 177.1$ Hz, $J_{^{125}Te-A} = 3630$ Hz, $J_{^{123}Te-B} = 3030$ Hz.

Results and Discussion

A method for the synthesis of SeF_5NCO was first suggested by the reaction of $Xe(OTeF_5)_2$ with HCN. The latter reaction was run in an attempt to prepare a xenon–carbon bond.

$$Xe(OTeF_5)_2 + HCN \rightarrow [F_5TeOXeCN] + HOTeF_5$$

$$[F_5TeOXeCN] \rightarrow Xe + [F_5TeOCN] \rightarrow F_5TeNCO$$

No direct evidence could be found for the suggested inter-

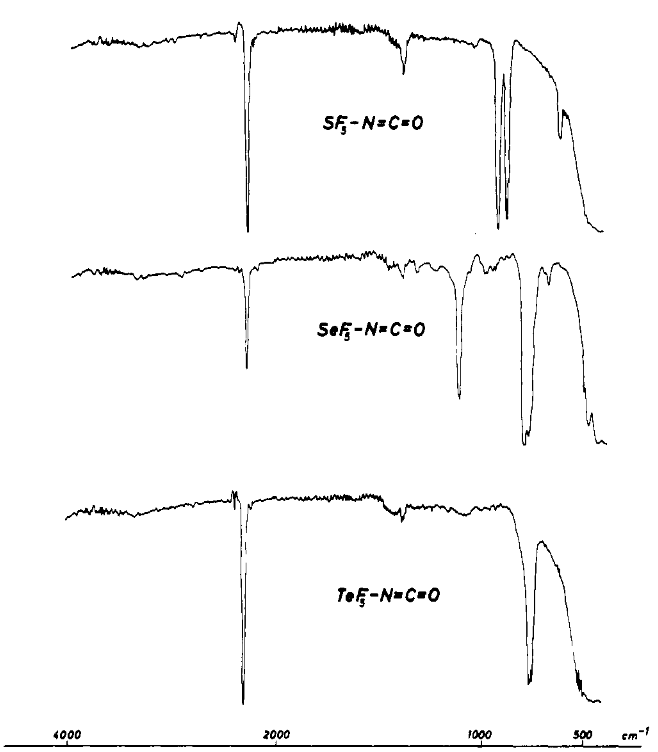

Figure 1. IR gas spectra of $F_5S-N=C=O$, $F_5Se-N=C=O$, and $F_5Te-N=C=O$, from top to bottom. Note that $\nu_{as,N=C=O}$ (2295, 2275 cm^{-1}, respectively) is strong in the sulfur and tellurium compounds, but rather weak in the selenium compound (2290 cm^{-1}). The absorptions at 1380, 1104, and 1365 cm^{-1}, respectively, are assigned to $\nu_{s,N=C=O}$. In $F_5Se-N=C=O$ this band is extremely strong. If it were not shown otherwise by the electron diffraction method, the IR spectra alone would suggest the material to be $F_5Se-O-C\equiv N$. All spectra are taken in 10-cm gas cells with KCl windows at a pressure of 3 mbar.

mediates, but the formation of F_5TeNCO would be an expected product of the decomposition of the intermediate xenon cyanide and of the isomerization of the cyanate. Divalent xenon compounds are known to lose xenon, forming the ligand dimer, e.g. $Xe(OSO_2F)_2 \rightarrow Xe + FSO_2OOSO_2F$.[11]

Application of the above reaction of HCN to $Xe(OSeF_5)_2$ followed a similar path resulting in the first synthesis of F_5SeNCO. As with $Xe(OTeF_5)_2$, no direct evidence could be found for the intermediacy of $[F_5SeOXeCN]$.

At the beginning of this work it was not clear whether $F_5Se-O-C\equiv N$ or $F_5Se-N=C=O$ is formed. As compared with $F_5S-N=C=O$ and $F_5Te-N=C=O$, $F_5Se-N=C=O$ showed a rather weak and sharp IR absorption at 2290 cm^{-1} and a strong one at 1104 cm^{-1}; see also Figure 1. These bands might readily be assigned to $\nu_{C\equiv N}$ and ν_{O-C} of $F_5Se-O-C\equiv N$, instead of $\nu_{as,\ N=C=O}$ and $\nu_{s,N=C=O}$ of $F_5Se-N=C=O$. Only electron diffraction of all three materials, $F_5S-N=C=O$, $F_5Se-N=C=O$, and $F_5Te-N=C=O$, proved unequivocally the isocyanate character of the selenium material.[7] The main difference is a rather small angle Se-N-C (116.9°), which is about 10° smaller than in $F_5S-N=C=O$ and $F_5Te-N=C=O$.[7] The connection between this angle and the unusual IR intensities is not yet fully understood. The formation of $F_5Se-N=C=O$ must include a step of cyanate–isocyanate isomerization. If so, the same is true for the corresponding reaction between $Xe(OTeF_5)_2$ and HCN, which also gives $F_5Te-N=C=O$. The nature of $F_5Te-N=C=O$ was not in doubt since the material was identical with the isocyanate prepared from $F_5Te-NH-Si(CH_3)_3$ and COF_2.[2] A cyanate–isocyanate isomerization is also observed if $Hg(OTeF_5)_2$ is reacted with cyanogen chloride.

$$Hg(OTeF_5)_2 + 2ClC\equiv N \rightarrow$$
$$HgCl_2 + 2[F_5TeO-C\equiv N] \rightarrow 2F_5Te-N=C=O$$

Again only the isocyanate is found. It is interesting to note that we could achieve no reaction between $Hg(OSeF_5)_2$ and ClCN. Therefore, the exotic reaction between $Xe(OSeF_5)_2$ and HCN remains the only way so far to prepare the F_5Se-N< configuration.

$F_5Se-N=C=O$ differs not only spectroscopically but also chemically from its sulfur and tellurium counterparts. First of all, it is explosive, especially if pure. Amounts of 0.5 g have caused considerable damage. Nothing like this has been observed with $F_5S-N=C=O$ or $F_5Te-N=C=O$.

$F_5S-N=C=O$ has been shown to undergo some typical isocyanate reactions.[5] Some of them have been tried here with $F_5Te-N=C=O$:

$$F_5Te-N=C=O + CH_3COOH \xrightarrow{-CO_2}$$
$$F_5Te-NH-CO-CH_3 \xrightarrow[-POCl_3,\ -HCl]{PCl_5}$$
$$F_5Te-N=CCl-CH_3$$

$$F_5Te-N=C=O + (CH_3)_2N-CHO \xrightarrow{-CO_2}$$
$$F_5Te-N=CH-N(CH_3)_2$$

$$F_5Te-N=C=O + C_6H_5-CHO \xrightarrow{-CO_2}$$
$$F_5Te-N=CH-C_6H_5$$

All these reactions are much slower than the corresponding reactions with $F_5S-N=C=O$, and the yields are much lower, even after prolonged reaction times.

The reaction of $TeF_5-N=C=O$ with C_2H_5-CHO, $CH_3COCH_2COCH_3$, C_6H_5SH, and PCl_5, respectively, did not lead to the expected products. With the organic materials reduction to elemental tellurium was observed.

None of the above mentioned reactions has been found to work with $F_5Se-N=C=O$; in general, reduction to elemental selenium is observed. Thus $F_5Se-N=C=O$, although having an isocyanate structure, is chemically the least isocyanate-like in its reactions. Only one reaction has been found during mass spectroscopy: it adds HF to form F_5Se-NH-COF. This new compound, however, has not been isolated macroscopically.

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Registry No. $F_5Se-N=C=O$, 88088-28-2; TeF_5NCO, 86024-46-6; $Xe(OSeF_5)_2$, 38344-58-0; HCN, 74-90-8; $Hg(OTeF_5)_2$, 87622-52-4; ClCN, 506-77-4; $Xe(OTeF_5)_2$, 25005-56-5; $TeF_5NHC(O)CH_3$, 89959-57-9; CH_3COOH, 64-19-7; $TeF_5N=C(Cl)CH_3$, 89959-58-0; $TeF_5N=C(H)N(CH_3)_2$, 89959-59-1; $(CH_3)_2N-CHO$, 68-12-2; $TeF_5N=C(H)C_6H_5$, 89959-60-4; C_6H_5-CHO, 100-52-7.

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(11) Bartlett, N.; Sladky, F. "Comprehensive Inorganic Chemistry; Pergamon Press: Oxford; p 272.