Isolation and Structure of the $OCNCO^+$ Ion**

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Carbon suboxide, C_3O_2, is a linear molecule. In a thorough theoretical investigation, Pyykkö and Runeberg calculated for the atomic sequence A=B=C=D=E that its minimum energy is almost always for a bent structure at the central atom. The linearity of C_3O_2 is almost the singular exception.[1] Our aim was to isolate in substance the ion $O{=}C{=}N{=}C{=}O^+$ as the closest relative to C_3O_2 and to establish its structure by experimental methods. The theoretical work cited above predicts an angle of 139° at the nitrogen atom.[1] $OCNCO^+$ has so far only been observed in the mass spectrometer as a decomposition product of various molecules generated by electron impact ionization.[2] An ion generated as such, which was initally assumed to be linear, reacts in the mass spectrometer with pyridine forming 1:1 and 1:2 adducts, in which the OCNCO moiety is now assumed to be bent.[3]

The starting point for our synthesis was the idea to generate the $OCNCO^+$ ion in the form of a salt by Cl^- or F^- abstraction from Cl−CO−N=C=O and F−CO−N=C=O with strong Lewis acids. Cl−CO−N=C=O,[4] however, did not react with any of the Lewis acids we tried, such as BCl_3, $AlCl_3$, or $SbCl_5$; thus, we chose F−CO−N=C=O[5] and the strong Lewis acids AsF_5 and SbF_5 as starting materials. The reaction of F−CO−N=C=O and AsF_5 in $CF_3CH_2CF_3$ resulted, however, in an adduct with O-coordinated AsF_5. A similar coordinated product was obtained in the reaction of F−CO−N=C=O and SbF_5 in a 1:1 molar ratio (Figure 1). In contrast, the desired reaction to give $OCNCO^+AsF_6^-$ occurred in the solvent $(CF_2Cl)_2$, as could be shown by Raman spectroscopy and in part by crystallography. The crystals were always twinned, and only an imperfect structure analysis could be obtained, which nevertheless showed the presence of bent $OCNCO^+$ ions and octahedral AsF_6^- ions. The use of excess AsF_5 resulted in $OCNCO^+As_2F_{11}^-$ whose crystals again were systematically twinned. Only by using an excess of the strongest Lewis acid SbF_5 were long colorless needles of $OCNCO^+Sb_3F_{16}^-$ obtained which were of a suitable quality to alleviate the crystallographic problem of twinning (Figure 2). The ion has a strongly bent (130.7°) C_{2v} structure. Other details of the structure are in full agreement with our and earlier calculations.

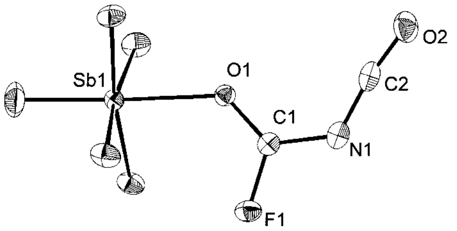

Figure 1. ORTEP plot of OCN−CFO·SbF_5, 50% probability ellipsoids. Distances [pm] Sb−F 185.1–186.4(1), Sb−O1 208.4(2), C1−O1 123.7(3), F2−C1 129.6(3), C1−N1 132.4(3), C2−N1 123.7(4), C2−O2 113.9(4). The structure of OCN−CFO·AsF_5 is practically identical, crystals are isomorphous to OCN−CFO·SbF_5. Distances: As−F 168.7–171.0(1), As−O1 199.6(1), C1−O1 123.1(2), C1−F1 129.2, C1−N1 133.7, C2−N1 123.2(3), C2−O2 113.9(3).

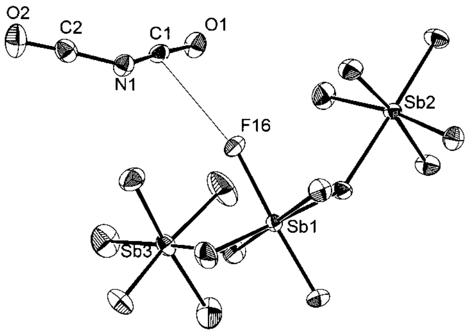

Figure 2. ORTEP plot of $OCNCO^+Sb_3F_{16}^-$, 50% probability ellipsoids. The shortest cation–anion contact is indicated by a thin line. Distances [pm]: C1−O1 111.8(4), C2−O2 111.4(5), C1−N1 125.0(4), C2−N1 125.0(5), F16−C1 268.6(4); angles [°]: O1-C1-N1 173.7(4), O2-C2-N1 173.1(4), C1-N1-C2 130.7(3)°.

In energetical terms, the qualitative large difference between the structures of linear C_3O_2 and bent $OCNCO^+$ is very small, and we have calculated the energy difference between linear and bent arrangements (Table 1).[6] Regardless of the basis set and method for approximation of the electron correlation, the energy difference is only a few kJ mol^{-1}. The potential of the deformation mode of the central atom is extraordinarily flat. The deformation mode is assigned to a Raman vibration at 130 cm^{-1}. A plausible explanation for the structural difference between $OCNCO^+$ and C_3O_2 could be the markedly higher electronegativity of the nitrogen atom with respect to the central carbon atom in C_3O_2, which leads to a higher localization of electron density in the sense of a

Table 1. Structure and vibrational data of $OCNCO^+Sb_3F_{16}^-$ determined by experiment and theory.

	Experiment $OCNCO^+Sb_3F_{16}^-$	Calculated[a] HF	MP2	CCD
r_{CO} [pm]	111.8, 111.3	110.8	115.4	113.6
r_{CN} [pm]	125.0, 125.0	124.5	126.5	126.4
$\sphericalangle$NCO [°]	173.1, 173.6	175.4	172.9	173.6
$\sphericalangle$NCN [°]	130.7	138.1	134.7	133.6
$\tilde{\nu}_{CO}A_1$ [cm^{-1}]	2359	2663	2349	2472
$\tilde{\nu}_{CO}B_2$ [cm^{-1}]	2320	2611	2415	2464
$\tilde{\nu}_{CN}B_2$ [cm^{-1}]	1512	1712	1529	1581
$\tilde{\nu}_{CN}A_1$ [cm^{-1}]	914	964	897	923
$\delta_{NCO}A1$ [cm^{-1}]	610	662	560	593
$\delta_{oop}A_2$[b] [cm^{-1}]	588	649	556	576
$\delta_{NCO}B_2$ [cm^{-1}]	560	631	541	560
$\delta_{oop}B_1$[b] [cm^{-1}]	514	626	499	530
$\delta_{NCN}A_1$ [cm^{-1}]	130	129	134	137
ΔE[c] [kJ mol^{-1}]		4.4	6.2	7.1

[a] Basis set 6-31G(d,p), Hf = Hartree–Fock approximation, MP2 = second order Møller–Plesset approximation, CCD = coupled cluster calculation with double substitution of the Hartree–Fock determinant. [b] Out-of-plane stretch. [c] Energy difference between linear and bent form.

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nonbonding electron pair. The calculation of the partial charges according Mullikan at the MP2 level for the central nitrogen atom gives the value of -0.36, in spite of the total change $+1$ of the $OCNCO^+$ ion. According to the analysis of the natural bond orbitals this is a result of the existence of two nonbonding electron pairs at nitrogen with an occupation of 1.6 and 1.5 e^-; the former has 23% s character and is responsible for the bending.

Finally it should be noted that the isoelectronic N_5^+ ion has recently been prepared in the form of the highly explosive $N_5^+AsF_6^-$, which is also strongly bent at the central nitrogen atom.[7]

Experimental Section

F–CO–NCO was prepared in 70% yield from Cl–CO–NCO by halogen exchange with an excess of $SF_3/SbCl_5$ at 75 °C. The product must be removed immediately from the reaction vessel in order to avoid decomposition into COF_2 and $OC(NCO)_2$. The latter polymerizes under these conditions. Further physical data see ref. [5].

$OCNCO^+Sb_3F_{16}^-$: By using a glass vacuum line under liquid nitrogen cooling, F–CO–NCO (60 mg, 0.67 mol), SbF_5 (600 mg, 7.76 mmol), and $CF_3–CH_2–CF_3$ (2–3 mL) were condensed into an 8 mL glass ampule, which was then sealed. At room temperature colorless crystals appeared which largely dissolved after brief heating to 60 °C, and the undissolved part melted. Slow cooling to 10 °C gave colorless needles, which decompose slowly at room temperature, and turn brown. Raman (Spex Industries 1403, 1064 nm excitation light, 300 mW, solid -90 °C): 2359(20), 2320(5), 1512(1), 1126(1), 1076(1), 914(40), 697(100), 674(60), 656(80), 610(15), 588(8), 560(1), 514(3), 350(5), 323(2), 298(30), 288(20), 271(5), 271(5), 232(10), 217(12), 190(30), 146(10), 130(5) cm^{-1}; ^{13}C NMR ($CF_3CH_2CF_3$): $\delta = 122.4$. Crystal structure analysis: A suitable crystal was adjusted under nitrogen and cooling on an Enraf Nonius CAD4 diffractometer (MoK_α, graphite monochromator). Lattice constants were obtained by fine adjustment of 25 reflections with $20° < \theta < 25°$. Intensities were measured with the ω scan method allowing a maximum of 60 s per reflection, of which 25% were used for the background measurement, psi scan absorption correction. Solution and refinement of the structure was done with the shelx programs.[8] $a = 954.8(1)$, $b = 735.8(1)$, $c = 2093.2(3)$ pm, $\beta = 94.65(1)°$, $V = 1465 \times 10^6$ pm^3, $P2_1/c$, 4688 measured, 4264 independent reflections, 218 parameters, $R_1 = 0.021$, $Rw^2 = 0.055$.

$OCN–FCO \cdot SbF_5$: The preparation was similar to that for $OCNCO^+Sb_3F_{16}^-$, only a 1:1 stoichiometry of F–CO–NCO and SbF_5 in the solvent $CF_3CH_2CF_3$ or $(CF_2Cl)_2$ was used. Colorless needles were obtained upon cooling to -40 °C which melt at 5–18 °C to give a viscous liquid. Raman (solid, -90 °C): 2271(5), 1662(10), 1509(1), 1490(2), 1273(5), 950(15), 754(2), 708(15), 679(45), 649(100), 594(20), 527(25), 299(15), 284(5), 265(5), 234(8), 196(4), 163(4), 125(70), 114(30) cm^{-1}. Crystal structure analysis: $a = 875.36(8)$, $b = 543.21(5)$, $c = 1503.1(1)$ pm, $\beta = 100.96(1)°$, $V = 701.7(1) \times 10^6$ pm^3, $P2_1/c$, 2125 measured, 1948 independent reflections, 110 parameters, $R_1 = 0.024$, $Rw^2 = 0.073$.

$OCNCO^+AsF_6^-$: Reaction of F–CO–NCO and AsF_5 in the stoichiometry 1:1 in $(CF_2Cl)_2$, as described above, crystallization, as described above, crystallization at -40 °C, colorless cubes that melt under gas evolution above O °C. Raman spectrum: 2366(10), 2287(1), 930(20), 915(15), 701(10), 685(100), 632(5), 613(2), 586(8), 573(4 =), 559(3), 518(4), 372(40), 205(50), 192(30), 124(80) cm^{-1}. Crystal structure analysis: $a = 1096.0(2)$, $b = 1118.3(3)$, $c = 1118.3(3)$ pm, $V = 1449.5 \times 1O^6$ pm^3, probably *Pnma*, pseudo-etragonal twinned with -1 0 0, 0 0 1, 0 1 0.

$OCNCO^+As_2F_{11}^-$: Reaction of F–CO–NCO and AsF_5 in 1:3 stoichiometry in $CF_3CH_2CF_3$, as described above, colorless platelets that melt above O °C under gas evolution, crystallization at -70 °C. Crystal structure analysis: $a = 566.5(2)$, $b = 1173.3(4)$, $c = 1612.9(7)$ pm, $\alpha = 110.60(3)$, $\beta = 90.74(3)$, $\gamma = 89.96(3)°$, $V = 1003.4 \times 10^6$ pm^3, $P\bar{1}$, pseudo-monoclinic twinned.

$OCN–FCO \cdot AsF_5$: Reaction of F–CO–NCO and AsF_5 in 1:1 stoichiometry in $CF_3–CH_2–CF_3$, as described above, colorless needles after cooling to -70 °C. Crystal structure analysis: $a = 855.2(1)$, $b = 525.42(6)$, $c = 1481.5(1)$, $\beta = 100.26(1)°$, $V = 655.1(1) \times 10^6$ pm^3, $P2_1/c$, 3296 measured, 2872 independent reflections, 110 parameters, $R_1 = 0.027$, $R_w{}^2 = 0.076$.

Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410736, CSD-410737, and CSD-410738.

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Stabilization of a Discrete Lanthanide(II) Hydrido Complex by a Bulky Hydrotris(pyrazolyl)borate Ligand**

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Organo f-element chemistry has witnessed spectacular growth in the past twenty years and, parallel with this development, hydrido complexes were synthesized for most of the lanthanides.[1] However, in spite of the importance of such species in various catalytic processes, often with activities

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[+] X-ray structure analysis.

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