cations and low surface areas are expected. However, at a loading of 33 mmol/100 g a N_2 BET surface area of approximately 180 m^2/g is expected, provided the clusters are uniformly distributed through the interlayers. Thus, the observed value of 58 m^2/g is only about one-third the value expected on the basis of cluster loading and size. This suggests that the clusters may tend to concentrate near the edges of certain interlayers and restrict access to those interlayers. Spatial redistribution of cluster cations within an interlayer can also lead to interstratification of collapsed and stuffed interlayers. Some degree of interstratification is suggested, in fact, by the asymmetry of the 001 and 002 X-ray reflections in Figure 3B. Nonuniformity in the cluster cation distribution, of course, will also result in interstratification and decreased surface areas for the thermolysis products containing metal oxide pillars.

Conclusion

This work demonstrates for the first time that metal cluster cations can be intercalated by an ion-exchange mechanism in a typical smectite clay and oxidized in situ to metal oxide aggregates that function as molecular size pillars. The intercalation chemistry for the particular niobium and tantalum clusters selected for study is complicated in part by hydrolysis, air oxidation, cluster migration, and nonuniform cluster distributions. Nevertheless, the synthetic approach may prove to be generally useful for the preparation of clays pillared by metal oxides that do not have stable polyoxycation precursors in aqueous solution.

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Pentafluoroselenium Cyanate, $F_5Se-O-C\equiv N$

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The previously described pentafluoroselenium isocyanate, $F_5Se-N=C=O$, has been demonstrated to be $F_5Se-O-C\equiv N$, according to electron diffraction, ^{77}Se and $^{14,15}N$ NMR, and vibrational spectroscopy. The other possible isomers, the nitrile oxide, $F_5Se-C\equiv N-O$, and the fulminate, $F_5Se-O-N\equiv C$, are excluded by means of geometrical and chemical reasons, respectively.

Introduction

Pentafluorosulfur isocyanate, $F_5S-N=C=O$,[1] and its tellurium analogue, $F_5Te-N=C=O$,[2] are best prepared from the corresponding amines F_5SNH_2 and F_5TeNH_2[4] and carbonyl halides. So, there was never any doubt about their isocyanate structure, and a recent electron diffraction work gave practically identical geometric parameters for the isocyanate parts in both molecules.[5] See also Table I.

F_5SeNH_2 does not exist. For the preparation of $F_5Se-N=C=O$ two reactions were tried that worked successfully in the preparation of $F_5Te-N=C=O$,[6] namely

$$Hg(OTeF_5)_2 + 2ClCN \rightarrow HgCl_2 + F_5Te-N=C=O$$

$$Xe(OTeF_5)_2 + HCN \rightarrow Xe + HOTeF_5 + F_5Te-N=C=O$$

Only the second reaction was successful in the case of the selenium system. The resulting material had the expected melting point, boiling point, mass spectrum, and IR absorption band at 2290 cm^{-1}, so we assumed that $F_5Se-N=C=O$ had been prepared. The electron diffraction structure on this material resulted in reasonable NC and CO distances. The SeNC angle, however, turned out to be almost 10° smaller than the corresponding angle in F_5SNCO and F_5TeNCO (Table I).

There were other doubts about the isocyanate nature of the novel material. There is a strong IR absorption at 1104 cm^{-1}, which was assigned to $\nu_s(N=C=O)$, but in $F_5S-N=C=O$ and $F_5Te-N=C=O$ this is very weak, as expected. Also, the selenium material was the only one that was exploive when pure. And despite many attempts, not a single chemical reaction occurred that was typical of an isocyanate.[6] With F_5SNCO and F_5TeNCO such reactions could well be performed.[6,7] In light of these results, we reviewed the electron diffraction and IR data and also measured ^{125}Te, ^{77}Se, ^{33}S, ^{14}N, and ^{15}N NMR spectra of these three materials.

Experimental Section

Pentafluorosulfur isocyanate and pentafluorotellurium isocyanate were prepared according to literature methods[1,2] from F_5SNH_2 and F_5TeNH_2. Pentafluoroselenium cyanate was prepared from $Xe(OSeF_5)_2$ and HCN, as described in ref 6. The electron diffraction data of Oberhammer et al.[5] were used in this analysis.

NMR spectra were taken on a JEOL FX90Q instrument equipped with a multinuclear probehead and operated at a frequency of 89.55 MHz for protons. Experimental conditions (10-mm sample diameter): ^{19}F, 84.25 MHz, 29-μs pulse width for a 90° pulse, 1–10 scans, no delay time between pulses on top of the acquisition time; ^{125}Te, 18.25 MHz, 36-μs pulse width, 1000–10000 scans, no further pulse delay, as above; ^{77}Se, 17.03 MHz, 17-μs pulse width, 10 000–20 000 scans, no further pulse delay, as above; ^{33}S, 6.83 MHz, 20-μs pulse, 100 000 scans, no further pulse delay; ^{15}N, 9.03 MHz, 26-μs pulse width, 1000scans, 100-s pulse delay; ^{14}N, 6.43 MHz, 37-μs pulse width, 2000 scans, no further delay.

The chemical shifts were measured externally against the standards $C^{19}FCl_3$ (neat), $^{125}Te(OH)_6/H_2O$, $^{77}SeOCl_2$ (neat), $(NH_4^+)_2{}^{33}SO_4^{2-}/H_2O$, and $^{14,15}NH_4^{+14,15}NO_3^-/H_2O$.

Results and Discussion

For a complete survey we took all possible isomers F_5SeXYZ into consideration: $F_5Se-N=C=O$, the isocyanate; F_5,Se—O—C≡N, the cyanate; $F_5Se-O-N\equiv C$, the fulminate; $F_5Se-C\equiv N-O$, the nitrile oxide.

The original electron diffraction data were used to determine the skeletal geometric parameters for all four isomers.[5] The details

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(1) Duncan, L. C.; Rhyne, T. C.; Clifford, A. F.; Shaddix, R. E.; Thompson, J. W. *J. Inorg. Nucl. Chem. Suppl.* **1967**, 33.
(2) Hartl, H.; Huppmann, P.; Lentz, D.; Seppelt, K. *Inorg. Chem.* **1983**, *22*, 2183.
(3) Clifford, A. F.; Duncan, L. C. *Inorg. Chem.* **1966**, *5*, 692.
(4) Seppelt, K. *Inorg. Chem.* **1973**, *12*, 2837.
(5) Oberhammer, H.; Seppelt, K.; Mews, R. *J. Mol. Struct.* **1983**, *101*, 325.
(6) Huppmann, P.; Klöter, G.; Thrasher, J. S.; Seppelt, K.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 2217.
(7) Thrasher, J. S.; Howell, J. L.; Clifford, A. F. *Inorg. Chem.* **1982**, *21*, 1616.

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Table I. Structural Models for SeF_5XYZ Consistent with Electron Diffraction Data as Compared with the Distances and Angles in SF_5NCO and TeF_5NCO

	SeX, Å	XY, Å	YZ, Å	SeXY, deg	XYZ, deg	R^a
SeF_5NCO	1.789 (6)	1.260 (11)	1.187 (9)	116.9 (0.8)	173 (4)	6.29
SeF_5OCN	1.794 (6)	1.257 (10)	1.181 (10)	116.8 (0.8)	172 (3)	6.44
SeF_5ONC	1.793 (6)	1.258 (9)	1.175 (10)	116.5 (0.7)	171 (4)	6.50
SeF_5CNO	1.793 (7)	1.270 (11)	1.184 (10)	115.6 (0.9)	172 (3)	6.39
SF_5NCO^b	1.668 (6)	1.234 (8)	1.179 (7)	124.9 (1.2)	173.8 (3.7)	
TeF_5NCO^b	1.859 (21)	1.244 (13)	1.186 (11)	126.5 (1.4)	175.7 (2.6)	

[a] Agreement factor. [b] See ref 5.

Table II. NMR Data of SF_5NCO, SeF_5OCN, and TeF_5NCO^a

	^{19}F	^{14}N	^{15}N	^{33}S, ^{77}Se, ^{125}Te
SF_5NCO	AB_4 spectrum; δ_a 68.1, δ_b 86.1; $J_{ab} = 146$ Hz	δ −271.8; lw ~ 120 Hz	not measd	δ −191.3; $J_{^{33}S-^{19}F}$ ~ 264 Hz; lw ~ 85 Hz
SeF_5OCN	AB_4 spectrum; δ_a 53.9, δ_b 83.3; $J_{ab} = 222.4$ Hz, $J_{^{77}Se-F_a} = 1417$ Hz, $J_{^{77}Se-F_b} = 1459$ Hz	δ −189.2; lw ~ 60 Hz	not measd	δ −913; $J_{^{77}Se-F_a} = 1426$ Hz, $J_{^{77}Se-F_b} = 1470$ Hz; lw ~ 3 Hz
TeF_5NCO	AB_4 spectrum; δ_a −46.4, δ_b −36.1; $J_{ab} = 177$ Hz, $J_{^{125}Te-F_a} = 3520$ Hz, $J_{^{125}Te-F_b} = 3528$ Hz	δ −303.9; lw ~ 130 Hz	δ 301.9; lw = 3.5 Hz	δ −140.8; $J_{^{125}Te-F_{a,b}} = 3545$ Hz, $J_{^{125}Te-^{14}N} = 153$ Hz; lw ~ 100 Hz (28 °C)

[a] lw = line width.

of the least-squares analyses are described in ref 5, and the results are summarized in Table I. For all four isomers the geometric parameters are equal within their error limits. The *R* factors, which measure the agreement between experiment and model, differ only very little (<3%) and cannot be used to select one of the models as superior to the others. The scattering intensities and radial distribution function (Figure 1) are very insensitive to the sequence in the XYZ group for two reasons: the contribution of the XYZ group is small, the main contribution being due to the SeF_5 group, and the atomic numbers of C, N, and O are very similar.

Nevertheless, the results permit exclusion of the nitrile oxide isomer. Here, a linear or almost linear configuration SeCNO is expected, which simply cannot be met with an SeCN angle of ~116°. This SeXY angle is somewhat smaller than the corresponding angles in Fe_5SNCO and F_5TeNCO. Indeed, a smaller angle is expected for a Se—O– instead of a Se—N= configuration.

In the previous electron diffraction study[5] the bond distances SeX and XY were used for the rejection of the $F_5Se{-}O{-}C{\equiv}N$ model. It was argued that a value of 1.79 Å is too long for an SeO bond and 1.26 Å is too short for an OC single bond. The former bond was compared to the SeO bond in SeF_5OSeF_5[8] (1.697 (13) Å), but the large decrease in the oxygen bond angle (142° in SeF_5OSeF_5 vs. 117° in SeF_5OCN) can account for the longer SeO bond in SeF_5OCN. No gas-phase structures of cyanates are available for comparison of OC bonds. In ionic cyanates coordination occurs frequently at both ends of the OCN group, and the distinction between cyanates and isocyanates is irrelevant. In the covalent 4-chloro-3,5-dimethylphenyl cyanate average bond lengths of 1.14 (C≡N) and 1.27 Å (C—O) have been determined. Several ab initio calculations for isocyanic and cyanic acid have been reported,[9] and the high-quality calculations of McLean et al. predict C≡N = 1.153 and C—O = 1.302 Å for H—O—C≡N. The difference between these bond lengths and those observed in the F_5SeXYZ material are certainly not significant, and our previous rejection of $F_5Se{-}O{-}C{\equiv}N$ was not justified. Furthermore, no bond length and angles are known for covalent R—O—N≡C compounds.

The IR spectrum of the F_5SeOCN material gives good arguments for rejection of the $F_5Se{-}N{=}C{=}O$ model. The two bands, attributable to the valency -XYZ vibrations are found at 2290 (m) and 1104 (str) cm^{-1}. The band at 2290 cm^{-1} can be similarly assigned to ν_s(NCO) of F_5SeNCO, ν(CN) of F_5SeOCN, and ν(NC) of F_5SeONC. The decrease in intensity as compared with F_5SNCO and F_5TeNCO already speaks against the isocyanate configuration. The strong band at 1104 cm^{-1} cannot be ν_s(NCO) of F_5SeNCO, since it is ~250 cm^{-1} away from the corresponding very weak bands in F_5SNCO and F_5TeNCO.[6] In organic cyanates a strong band at ~1100 cm^{-1} is observed for ν(C–O) as a characteristic and strong absorption;[10] in silyl cyanates this band is observed at 1160 cm^{-1} (vs).[11] Unfortunately, nothing again is known about IR spectra of covalent fulminates.

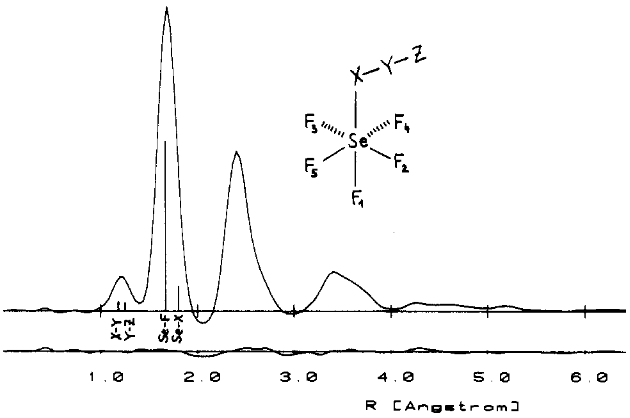

Figure 1. Experimental radial distribution function and difference curve for $SeF_5{-}O{-}C{\equiv}N$. The difference curves for the other isomers are very similar.

The strongest evidence for rejection of the F_5SeNCO model can be obtained from the various NMR spectra (Table II).

^{19}F Spectra. All four possible isomers would have typical AB_4 patterns in typical regions. This fact does not allow any conclusions.

The ^{14}N spectrum of the selenium material is not compatible with the F_5SeNCO model: The chemical shift range for -NCO groups is normally −300 to −350 ppm[12] (Table II), and F_5TeNCO falls into this range, while F_5SNCO is on the border. F_5SeOCN,

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(8) Oberhammer, H.; Seppelt, K. *Inorg. Chem.* **1978**, *17*, 1435.

(9) McLean, A. D.; Loew, G. H.; Berkowitz, D. S. *J. Mol. Spectrosc.* **1977**, *64*, 184. Poppinger, D.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 7806. Rank, A.; Alewood, P. F. *Can. J. Chem.* **1977**, *55*, 1498. Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 3674.

(10) Groving, N.; Holm, A. *Acta Chem. Scand.* **1965**, *19*, 443.

(11) Eaborn, C.; Lickiss, P. D.; Marquina-Chidsey, G.; Thorli, E. Y. *J. Chem. Soc., Chem. Commun.* **1982**, 1326.

(12) "NMR and the Periodic Table"; Mann, B. E., Eds., Harris, V. K., Academic Press: London, New York, San Francisco, 1978; p 97.

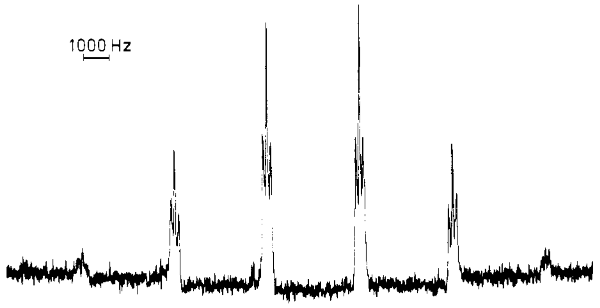
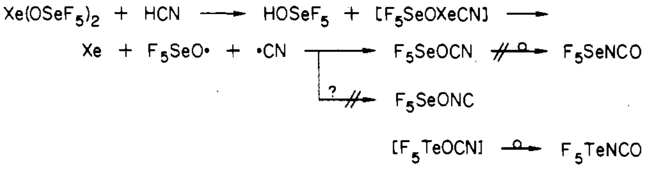


Figure 2. ^{125}Te NMR spectrum of TeF_5—N=C=O. The large splitting shows the coupling to the directly bonded five fluorine atoms with virtually identical coupling constants: $J_{^{125}Te-F_{ax}} = 3520$, $J_{^{125}Te-F_{eq}} = 3528$ Hz (from the ^{19}F NMR).[2] The broadening with some fine structure is due to the coupling ^{125}Te–^{14}N, here at 28°.

Scheme I



however, lies 100 ppm out of this range, in fact right into the region where –O—C≡N, –C≡N—O, or –N≡C compounds are found.[12]

The ^{15}N spectrum was only obtained on a neat, 20-g sample of F_5TeNCO, which gives a sharp, single line. No more information seems obtainable from such measurements, especially since any ^{15}N–^{19}F coupling constant is too small to be observed. ^{13}C measurement does not give more information, especially because of lack of material for comparison.

The ^{125}Te spectrum of F_5Te—N=C=O shows the coupling to both the directly bonded fluorine atoms on the Te and to the ^{14}N nucleus. Because of a nuclear spin of 1 and the quadrupole moment of the latter nucleus, the lines are broad. At 30° the 1:1:1 splitting becomes evident, on further warming it got even better resolved, and on cooling to –30 °C it disappears reversibly (Figure 2). A similar ^{33}S–^{14}N coupling in F_5SNCO is probably hidden under the natural line width of the ^{33}S spectrum. But, the magnitude of $J_{^{125}Te-^{14}N}$ in F_5TeNCO can be used for a prediction of the corresponding ^{77}Se–^{14}N coupling in F_5Se—N=C=O. In homologous compounds the ratio of corresponding coupling constants is equivalent to the ratio of the gyromagnetic factors; here, ^{125}Te:^{77}Se = 0.8871:0.534 = 1.66. A coupling constant so obtained must further be corrected for relativistic effects on such heavy elements.[13] An estimated value of 50 Hz is so obtained for $J_{^{77}Se-^{14}N}$ in F_5Se—N=C=O. The ^{77}Se spectra clearly show no such coupling or at least broadening. The lines are very sharp. A coupling of ~3 Hz would have been observed (Figure 3).

While the NMR spectra allow rejection of the isocyanate model, a distinction between cyanate and fulminate model still has to be made. At present we see no clear and simple physical method for a clear decision. But, chemical reasons strongly favor the

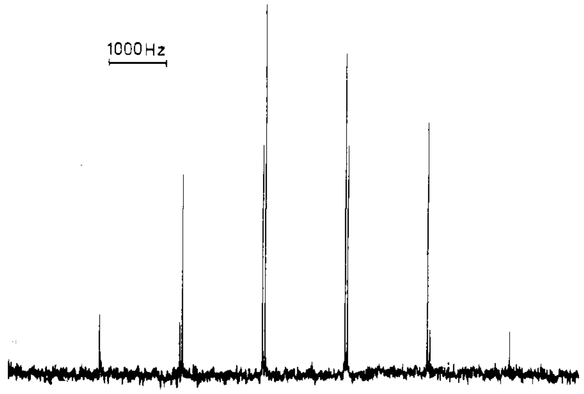


Figure 3. ^{77}Se NMR spectrum of SeF_5—O—C≡N. The very sharp lines exclude a direct coupling ^{77}Se–^{14}N. The fine structure is due to the directly bonded axial and four equatorial fluorine atoms.

cyanate over the fulminate model. The formation of F_5SeOCN or F_5SeONC from $Xe(OSeF_5)_2$ and HCN would be a stepwise process (Scheme I).

Dissolution of $Xe(OSeF_5)_2$ in excess HCN might give small amounts of an intermediate xenon cyanide. But, this cyanide should decompose spontaneously into free radicals, as it is known for quite a few xenon compounds of similar type, e.g. $Xe(OSO_2F)_2$, $Xe[N(SO_2F)_2]_2$, $Xe(OSeF_5)_2$,[14] and others. The recombination of these radicals should give the cyanate as the thermodynamically more stable material than the fulminate.

In the case of similar reaction between $Xe(OTeF_5)_2$ and HCN, only F_5TeNCO is observed. Certainly all steps are alike until the proposed intermediate F_5TeOCN. But, tellurium is larger than selenium; the existence of the complexes TeF_8^{2-} and $(R_3N)_2TeF_6$ demonstrate this, while SeF_6 or SF_6 do not undergo any coordination increase. Therefore, the rearrangement $F_5TeOCN \rightarrow F_5TeNCO$, be it in an intra- or intermolecular manner, is easily conceivable. F_5Te—N=C=O, however, cannot come from F_5Te—O—N≡C; so, if the analogy is correct, the F_5SeXYZ material cannot be the fulminate.

Also, fulminates (–ON≡C) or isocyanides (–N≡C) should be sensitive to strong oxidation. The preparation reaction is done in the presence of the very highly oxidizing $Xe(OSeF_5)_2$, which is consumed only slowly. So, any fulminate formed should be oxidized. The explosivity of the F_5SeOCN material remains to be explained. This, of course, has always tempted us to think of a fulminate. But, six-valent selenium compounds are known to be less stable than the corresponding sulfur and tellurium compounds. So, the decomposition of F_5SeOCN into the stable species N_2, COF_2, SeF_4, and Se could well be explosive.

Conclusion

While we have demonstrated that the questionable material is indeed F_5Se—O—C≡N, chemistry in this area is back to the point that no F_5Se–nitrogen compounds exist so far, in spite of several derivatives with the F_5S—N= and F_5Te—N= configurations. Numerous attempts to attach a SeF_5 group to nitrogen with SeF_6 or SeF_5Cl have failed.

Registry No. F_5Se—N=C=O, 88088-28-2; F_5Se—O—C≡N, 94994-37-3; F_5TeNCO, 86024-46-6; F_5SNCO, 2375-30-6.

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(13) This calculation is a simple version of the theory of reduced coupling constants. See also: Webb, G. A. In "NMR and the Periodic Table"; Harris, V. K., Mann, B. E., Eds.; Academic Press: London, New York, San Francisco, 1978; p 66.

(14) Seppelt, K.; Lentz, D. *Prog. Inorg. Chem.* **1982**, 167 and literature cited therein.