δ-$SrSiO_3$:Eu^{2+} (ca. 300 K) means that the quenching effect via lattice vibrations of $(Si_3O_9)^{6-}$ rings is greater than that of $(Si_4O_{12})^{8-}$ rings. Therefore, δ′-$SrSiO_3$:Eu^{2+} gives an emission with high quantum efficiency compared with δ-$SrSiO_3$:Eu^{2+}.

The Eu^{2+} ions in δ-$CaSiO_3$:Eu^{2+} must selectively occupy the eightfold sites rather than the sixfold sites. As the dispersion of the Eu^{2+} ions in the matrix is expected to be good, the quenching effect of the energy transfer seems to be smaller than that of δ-$SrSiO_3$:Eu^{2+}. The great T_{50} value (ca. 420 K) indicates that the quenching effect of lattice vibration is relatively small. We can interpret from these considerations that δ-$CaSiO_3$:Eu^{2+} gives strong emission similar to δ′-$SrSiO_3$:Eu^{2+} in spite of the crystallographic mismatch between Ca^{2+} and Eu^{2+} ions.

Conclusion

Both $SrSiO_3$ and $EuSiO_3$ show similar high-pressure polymorphisms to that of $CaSiO_3$ and transform into the δ and δ′ phases at a pressure of 35–70 kbar. The δ form is isostructural with δ-$CaSiO_3$, but the δ′ phase is not formed for $CaSiO_3$, and hence it is a phase characteristic of $SrSiO_3$ or $EuSiO_3$. The ϵ (perovskite) form of $SrSiO_3$ or $EuSiO_3$ is not obtained because of the large ionic radius of Sr^{2+} or Eu^{2+}. The structures of δ-$SrSiO_3$ and δ-$EuSiO_3$ consist of $(Si_3O_9)^{6-}$ rings in a similar manner as δ-$CaSiO_3$ while δ′-$SrSiO_3$ and δ′-$EuSiO_3$ contain $(Si_4O_{12})^{8-}$ rings. The Sr or Eu atoms in these phases are surrounded by eight or six oxygens for the δ form and eight oxygens for the δ′ form.

The luminescence properties of $CaSiO_3$:Eu^{2+} and $SrSiO_3$:Eu^{2+} phosphors change considerably following the phase transformations. The excitation and emission spectra of δ-$CaSiO_3$:Eu^{2+} and δ′-$SrSiO_3$:Eu^{2+} are responsible for the Eu^{2+} ions that occupy the eightfold sites in the matrices while the Eu^{2+} ions on the eightfold and sixfold sites in δ-$SrSiO_3$:Eu^{2+} contribute to its luminescence spectra. For the α phases of $CaSiO_3$:Eu^{2+} and $SrSiO_3$:Eu^{2+}, the reflection spectra disagree with their excitation spectrum patterns. This means that there are two kinds of Eu^{2+} ions in the matrices: one contributes as the luminescence center whereas the other does not. Most of the Eu^{2+} ions belong to the latter type, and hence the emission intensity of this phase is weak. The experimental observation that the quantum efficiency of the sample appreciably increases with transformation into the δ-$CaSiO_3$ or δ′-$SrSiO_3$ phase is qualitatively interpreted by considering the crystal structure of the host lattice and the dispersion of Eu^{2+} ions in the matrix.

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Registry No. $EuSiO_3$, 15060-38-5; $CaSiO_3$, 10101-39-0; $SrSiO_3$, 13451-00-8.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Matrix Infrared Spectra of the NCl_2 and NBr_2 Free Radicals

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Mixtures of argon/chlorine/nitrogen were passed through a microwave discharge and condensed on a 15 K substrate. In addition to the NCl doublet at 823.5 and 817.2 cm^{-1}, a sharp new absorption with 9/6/1 relative intensity splittings appeared at 679.1, 677.4, and 675.8 ± 0.2 cm^{-1}. A nitrogen-15-enriched experiment produced a doublet of triplets and provided the NCl_2 identification and a 111 ± 4° calculation of the valence angle. Similar experiments with argon/bromine/nitrogen mixtures produced a sharp 603.5-cm^{-1} absorption with the appropriate nitrogen-15 shift for NBr_2.

Introduction

Much work has been done on electrical discharges in nitrogen since they were first reported in 1884,[1] and several reviews of their physical and chemical properties have appeared.[1-3] Experience has shown that these electrical discharges, microwave and radio frequency, are the only practical sources of nitrogen atoms in the gas phase. Ground-state nitrogen atoms are probably the main reactive species in "active" nitrogen,[2] as the discharge gas is often called, but other species, including vibrationally excited ground-state N_2 molecules and electronically excited N_2 molecules ($A^3\Sigma_u{}^+$), are present, and may also be significant.[4] Reactions of nitrogen atoms with other molecules in discharges have been studied, including the reaction with halogen molecules.[4] Raxworthy and Phillips[5] formed NCl and NBr in N_2 discharges with Cl_2 and Br_2. Using this approach, Miller and Andrews[6] trapped NCl, NBr, and NI in solid argon for laser-induced fluorescence study by condensing the effluent from an argon discharge containing the elements. The first identification of NCl_2 was provided by Briggs and Norrish[7] from flash photolysis of a NCl_3 and Cl_2 mixture. Clark and Clyne[8] later studied kinetics of the NCl_2 radical through the disappearance of a transient absorption at 299 nm; these workers prepared NCl_2 by reacting NCl_3 with Cl atoms from a microwave discharge. The NCl_2 radical has also been observed in the decomposition of NCl_3 in a helium atmosphere at room temperature,[9] and the matrix ESR spectrum of NCl_2 has been

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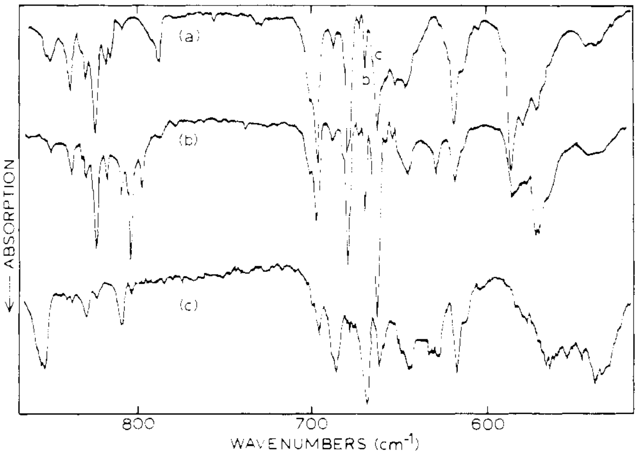

Figure 1. Infrared spectra in the 520–860-cm^{-1} region for a sample prepared by passing argon/chlorine/nitrogen mixtures through a microwave discharge and condensing the flowing gas on a CsI window at 15 K: (a) $Ar/Cl_2/N_2$ = 500/5/1; (b) $Ar/Cl_2/N_2$ = 200/2/1, 60% ^{15}N enrichment; (c) sample from (b) after temperature cycling to 46 ± 2 K and back to 15 K. In trace (a), "b" denotes the 669-cm^{-1} "band" contributed by improper instrument balance and "c" denotes the 663-cm^{-1} CO_2 absorption.

observed as a decomposition product during matrix deposition.[10] Finally, the geometry of NCl_2 (109.8° angle, 173-pm bond length) has been predicted from SCF-MO calculations.[11]

This work reports the infrared spectrum of NCl_2 in an argon matrix; the NCl_2 radical was prepared by passing nitrogen and chlorine gases through a low-pressure microwave-induced discharge of argon and trapping the effluent on a 15 K CsI window. Similar experiments with nitrogen and bromine provide infrared spectroscopic observation of the NBr_2 radical in solid argon.

Experimental Section

The cryogenic and vacuum apparatus have been previously described.[12] In most experiments, an $Ar/Cl_2/N_2$ mixture (usually 100/1/1) was passed through a microwave discharge (50–80 W, 2450 MHz) tube (12-mm o.d. × 8-mm i.d. quartz) and immediately deposited (1–2 mM/h for 20–24 h) on a CsI window at 15 K. Chlorine (Matheson) and bromine (Mallinckrodt) were outgassed at 77 K before use; the nitrogen gases (Air Products, 99.99%; $^{15}N_2$, Isomet Corp., ~60% ^{15}N) were used without further purification.

In some experiments, a modified surfatron wave guide[13] powered by a microwave oven magnetron and supply (nominal 650 W) was used as the discharge source. Preliminary results have been promising, but difficulty in keeping the gas pressure high enough to sustain the discharge without warming the matrix has been encountered. The spectra shown were produced with the microwave source, although similar results were obtained with the surfatron.

Results

Observations from the nitrogen–chlorine and nitrogen–bromine discharge systems will be described in turn.

Nitrogen–Chlorine System. Eight experiments were performed with the nitrogen–chlorine discharge system under different discharge and concentration conditions. The infrared spectrum from 520 to 860 cm^{-1} for an experiment using a 1% Cl_2, 0.2% N_2 mixture in argon is shown in Figure 1a, and the product bands are listed in Table I. The multiplet with the most intense component at 823.5 cm^{-1} is in agreement with the spectrum of NCl in solid argon[14] produced by photolysis of N_3Cl. The weak 838-cm^{-1} band and a stronger absorption near 1820 cm^{-1} are due to phosgene.[15] The weak 788-cm^{-1} absorption is due to CCl_4 produced by reaction of trace carbon impurity with chlorine in the discharge tube. The strong absorption at 697 cm^{-1} is due to the HCl_2^- anion,[16] and the 618- and 586-cm^{-1} absorptions are contributed by $SiCl_4$ and $SiCl_3$, respectively, from the reaction of chlorine with the discharge tube.[17,18] The weak 570-cm^{-1} absorption and a stronger band at 1875 cm^{-1} are due to the ClCO free radical.[19] Of particular interest here is the sharp, strong new absorption at 679 cm^{-1}. The sample was warmed to 46 ± 2 K to allow diffusion and reaction of trapped chlorine atoms, and changes in product band absorbances can be seen by comparison of absorbances given in Table I. In conclusion, the NCl multiplet and new 679- and 586-cm^{-1} bands decreased markedly on sample warming whereas new bands at 687.5 and 646 cm^{-1} markedly increased. In a 2% nitrogen–1% chlorine discharge experiment, the deposited sample was photolysed by a water-filtered high-pressure mercury arc; the 646-cm^{-1} band was increased by 50%, the 788-cm^{-1} band was increased slightly, the 829 cm^{-1} band was decreased slightly, and the other absorptions were unchanged. The production of HCl_2^- in this experiment was markedly reduced.

Table I. Infrared Absorptions in Argon/Nitrogen/Chlorine Discharge Experiments

$^{14}N_2$[a]			^{15}N-enriched N_2[b]			
ν, cm^{-1}	A (15 K)[c]	A (46 K)[d]	ν, cm^{-1}	A (15 K)[c]	A (46 K)[d]	ident
850	0.08	0.18	850	0.02	0.12	aggregate
838	0.08		838	0.05	0.01	Cl_2CO
829	0.06	0.04	829	0.05	0.05	NCl
823.5	0.20	0.01	823.5	0.18		$^{14}N^{35}Cl$
817.2	0.06		817.2	0.05		$^{14}N^{37}Cl$
815	0.05					NCl
			809	0.07	0.07	^{15}NCl
			803.6	0.24		$^{15}N^{35}Cl$
			797.3	0.07		$^{15}N^{37}Cl$
788	0.06	0.05				CCl_4
697	0.28	0.11	697	0.15	0.09	HCl_2^-
687.5	0.03	0.13	687.0	0.02	0.10	$[(^{14}NCl_2)_2]$
679	0.26	0.02	679.1	0.24	0.03	$^{14}NCl_2$
			669.5		0.16	$[(^{15}NCl_2)_2]$
			661.9	0.39	0.07	$^{15}NCl_2$
646	0.10	0.20	646	0.04	0.05	$^{14}NCl_3$
			629	0.05	0.07	$^{15}NCl_3$
618	0.18	0.30	618	0.07	0.12	$SiCl_4$
586	0.25	0.03	586	0.08		$SiCl_3$
571	0.05		571	0.12		ClCO
565		0.15	565		0.1	aggregate
535		0.15	535		0.1	aggregate

[a] Figure 1a. [b] Figure 1b. [c] Initial absorbance at 15 K. [d] Absorbance after temperature cycle to 46 K.

A 2% chlorine sample in nitrogen was discharged and condensed at 15 K. The spectrum contained N_2O absorptions[20] at 590, 1291, and 2236 cm^{-1}, a weak phosgene band at 835 cm^{-1}, the NCl multiplet with the most intense feature at 826 cm^{-1} (A = 0.12), new bands at 684 (A = 0.07) and 645 (A = 0.04), and $SiCl_4$ at 618 cm^{-1}; HCl_2^- was absent from the spectrum.

The best experiment with nitrogen-15 (60%) utilized a 1% Cl_2, 0.5% N_2 mixture; the spectrum is shown in Figure 1b, and

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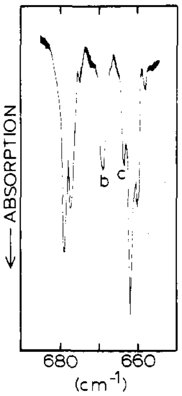

Figure 2. Expanded scale spectrum from 655 to 685 cm^{-1} with use of 0.5-cm^{-1} spectral slit width and 3 cm^{-1}/min scan speed for $Ar/Cl_2/N_2$ = 200/2/1 sample with 60% ^{15}N enrichment.

Table II. Infrared Absorptions in Argon/Nitrogen/Bromine Discharge Experiments

ν, cm^{-1}	125/1/1 concn[a]	100/1/2 concn[a]	Δ[b]	ident
728	0.06	0.0	dec	HBr_2^-
690	0.16	0.01	dec	NBr
679	0.09	0.07	dec	NBr
618	0.02	0.25	inc	$[(NBr_2)_2]$
603.5	0.37	0.55	dec	NBr_2
563	0.02	0.20	inc	aggregate
535	0.17	0.03	dec	?
523		0.2	con	?
497		1.0	inc	$SiBr_4$
315		1.0	inc	aggregate

[a] Absorbance units in experiment with concentrations. [b] Behavior on sample warming to 46 ± 2 K: dec = decrease, inc = increase, con = constant.

the new bands are listed in Table I. Obvious ^{15}N counterparts were observed at 803.6 and 797.3 cm^{-1} for the ^{14}NCl doublet at 823.5 and 817.2 cm^{-1}, at 662 cm^{-1} for the 679-cm^{-1} band, and at 629 cm^{-1} for the 646-cm^{-1} absorption. The expanded scale spectrum, recorded at reduced slit width and slow scanning speed, for the new product multiplet at 679 cm^{-1} is shown in Figure 2. Each nitrogen isotopic multiplet clearly exhibits a 9/6/1 relative intensity triplet appropriate for the vibration of two equivalent chlorine atoms. The components in the ^{14}N triplet were measured at 679.1, 677.4, and 675.8 ± 0.2 cm^{-1}, and the ^{15}N components were 661.9, 660.2, and 657.9 ± 0.2 cm^{-1}. Sample warming to 46 ± 2 K, illustrated in Figure 1c, had the same general effect as in the normal isotopic experiments. The band that increased markedly at 687.0 cm^{-1} exhibited a ^{15}N counterpart at 669.5 cm^{-1}.

Nitrogen–Bromine System. Four similar experiments were performed with the nitrogen–bromine–argon discharge system. The spectrum from an experiment using a 1/1/125 mixture is illustrated in Figure 3a, and the product absorptions are listed in Table II. A 728-cm^{-1} band (not shown) is due to the HBr_2^- anion.[21] The 690, 679 cm^{-1} doublet is in agreement with the spectrum of NBr produced from photolysis of N_3Br.[14] A sharp new product band was observed at 603.5 cm^{-1}. A similar experiment was performed with a 2% Br_2, 1% N_2 mixture; the band absorbances are also listed in Table II. Sample warming destroyed the NBr bands and the sharp 603.5-cm^{-1} feature and increased the 618-cm^{-1} band and other absorptions identified as aggregates in the table. The best experiment with ^{15}N is illustrated in Figure 3b; ^{15}N counterparts of the NBr multiplet were observed at 670 and 660 cm^{-1}; and the sharp 603.5-cm^{-1} band exhibited a ^{15}N counterpart at 585.8 cm^{-1}. The 523-cm^{-1} band and the 497-cm^{-1} absorption due to $SiBr_4$[22] were also observed in the 2% Br_2, 1% $^{14}N_2$ study.

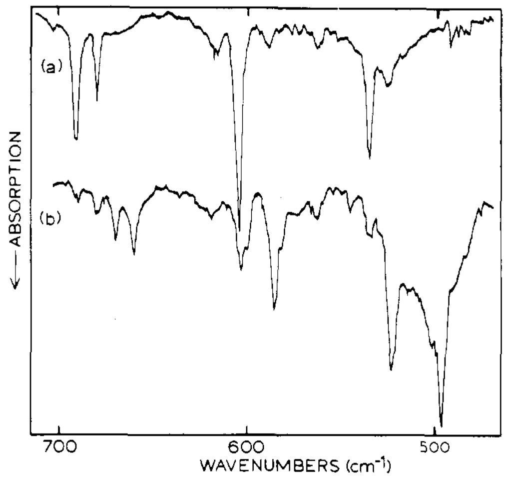

Figure 3. Infrared spectra in the 480–700-cm^{-1} region for a sample prepared by flowing argon/bromine/nitrogen mixtures through a microwave discharge and condensing the resulting mixture at 15 K: (a) $Ar/Br_2/N_2$ = 125/1/1; (b) $Ar/Br_2/N_2$ = 100/1/1, 60% ^{15}N enrichment.

Discussion

The new absorptions will be identified, and structure and bonding in the NCl_2 free radical will be considered.

Identification. The sharp new 679-cm^{-1} absorption exhibits isotopic components at 679.1, 677.4, and 675.8 cm^{-1} with the approximate 9/6/1 relative intensity ratios appropriate for a vibration of two equivalent chlorine atoms (Figure 2). The observation of two strong 679.1- and 661.9-cm^{-1} bands with the ^{15}N-enriched sample demonstrates the involvement of a single nitrogen atom in the vibrational mode. The molecular species responsible for the sharp 679-cm^{-1} absorption is, therefore, identified as the NCl_2 free radical. The substantial decrease of this absorption on sample warming is consistent with its identification as a reactive species. The strong 679-cm^{-1} absorption is ν_3, the antisymmetric N–Cl stretching mode. On the basis of the similar CCl_2 species,[23] the ν_1 mode will be substantially weaker and near 650 cm^{-1}, where it is probably obscured by other absorptions in the spectrum.

The NCl radical is probably formed from the elements in the argon discharge. The dichloroamine free radical is probably formed by diffusion and reaction of chlorine atoms, from the discharge stream, with NCl on the matrix surface during sample condensation (reaction 1).

$$NCl + Cl \rightarrow NCl_2 \qquad (1)$$

The 646-cm^{-1} absorption exhibits a ^{15}N counterpart at 629 cm^{-1}, which suggests a nitrogen–chlorine product. Based on agreement with the 652-cm^{-1} gas-phase ν_3 fundamental of NCl_3,[24] the 646-cm^{-1} argon matrix band is assigned to NCl_3. This absorption grows on sample warming, presumably from the diffusion and reaction of trapped chlorine atoms with NCl_2, and it grows on photolysis at the expense of the 829-cm^{-1} site of NCl, presumably due to the photolysis reaction of nearby NCl and Cl_2 reagents. It is perhaps surprising that NCl_3 survives mercury arc photolysis, particularly in view of its thermodynamic instability;[10] however the matrix cage may retain the photofragments for recombination.

The 687.5-cm^{-1} absorption, present as a weak band in the initial sample deposit, increased a factor of 4 and retained its

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sharp band contour upon sample warming to 46 ± 2 K. This evidence suggests a new well-defined higher species such as $(NCl)_2$ or $(NCl_2)_2$, whose fluorine analogues are known.[25] The $^{14}N/^{15}N$ ratio of 1.0269 is suggestive of an antisymmetric $N-Cl_2$ vibration that requires more nitrogen involvement (for NCl_2 the isotopic ratio is 1.0260) rather than a simple N–Cl vibration (for NCl the isotopic ratio is 1.0248). In the $(NCl_2)_2$ species the N–N single bond is expected to be weak such that the vibrations of each NCl_2 subgroup cannot significantly couple. Accordingly the $^{14}NCl_2{}^{15}NCl_2$ species is not resolved from the $^{14}N_2Cl_4$ species. (The absorption at 687.0 cm^{-1} in the 60% ^{15}N experiment may reveal this weak coupling if the 0.5-cm^{-1} displacement is not due to scatter in the data.) This conclusion is consistent with the spectrum of the $^{12}CCl_2{}^{13}CCl_2$ isotopomer in a 51% ^{13}C-enriched experiment.[23] Even with a double bond between CCl_2 submolecules, the outside components (913, 911 cm^{-1} and 881, 878 cm^{-1}) are separated by only 2–3 cm^{-1}. The 687.5-cm^{-1} band is tentatively identified as $(NCl_2)_2$; the growth on sample warming to 46 ± 2 K is reminescent of earlier experiments[23] with CCl_2, which was converted to C_2Cl_4 upon sample warming to 47 ± 2 K.

The NCl absorption multiplet was first identified by Milligan and Jacox[14] from photolysis of N_3Cl in solid argon. The present observation of the ^{15}N counterpart strengthens the earlier assignment. Three different $^{14}N^{35}Cl$ fundamental sites were observed at 829, 823.5, and 815 cm^{-1}. The 829-cm^{-1} site is apparently more stable as it was little affected by sample warming that almost destroyed the other two sites. Recent laser-induced fluorescence studies in this laboratory[6] identified at least three sites of NCl in solid argon; the major site exhibited a fundamental at 825.0 cm^{-1} in agreement with the present absorption measurement of 823.5 cm^{-1} within experimental error. In the emission work, each site and isotope was selectively excited by a tunable laser and its fluorescence spectrum observed independent of the other sites and isotopes. The excitation spectrum (Figure 6 of ref 6) shows that the site structure in the excited electronic state is similar to that of the ground state recorded here by infrared absorption.

By analogy with NCl_2 below the NCl fundamental, the sharp 603.5-cm^{-1} band below the NBr fundamental is assigned to NBr_2. This assignment is supported by the large ^{15}N shift and the disappearance of the 603.5-cm^{-1} band with marked growth of the 618-cm^{-1} absorption. Following a similar rationale to that presented above, the 618-cm^{-1} absorption is tentatively assigned to $(NBr)_2$.

The 690- and 679-cm^{-1} sites for NBr are in agreement with the results of Milligan and Jacox.[14] Laser-induced fluorescence studies again found evidence for three sites of NBr in solid argon; the major site exhibited a 685-cm^{-1} ground-state fundamental[6] intermediate between the two sites observed by infrared absorption.

The remaining absorptions in these experiments cannot be identified without additional information. The 535-cm^{-1} band in Figure 3a was weak in subsequent N_2-Br_2 experiments which produced a substantial yield of $SiBr_4$. The broad bands that grow upon sample warming are identified as aggregates.

Structure and Bonding. The sharp 679.1-cm^{-1} band is assigned to the ν_3 mode of NCl_2 on the basis of its intensity and ^{15}N isotopic shift. In fact the valence angle can be calculated to a very good approximation from apex and terminal atom isotopic data for a C_{2v} molecule.[26] The 15–35/15–37 and 14–35/14–37 isotopic data give 119.6 and 119.2° upper limits to the valence angle, and the 14–35/15–35 and 14–37/15–37 isotopic fundamentals give 102.7 and 102.1° lower limits. The mean value 111° averages the differences in anharmonicity between the isotopes and provides a reliable estimate of the NCl_2 valence angle as calculations for ozone demonstrate.[27,28] The 111 ± 4° value for the NCl_2 valence angle determined from matrix data is in excellent agreement with the 110° value from SCF–MO calculations.[11] The sharp ν_3 fundamentals for $^{14}NBr_2$ and $^{15}NBr_2$ predict a lower limit of 99.6° for the valence angle. On the basis of the above discussion for NCl_2, the valence angle of NBr_2 is approximately the same as the valence angle of NCl_2.

The ν_3 fundamentals of CCl_2, NCl_2, and OCl_2 in solid argon are 746, 679, and 671 cm^{-1} and the valence angles are 106 ± 4, 111 ± 4, and 110°.[29,30] The lower fundamentals for NCl_2 and OCl_2 are consistent with their being less stable compounds than chlorocarbons. The p-orbital spin densities for NCl_2 radical from ESR studies (0.22 on Cl, 0.57 on N)[10] show substantial delocalization in the π-orbital system, which is antibonding, again suggesting weaker bonding in NCl_2 than, for example, in CCl_2.

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Registry No. NCl_2, 25938-83-4; NBr_2, 77318-96-8.

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