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Crystal Structures and Bonding in NOCl, NO_2Cl, and NO_3Cl[†]

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Abstract: The crystal structures of NOCl, NO_2Cl, and NO_3Cl have been determined. NOCl forms a high-temperature phase (*Cmcm*, $a = 413.2(1)$ pm, $b = 1082.9(3)$ pm, $c = 546.1(1)$ pm at -125 °C) with the NO moiety showing 2-fold disorder while in the low-temperature modification (*Pnma*, $a = 1085.6(2)$ pm, $b = 539.93(9)$ pm, $c = 406.63(8)$ pm at -160 °C) continuous ordering is observed. The structure of the molecule is remarkably different in the solid state as compared to the gas phase. NO_2Cl crystallizes in the triclinic system ($P\bar{1}$, $a = 543.1(1)$ pm, $b = 737.4(1)$ pm, $c = 758.1(1)$ pm, $\alpha = 72.39(1)°$, $\beta = 78.88(2)°$, $\gamma = 89.56(2)°$ at -170 °C) with two crystallographically independent molecules in the asymmetric unit. NO_3Cl is best described as an adduct of the radicals NO_2 and ClO ($P2_12_12_1$, $a = 385.6(1)$ pm, $b = 675.5(2)$ pm, $c = 1207.6(3)$ pm at -166 °C).

Introduction

The structures of NOCl, NO_2Cl, and NO_3Cl are of interest for several reasons. These compounds caught the interest of chemists from early on until very recently as NOCl is a major component of aqua regia, probably the most reactive one, and NO_3Cl is considered to play an essential role for ozone depletion in the stratosphere as reaction product of ClO radicals with NO_2.[1] The nitrogen–oxygen bond is one of the most fascinating and puzzling problems in our understanding of chemical bonding. Similarly intriguing are the chlorine–oxygen bond and the nitrogen–chlorine bond which up to now have been studied only in a small number of compounds. As all three types of bonding are found in the series NOCl, NO_2Cl, and NO_3Cl precise structural data are highly desirable. Furthermore, this series of compounds nicely illustrates inconsistencies in chemical nomenclature. The names nitrosyl chloride for NOCl and nitryl chloride for NO_2Cl, respectively, suggest combinations of "cationic" nitrogen oxides and "anionic" chlorine. On the other hand, the name chlorine nitrate for NO_3Cl is indicative of a combination of chlorine cations and nitrate anions. This difference even manifests itself in many textbooks where NOCl and NO_2Cl are listed with nitrogen compounds, while NO_3Cl is discussed in context with chlorine compounds.[2,3] The (over)-simplified ionic classification of these polar molecules is as in many other cases based on their reactivity in chemical reactions, yet structural conclusions from chemical reactivity may be misleading. Indeed, the traditional nomenclature does not cope with the specific bonding features of NOCl, NO_2Cl, and NO_3Cl.

Results and Discussion

Single crystals of all three low-melting compounds were grown in situ on a four-circle diffractometer. To optimize growth conditions (and to avoid interference from solid-state transitions) investigations at continuously changing temperatures were performed with the modified Guinier technique[4] and differential thermal analysis.[5]

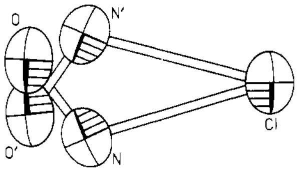

Figure 1. Disordered molecule in the high-temperature (HT) form of NOCl at -125 °C. Both orientations of the NO moiety are equally occupied. The ellipsoids are drawn on the 50% probability level. N–Cl 217.3(2) pm, N–O 108.9(2) pm; Cl–N–O 110.8(2)°.

Caution. The compounds are highly corrosive and strong oxidizers. They must be handled with care in an efficient fume hood.

NOCl was prepared[6] from NO_2/N_2O_4 and KCl and formed ruby red crystals on cooling. Thermal analysis revealed an endothermic phase transformation at -131 °C and the melting point at -61 °C. X-ray powder diffraction confirmed these results. Another phase transformation at -64 °C as described in the literature[7] was not observed. A single crystal was grown in an X-ray capillary from the melt and measured at six different temperatures between -75 and -125 °C. Ag Kα radiation was used to minimize photochemical decomposition. The structure at -125 °C was solved and refined in space group *Ama*2 with four molecules in the orthorhombic unit cell. As the NO "cations" showed 2-fold disorder in the high-temperature (HT) modification with both orientations being equally occupied and related by a pseudo mirror plane, final refinements were performed in space group *Cmcm* (Table 1). The refined parameters are given in Table 2, and the geometry of the molecule is shown in Figure 1 and the arrangement in the unit cell in Figure 3.

When the crystal was cooled below -125 °C additional reflections emerged, indicating the loss of the centering of the unit cell. *Pbnm* (standard setting *Pnma*) results as a possible space group for the low-temperature phase.[8] At -135 °C the 50:50 disorder of the high-temperature phase had changed to 85:15 and at -160 °C the structure was almost ordered with

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[†] Dedicated to Professor Gerhard Fritz on the occasion of his 75th birthday.

[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1995.

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(8) Group–subgroup relation: $Cmcm \xrightarrow{k2} Pbnm$.

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Table 1. Crystal Data and Structure Refinements

	HT-NOCl	LT-NOCl	NO_2Cl	NO_3Cl
empirical formula	NOCl	NOCl	NO_2Cl	NO_3Cl
formula wt	65.46	65.46	81.46	97.46
temp (°C)	−125	−160	−170	−166
diffractometer	Syntex/Siemens $P2_1$, graphite monochromator			
wavelength (pm)	56.087		71.073	
crystal system	orthorhombic		triclinic	orthorhombic
space group (No.)	*Cmcm* (63)	*Pnma* (62)	$P\bar{1}$ (2)	$P2_12_12_1$ (19)
unit cell dimens				
a (pm)	413.2(1)	1085.6(2)	543.1(1)	385.6(1)
b (pm)	1082.9(3)	539.93(9)	737.4(1)	675.5(2)
c (pm)	546.1(1)	406.63(8)	758.1(1)	1207.6(3)
α (deg)	90	90	72.39(1)	90
β (deg)	90	90	78.88(2)	90
γ (deg)	90	90	89.56(2)	90
vol (nm^3)	0.2444(1)	0.23835(8)	0.28354(9)	0.3145(2)
formula units *Z*	4	4	4	4
density (calc) (g/cm^3)	1.779	1.824	1.908	2.058
abs coeff (mm^{-1})	0.607	0.622	1.076	1.011
F(000)	128	128	160	192
$2\theta_{max}$ (deg)	45	54	55	75
reflcns collected	357	1974	1314	3577
independent reflcns	203	580	1310	1628
R_{int}	0.0208	0.0426		0.0166
structure solution	direct methods			
refinement method	full-matrix least-squares on F^2			
parameters	18	26	74	47
goodness-of-fit on F^2	1.245	1.385	1.237	1.613
R indices R_1, wR_2 [$I > 2\sigma(I)$]	0.0155, 0.0363	0.0225, 0.0460	0.0203, 0.0518	0.0161, 0.0385
R indices R_1, wR_2 [all data]	0.0163, 0.0366	0.0241, 0.0469	0.0213, 0.0524	0.0167, 0.0387
extinction coeff	0.066(11)		0.009(4)	0.003(5)
absolute structure parameter				0.04(3)
programs used	SHELXTL-Plus and SHELXL-93			

Table 2. Final Positional and Displacement Parameters

atom	*x*	*y*	*z*	$U_{eq}{}^{a}$ (pm^2)
		HT-NOCl		
Cl	0.5	0.35528(2)	0.25	405(2)
N	0.6400(5)	0.1619(2)	0.25	371(3)[b]
O	0.4273(4)	0.1025(2)	0.25	465(5)[b]
		LT-NOCl		
Cl	0.14385(2)	0.25	0.03317(5)	218.9(8)
N	0.33734(7)	0.25	0.1733(2)	217(1)
O	0.39882(7)	0.25	−0.0424(2)	260(2)
N′	0.3385(5)	0.25	−0.095(5)	217(1)
O′	0.401(2)	0.25	0.119(5)	260(2)
		NO_2Cl		
Cl1	0.50222(5)	0.25854(5)	0.79728(4)	304(1)
N1	0.1914(2)	0.2645(1)	0.7411(1)	215(2)
O1	0.0243(2)	0.2019(1)	0.8748(1)	271(2)
O2	0.1865(2)	0.3289(2)	0.5774(1)	343(2)
Cl2	−0.30289(5)	0.20116(5)	0.28830(4)	324(1)
N2	0.0388(2)	0.2383(1)	0.2505(1)	214(2)
O3	0.1464(2)	0.0956(1)	0.2981(1)	278(2)
O4	0.1155(2)	0.4001(1)	0.1818(1)	340(2)
		NO_3Cl		
Cl	0.20799(4)	0.56031(2)	0.238859(10)	207.9(4)
N	0.1526(1)	0.51164(7)	0.45371(4)	184.7(7)
O1	0.0228(1)	0.62738(7)	0.35939(3)	233.7(8)
O2	0.0141(1)	0.56773(9)	0.53730(3)	270.7(9)
O3	0.3603(2)	0.38563(8)	0.43643(4)	280.0(10)

[a] U_{eq} defined as 1/3 of the trace of the orthogonalized U_{ij} tensor. [b] Both positions are only half occupied.

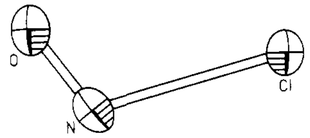

Figure 2. Molecule in the low-temperature (LT) form of NOCl at −160 °C. The disordered part (3%) is not shown. The ellipsoids are drawn on the 70% probability level. N−Cl 217.65(9) pm and N−O 110.2(1) ppm; Cl−O−N 112.10(6)°.

96.9(2)% of the NO groups occurring in just one orientation. To assure that the geometry of the molecule is not falsified by errors in the refined model we gradually increased the number of constraints. However, even completely neglecting the disorder at −160 °C does not change the geometry but increases the wR_2 index by about 1.5%. Final parameters are given in Table 2 and in Figure 2. The geometry of the NOCl molecule in the solid state (N−O 108.9(2) pm, N−Cl 217.3(2) pm) is remarkably different from that determined by microwave spectroscopy in the gas phase where an N−O interatomic distance of 113.9(12) pm and an N−Cl distance of 197.5(5) pm were observed.[9] Despite these big differences in bond distances the enclosed angle shows only a small difference with 110.8(2)° in the solid state and 113.3(7)° in the gas phase. The N−O distances lie between those in the neutral molecule NO (115 pm)[10] and the NO^+ cation (106.3 pm).[11] Assuming a linear correlation between charge and distance, a 55% positive charge results for solid NOCl and 12.5% for gaseous NOCl. The considerable amount of covalent bonding in solid NOCl is also reflected in the fact that it crystallizes in a typical molecular structure (Figures 3 and 4) and not in the rocksalt type structure while nitrosyl compounds with complex anions like BF_4^- or ClO_4^- are isostructural with their potassium analogs.[12,13]

It is of interest that $NaNO_2$ shows a very similar phase transition that was studied in detail. Above the transition temperature the NO_2^- anion shows a 2-fold disorder while continuous ordering is observed below the transition temperature

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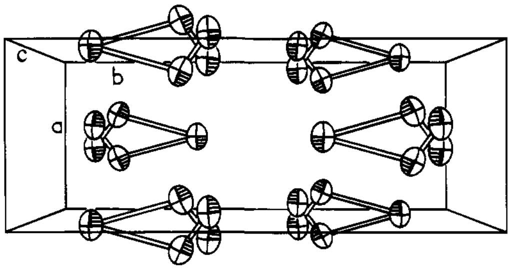

Figure 3. Unit cell of HT-NOCl projected onto (001). The disordered NO units are related by a mirror plane.

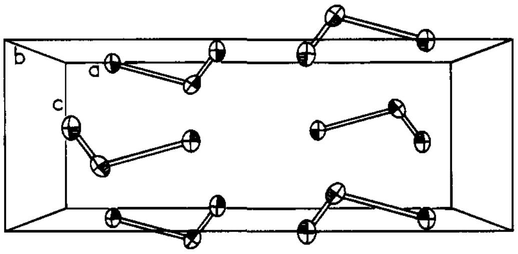

Figure 4. Unit cell of LT-NOCl projected onto (010). The small amount of disorder is neglected. Next nearest NCl distances are at 307.8 pm, which is even longer than the ClO distance within the molecule (278.5 pm).

to the ferroelectric phase.[14] However, for NOCl ferroelectric behavior was not observed in agreement with its refinement in a centrosymmetric space group. To elucidate the type of disorder and more details of the phase transition we are currently planning further experiments. A study on NOBr was started which seems to show very similar crystal chemistry.[15]

NO_2Cl was prepared from nitric acid and chlorosulfuric acid.[16] The colorless samples were manipulated only on dry ice to prevent irreversible decomposition. The reddish color of slightly decomposed samples indicated the formation of NOCl which was clearly observed in powder diffraction patterns. This indicates that the decomposition of nitryl chloride proceeds differently in the condensed phase compared to the gas phase where NO_2 and Cl_2 were described as the only reaction products.[17] Thermal analysis and Guinier powder photographs did not show any phase changes below the melting point at −145 °C down to −180 °C. A single crystal was grown close to the melting point. The volume of the triclinic unit cell already indicated two crystallographically independent molecules which was verified during the course of the refinement in space group $P\bar{1}$. Both molecules (Figure 5) exhibit only slight deviations from C_{2v} symmetry as well as from planarity as is expected for a molecule which is isoelectronic to NO_3^- and $NOCl_2^+$.[18]

Geometric details are in close agreement with those from microwave spectroscopy[19] and ab initio calculations.[20] The N−Cl distances (181.7, 183.3 pm) are considerably shorter compared to solid NOCl (217.5 pm), indicating mainly covalent bonding; however, they are still somewhat longer in comparison to solid NCl_3 (175 pm).[21] The interpretation in terms of covalency is supported by the geometry of the NO_2 moiety which is almost identical to that in N_2O_4;[22] the slightly smaller angle argues against a positive charge on the "nitryl" group of NO_2Cl. The molecular structure of NO_2Cl again as in the case of NOCl contrasts the typical salt-like structures of nitryl compounds with stable complex anions which are isostructural to their analogs of the heavier alkali metals (Figure 6).[23] The packing diagram of NO_2Cl shows all N−Cl interatomic bonds oriented parallel to the *a* axis. Accordingly, the view along [100] exhibits a hexagonal rod packing of the ribbons of molecules.

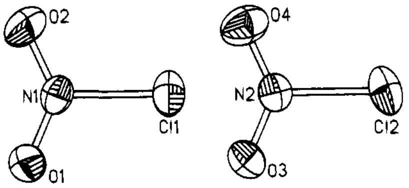

Figure 5. The two independent molecules of NO_2Cl at −170 °C. The ellipsoids are drawn at the 70% probability level. N1−Cl1 181.6(1) pm, N2−Cl2 183.2(1), N1−O1 119.7(1), N1−O2 119.3(1), N2−O3 119.2(1), N2−O4 119.0(1); Cl1−N1−O1 114.57(8)°, Cl1−N1−O2 115.04(9), O1−N1−O2 130.4(1), Cl2−N2−O3 114.24(8), Cl2−N2−O4 114.71(9), O3−N2−O4 131.1(1).

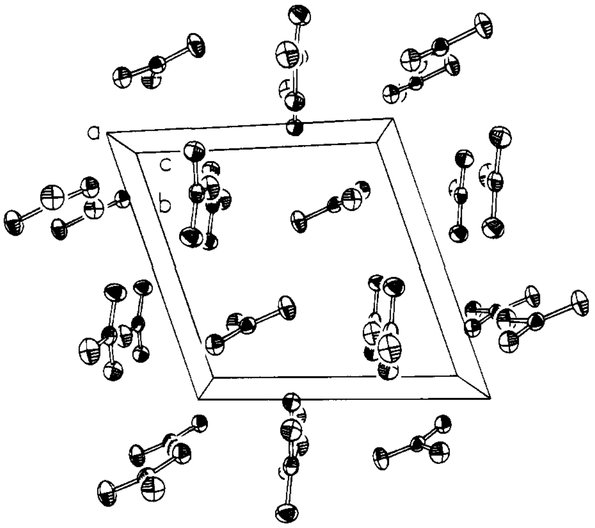

Figure 6. Packing diagram of NO_2Cl with the triclinic unit cell projected along [100].

NO_3Cl was prepared from nitric acid and ClF in a Teflon FEP tube.[24] Surprisingly the reaction products HF and NO_3Cl are not miscible and the more dense NO_3Cl collects at the bottom of the vessel. This unusual behavior makes it somewhat tedious to distill off the more volatile NO_3Cl, especially in a narrow reaction tube. Therefore the reaction vessel was vigorously agitated while the NO_3Cl was distilled from −78 to −196 °C in vacuum. To remove the last traces of HF the product was allowed to stand over NaF for about 5 h at −30 °C before it was condensed into the storage vessel. The slightly yellow sample showed only one crystalline phase in the interval from the melting point at −101 to −170 °C. A data set of a single crystal was collected at −166 °C. The structure was solved and refined in the orthorhombic space group $P2_12_12_1$.

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(15) NOBr shows a phase transition at −135 °C with the high-temperature phase being isostructural with that of NOCl. More pronounced light sensitivity, considerable dissociation in the gas phase, and the existence of additional phases like $NOBr_2$ and $NOBr_3$ in the NO/Br_2 system have so far hindered a high-quality structure determination.

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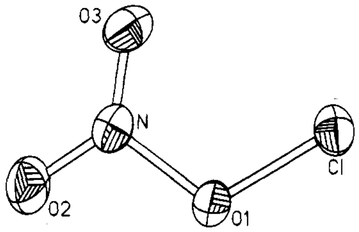

Figure 7. NO_3Cl molecule at −166 °C. The ellipsoids are drawn at the 70% probability level. Cl1−O1 168.34(6) pm, N−O1 146.94(7), N−O2 120.30(7), N−O3 118.72(7); Cl−O1−N 112.49(4)°, O1−N−O2 109.37(5), O1−N−O3 118.36(5), O2−N−O3 132.27(5).

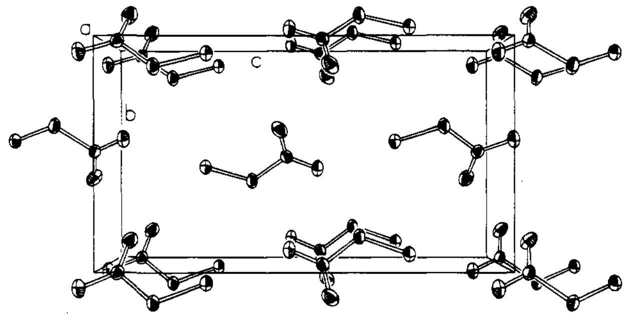

Figure 8. Unit cell of NO_3Cl projected onto (100).

In the structure all three oxygen atoms are bonded to the nitrogen atom and the chlorine atom is connected to one oxygen atom (Figure 7). Obviously the particular isomer was crystallized which is considered the most stable one.

The chlorine atom is only slightly (2.7 pm) out of the plane through the NO_3 group in contrast to some spectroscopic experiments where the nonplanar arrangement was favored[25,26] but in accordance with other investigations.[27−30] Distances and angles are in fair agreement with those deduced from earlier experiments[31] and calculations.[20] The structural details are best interpreted in terms of an NO_2 radical bonded to a ClO radical with a small negative charge on the NO_2 moiety. Especially the much longer N−O1 interatomic distance at 146.94(7) pm compared to N−O2 at 120.30(7) and N−O3 at 118.72(7) pm clearly contrasts the regular triangle of a typical nitrate. Accordingly, the angles span a rather large range from 109.37(5)° to 132.27(5)° around the ideal value of 120°. In the crystal structure the molecules are arranged head to tail in ribbons parallel to the *c* axis (Figure 8).

Concluding Remarks

NOCl, NO_2Cl, and NO_3Cl all form molecular structures in the solid state. In the case of NOCl the differences of the N−O and N−Cl interatomic distances respectively between the gas phase and the crystal indicate a tendency toward ionic dissociation in the solid state. Whereas the description of NOCl as nitrosyl chloride seems adequate, the name nitryl chloride for NO_2Cl is misleading for a rather nonpolar molecule that does not contain a positively charged NO_2 group. Last but not least "chlorine nitrate" is better described as an association of NO_2 and ClO radicals. These findings corroborate the dominant influence of the nitrogen−oxygen bond on the geometries of these molecules which is also reflected in the unexpected structure of the PNO molecule.[32]

Supporting Information Available: Tables SI to SVI, listing lattice parameters of NOCl at different temperatures as well as anisotropic displacement coefficients (2 pages); listing of structure factors (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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