

Matrix Isolation Study of the Reaction of CrCl_2O_2 with NH_3 : Synthesis and Characterization of $\text{ClCr(O)}_2\text{NH}_2$

Susan R. Anderson and Bruce S. Ault*

Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnati, Ohio 4522-0172

Received: September 24, 2001; In Final Form: November 28, 2001

Initial and secondary intermediates in the reaction of CrCl_2O_2 with NH_3 have been characterized by matrix isolation infrared spectroscopy and density functional calculations. Twin-jet co-deposition of these two reagents led to a series of infrared absorptions that are assigned to the 1:1 molecular complex between these two species. The shift of ν_2 of NH_3 in the complex was $+218\text{ cm}^{-1}$, indicating that CrCl_2O_2 is a moderately strong Lewis acid. Irradiation of these matrices with light of $\lambda > 300\text{ nm}$ led to complete destruction of the complex and the growth of a number of new bands. These are assigned to the $\text{ClCr(O)}_2\text{NH}_2$ species, as well as to HCl arising from destruction of the complex. Identification of these species was supported by isotopic labeling (^{15}N and ^2H), as well as by B3LYP/6-311G+(2d,3p) density functional calculations. Good agreement was observed between the experimental and computed frequencies.

Introduction

High-valent transition metal oxo compounds, including OVCl_3 and CrCl_2O_2 , have been used on many occasions as potent yet selective oxidizing agents in organic synthesis.^{1,2} However, the high reactivity of these systems have prevented researchers in many cases from determining the mechanistic details of these oxidation reactions. In contrast, several detailed theoretical studies^{3–7} have explored such systems and postulated the existence of multiple intermediates in model systems involving high-valent transition metal oxo compounds. While the reactions of CrCl_2O_2 with a number of small molecules are known, the reaction of CrCl_2O_2 with NH_3 has not been reported to date, although substantial reactivity might be anticipated based on related studies.

The matrix isolation technique^{8–10} was developed to facilitate the isolation and spectroscopic characterization of reactive intermediates. This approach has been applied to the study of a wide range of species, including radicals, weakly bound molecular complexes, and molecular ions. Recent studies^{11–14} from this laboratory have focused on the sequence of intermediates formed in the reactions of OVCl_3 and CrCl_2O_2 with small organic substrates, and the thermal and photochemical reaction of OVCl_3 with NH_3 , leading to the $\text{Cl}_2\text{V(O)NH}_2$ intermediate species, was recently reported.¹⁵ While CrCl_2O_2 is generally somewhat less reactive than OVCl_3 , the origins of the differences between these two compounds is not clear. Consequently, a study was undertaken to identify and characterize initial and secondary intermediates in the reaction of CrCl_2O_2 with NH_3 and to compare this system to the previously studies $\text{OVCl}_3/\text{NH}_3$ system. Density functional calculations were also carried out in support of the experimental observations.

Experimental Details

All of the experiments in this study were carried out on conventional matrix isolation apparatus that has been described.¹⁶ Chromyl chloride, CrCl_2O_2 (Aldrich), was introduced into the vacuum system as the vapor above the room-temperature

liquid, after purification by freeze–pump–thaw cycles at 77 K. NH_3 (Matheson). $^{15}\text{NH}_3$ (99% ^{15}N) and ND_3 (99% D) (both Cambridge Isotope Laboratory) were introduced from lecture bottles into a separate vacuum manifold and were purified by repeated freeze–pump–thaw cycles at 77 K. Argon and nitrogen (Wright Brothers) were used as the matrix gas in different experiments and were used without further purification.

Matrix samples were deposited in both the twin-jet and merged-jet modes. In the former, the two gas samples were deposited from separate nozzles onto the 14 K cold window, allowing for only a very brief mixing time prior to matrix deposition. A number of these matrices were subsequently warmed to 33–35 K to permit limited diffusion and then recooled to 14 K and additional spectra recorded. In addition, most of these matrices were irradiated for 1.0 or more hours with the $\text{H}_2\text{O/Pyrex}$ filtered output of a 200 W medium-pressure Hg arc lamp, after which additional spectra were recorded.

Several experiments were conducted in the merged-jet mode,¹⁷ in which the two deposition lines were joined with an UltraTorr tee at a distance from the cryogenic surface, and the flowing gas samples were permitted to mix and react during passage through the merged region. The length of this region was variable; lengths between 15 and 90 cm were employed. In both twin and merged jet, matrices were deposited at the rate of 2 mmol/h from each sample manifold onto the cold window. Final spectra were recorded on a Perkin-Elmer Spectrum 2000 or a Bruker 113 Fourier transform infrared spectrometer at 1 cm^{-1} resolution.

Theoretical calculations were carried out on likely intermediates in this study, using the Gaussian 94 suite of programs.¹⁸ Density functional calculations using the Becke B3LYP functional were used to locate energy minima, determine structures, and calculate vibrational spectra. Final calculations with full geometry optimization employed the 6-311G+(2d, 3p) basis set, after initial calculations with smaller basis sets were run to approximately locate energy minima. Calculations were carried out on a Silicon Graphics Indigo 2 workstation.

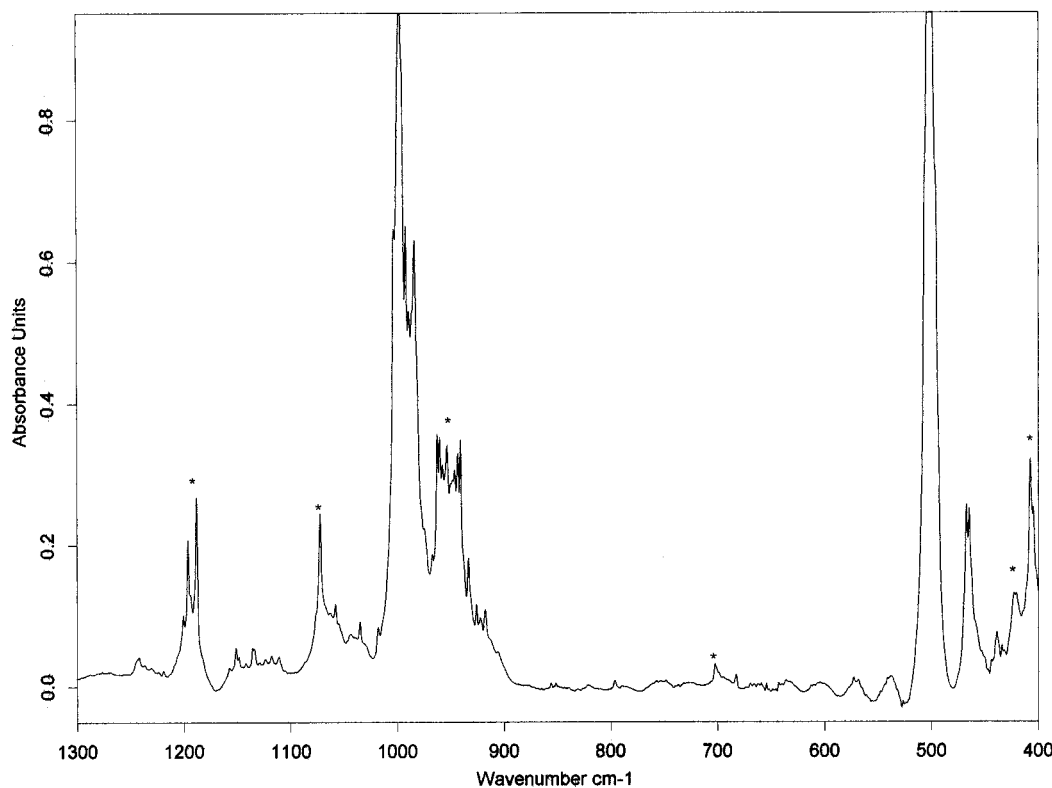


Figure 1. Infrared spectrum, between 400 and 1300 cm^{-1} , of the matrix formed by the twin-jet co-deposition of a sample of $\text{Ar}/\text{NH}_3 = 250$ with a sample of $\text{Ar}/\text{CrCl}_2\text{O}_2 = 150$. Bands marked with an * are not present in the blank spectra of the reagents, and are due to the 1:1 complex.

Results

Prior to any co-deposition experiments, blank experiments were run on each of the reagents used in this study. In each case, the blanks were in good agreement with literature spectra^{19–21} and with blanks run previously in this laboratory. The actual $^{15}\text{N}/^{14}\text{N}$ ratio in the $^{15}\text{NH}_3$ blank, as determined by relative parent band intensities, was approximately $2/1$, while in the ND_3 experiments the D/H ratio was approximately $4/1$, after extensive conditioning. Each blank experiment was then irradiated by the $\text{H}_2\text{O}/\text{Pyrex}$ filtered output of a 200 W Hg arc lamp for 1.0 h. No changes were observed in any of the blank spectra as a result of irradiation. Weak bands due to HCl impurity were noted in all of the CrCl_2O_2 blank experiments.²²

$\text{CrCl}_2\text{O}_2 + \text{NH}_3$. In an initial twin-jet experiment, a sample of $\text{Ar}/\text{NH}_3 = 250$ was co-deposited with a sample of $\text{Ar}/\text{CrCl}_2\text{O}_2 = 150$. A number of new, moderately intense infrared bands were seen in the resulting infrared spectrum, at 407, 427, 702, 950 (multiplet), 1072, 1188, 1196, 1589, 1600, 3295, 3401, and 3407 cm^{-1} (hereafter referred to as set A), as shown in Figure 1. Several groups of these bands appeared as site split pairs (e.g., 1188, 1196 and $3401, 3407\text{ cm}^{-1}$). This matrix was then irradiated with the $\text{H}_2\text{O}/\text{Pyrex}$ filtered output of a medium-pressure Hg arc lamp for 1.0 h ($\lambda > 300\text{ nm}$), and additional spectra were then recorded. The above set A bands were dramatically reduced, to about 25% of their initial intensity. At the same time, numerous new bands grew in as a result of irradiation, at 431, 546, 558, 733, 755, 1009, 1450, 2733, 2764, 3307, 3337, and 3437 cm^{-1} , as shown in Figures 2 and 3. The 1450 cm^{-1} was very broad, while the 3437 cm^{-1} appeared as a sharp triplet and several appeared as site split doublets (e.g., 546, 558 and 733, 755 cm^{-1}). These new bands will hereafter referred to as set B.

Numerous additional experiments were conducted, depositing these two reagents into argon matrices at different concentra-

tions, using twin-jet deposition. The same results were obtained throughout. The set A bands were formed upon initial deposition; these bands maintained a constant intensity ratio with respect to one another in all of these experiments. The set A bands were diminished greatly by Hg arc irradiation, while bands of set B grew in. The bands of set B maintained a constant intensity ratio with respect to one another in all of these experiments.

NH_3 is known to undergo hindered rotation in solid argon,²⁰ leading to a complex spectrum in the regions of the NH_3 fundamentals. This rotation is quenched in N_2 matrices,²¹ leading to a simpler spectrum. Consequently, several twin-jet experiments employing samples of $\text{N}_2/\text{CrCl}_2\text{O}_2$ and N_2/NH_3 were carried out. The results were very similar to those reported above in solid argon, with a nitrogen matrix counterpart to each of the set A and set B bands, while no new bands were observed. However, the bands in N_2 matrices tended to be somewhat broader than those in argon. Consequently, no additional nitrogen matrix experiments were carried out.

Several merged-jet experiments were also carried out with these two reagents and argon as the matrix gas. In the first, the merged region was 90 cm in length, and the region was held at room temperature. At the conclusion of the first experiment, no product bands were observed. In addition, no parent bands of NH_3 were seen, and the bands of parent CrCl_2O_2 were relatively weak (certainly much weaker than in the blank spectra). In the second experiment, identical conditions were employed. However, in this experiment a spectrum was recorded after 10 h of deposition. This spectrum was very similar to that in the first experiment, with no product bands, no NH_3 parent bands, and weak CrCl_2O_2 parent bands. The flow of $\text{Ar}/\text{CrCl}_2\text{O}_2$ was then stopped, while the flow of Ar/NH_3 was allowed to continue for an additional 10 h (to verify that the sample was

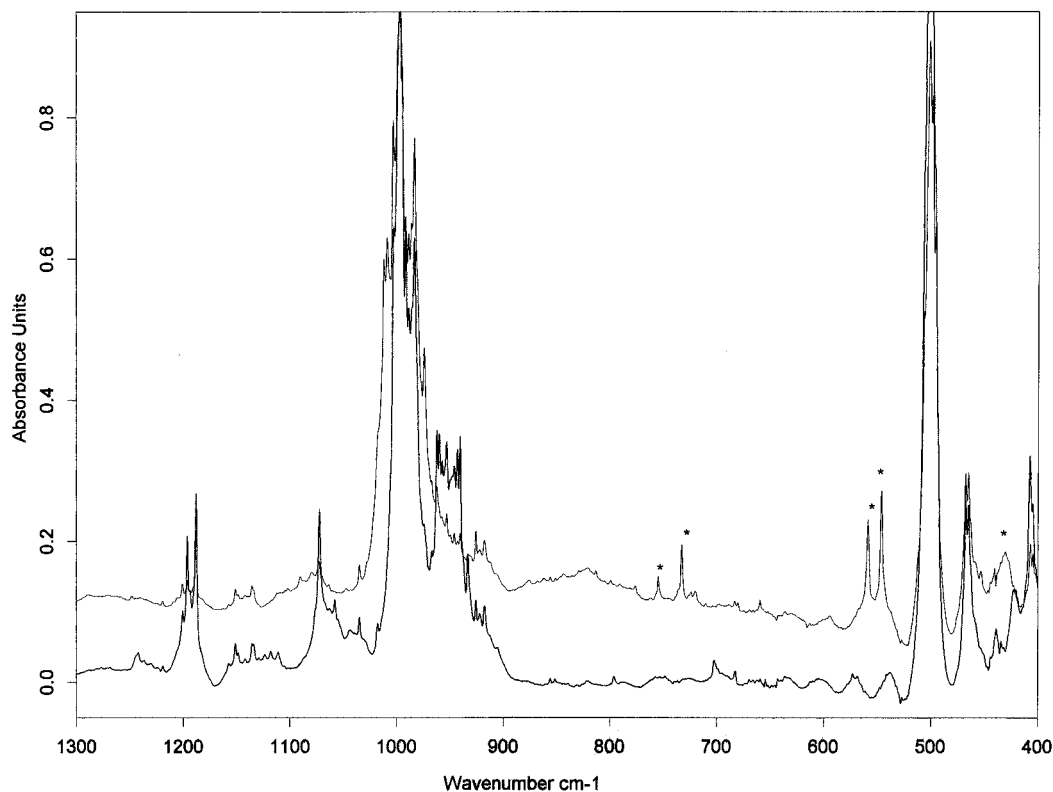


Figure 2. Comparison of the spectra, between 400 and 1300 cm^{-1} , of the matrix formed by the twin-jet co-deposition of a sample of $\text{Ar}/\text{NH}_3 = 250$ with a sample of $\text{Ar}/\text{CrCl}_2\text{O}_2 = 150$ (lower trace) and the same matrix after 1.0 h irradiation with the H_2O /Pyrex-filtered output of a medium-pressure Hg arc (upper trace). Bands marked with an * are produced as a result of irradiation.

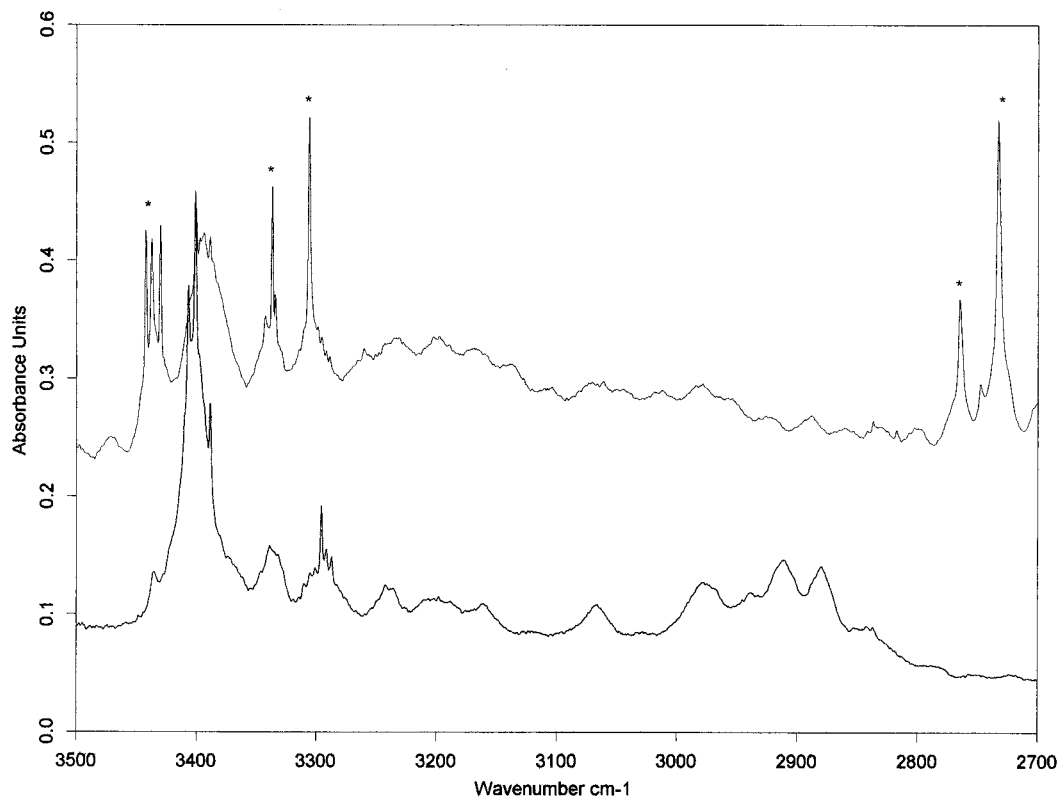


Figure 3. Comparison of the spectra, between 2700 and 3500 cm^{-1} , of the matrix formed by the twin-jet co-deposition of a sample of $\text{Ar}/\text{NH}_3 = 250$ with a sample of $\text{Ar}/\text{CrCl}_2\text{O}_2 = 150$ (lower trace) and the same matrix after 1.0 h irradiation with the H_2O /Pyrex-filtered output of a medium-pressure Hg arc (upper trace). Bands marked with an * are produced as a result of irradiation.

prepared properly and did contain NH_3). The spectrum recorded at the conclusion of this second 10 h segment showed strong bands due to parent NH_3 . An additional merged-jet experiment

was conducted using a short, 15 cm merged region. Essentially identical results were obtained. In all of these merged-jet experiments, growth of bands due to HCl was not observed.

TABLE 1: Band Positions and Assignments for the 1:1 Complex $\text{CrCl}_2\text{O}_2\text{:NH}_3$ in Solid Argon

$\text{CrCl}_2\text{O}_2\text{:NH}_3$	$\text{CrCl}_2\text{O}_2\text{:}^{15}\text{NH}_3$	$\text{CrCl}_2\text{O}_2\text{:ND}_3$	assignment
407 cm^{-1}	406	404	— CrCl_2 sym. st.
427	427	421	— CrCl_2 asym. st.
702	698		NH_3 rock
950 ^a	950 ^a	951 ^a	CrO_2 asym. st.
1072	1072		CrO_2 sym. st.
1188, 1196	1182, 1190		ν_2 , NH_3
1589, 1600	1589		ν_4 , NH_3
3295	3290	2541	ν_1 , NH_3
3401, 3407	3392		ν_3 , NH_3

^a — multiplet.**TABLE 2: Band Positions and Assignments^a for Argon Matrix Isolated $\text{ClCr}(\text{O})_2\text{NH}_2$**

$\text{ClCr}(\text{O})_2\text{NH}_2$	$\text{ClCr}(\text{O})_2^{15}\text{NH}_2$	$\text{ClCr}(\text{O})_2\text{ND}_2$	assignment
431	431		Cr—Cl stretch
546, 558 cm^{-1}	543		— NH_2 wag
733, 755	719, 732		Cr—N stretch
1009	1008	1008	— CrO_2 asym. st.
1486	1480		— NH_2 bend
3306, 3337	3331	2443	— NH_2 sym. st.
3437 ^a		3423	— NH_2 asym. st.

^a — multiplet.

Isotopic Studies. Several twin-jet experiments were conducted employing samples of $\text{Ar/CrCl}_2\text{O}_2$ and $\text{Ar/}^{15}\text{NH}_3$. As noted above, bands due to residual $^{14}\text{NH}_3$ were present as well, although weaker than the $^{15}\text{NH}_3$ bands. Upon initial deposition, bands analogous to the set A bands described above were seen at 406, 429, 698, 1072, 1182, 1190, 1589, 3290, and 3392 cm^{-1} , as well as weak ^{14}N product bands at 702, 1196, 1600, 3295, and 3407 cm^{-1} . The relative intensities were in the same ratio as in the $^{14}\text{NH}_3$ experiments described above. Irradiation of these matrices led to complete destruction of these product bands, and the growth of new bands corresponding to the sets B bands described above. Set B ^{15}N bands were located at 431, 543, 719, 732, 1008, 1072, 1480 (br), 2733, 2764, 3331, and 3437 cm^{-1} . Additional experiments with this pair of reagents at different sample concentrations led to very similar results.

Several experiments were conducted using samples of Ar/ND_3 . Due to rapid exchange, these samples contained a statistical distribution of ND_3 , ND_2H , NDH_2 , and NH_3 . This, combined with rotational substructure to the vibrational transitions, led to a rather complicated spectrum, relative to the NH_3 experiments. In addition, the total absorption intensity was distributed over different species, leading to weaker bands; also, an N—D oscillator has approximately an absorption coefficient that is about 50% of an N—H oscillator, weakening the product spectrum further. Consequently, shifted bands due to deuterium substitution were seen for some but not all of the product bands. Shifted product bands were observed at 404, 421, 952 (multiplet), and 2541 cm^{-1} upon initial twin-jet deposition (i.e., set A bands). Irradiation of these matrices led to destruction of these bands, and growth of bands at 686, 720, 1008, 1979, 1983, 2443, 2733, and 2764 cm^{-1} . These bands, while weak, were reproducible in the several experiments that were conducted. Set A bands for all isotopes are listed in Table 1, while set B bands are collected in Table 2.

Computational Results

The discussion section to follow will demonstrate that the photoproduct bands at 2733 and 2764 cm^{-1} with NH_3 and 1979 and 1983 cm^{-1} with ND_3 are due to the formation of HCl upon irradiation. On the basis of this fact and previous findings,^{11–15}

TABLE 3: Key Computed Structure Parameters

parameter	$\text{ClCr}(\text{O})_2\text{NH}_2$	$\text{Cr}(\text{O})_2\text{NH}$
$R(\text{Cr—Cl})$	2.16 Å	—
$R(\text{Cr=O})$	1.56	1.58 Å
$R(\text{Cr—N})$	1.71	1.67
$R(\text{N—H})$	1.04	1.02
$\alpha(\text{O—Cr—O})$	109.1°	119.7°
$\alpha(\text{Cl—Cr—O})$	108.8	—
$\alpha(\text{H—N—H})$	113.4	—
spin multiplicity	1	1

the two HCl elimination products, $\text{ClCr}(\text{O})_2\text{NH}_2$ and $\text{Cr}(\text{O})_2\text{NH}$, are two potential intermediates in this system. Both were studied using density functional methods (B3LYP) and the 6-311G+(d,2p) basis set. Both species optimized to stable minima, with a positive vibrational frequencies. The optimized structures for both are presented in Table 3, while the computed vibrational spectrum (above 400 cm^{-1}) is presented, along with computed isotopic shifts in Table 4. In Table 4, comparison to the observed spectral features is made as well.

Discussion

Numerous product bands and several product species were isolated in the reaction of CrCl_2O_2 with NH_3 under a range of reaction conditions. As noted above, the product bands can be grouped into sets A, B, and C, based on the conditions under which they appeared and the fact that bands within a given set maintained a constant intensity ratio with respect to other bands in that set. It is also apparent that the different product species are formed in sequence, i.e., that sets B and C are formed at the same time that set A bands are destroyed. The identity of the species responsible for each set of product bands will be discussed, supported by the results of ab initio calculations and followed by an overview of the mechanism of reaction.

Initial Intermediate. The bands in set A were formed under the conditions of shortest reaction time and lowest reaction temperature, namely, in the twin-jet deposition experiments where mixing of the two reactants occurs on the surface of the condensing matrix. This indicates the species A is the initial intermediate in the reaction between CrCl_2O_2 and NH_3 . It is also noteworthy that each of these bands (except for the band at 702 cm^{-1}) was observed relatively near a parent mode of either CrCl_2O_2 or NH_3 . For example, the 407 and 427 cm^{-1} bands are shifted from the parent CrCl_2 stretching modes near 500 and 470 cm^{-1} , while the 3295 and 3401/3407 cm^{-1} bands lie near the NH_3 stretching modes of ammonia. Further, the isotopic dependence of each of the set A bands mirrored closely the isotopic dependence of the nearby parent mode. These observations are indicative of the formation of a molecular complex between the two reacting species, where each subunit is perturbed in the complex, yet maintains its molecular identity.²³ On this basis, the bands in set A are assigned to a molecular complex between CrCl_2O_2 and NH_3 and its isotopomers in argon and nitrogen matrices.

The stoichiometry of the complex is not as readily determined. However, the observation of only a single product after co-deposition over a wide range of concentrations suggest that the stoichiometry is 1:1. Certainly, it would be difficult to envision formation of higher complexes (e.g. 2:1 or 1:2) without also forming the 1:1 complex. The observation of a single product argues against this, and for the formation of the 1:1 complex. Consequently, the set A bands described above are assigned to the 1:1 molecular complex between CrCl_2O_2 and NH_3 . This species represents the initial intermediate in the reaction between these two compounds.

TABLE 4: Computed ($>400\text{ cm}^{-1}$) and Observed Frequencies for $\text{ClCr}(\text{O})_2\text{NH}_2$ in Argon Matrices

computed	$\text{ClCr}(\text{O})_2\text{NH}_2$			$\text{ClCr}(\text{O})_2^{15}\text{NH}_2$		$\text{ClCr}(\text{O})_2\text{ND}_2$		assignment
	intensity	scaled	expt.	comp. shift	expt. shift	comp. shift	expt. shift	
427	0.12	414		0		-98		NH ₂ wag
444	25.2	431	431	-1	-1	-58		Cr-N stretch
512	178	497	552	-3	-3	-32		NH ₂ wag
707	2	686		-4		-161		NH ₂ rock
764	77.4	741	744	-15	-18	-49		Cr-N stretch
1083	100.9	1051		0		-3		CrO ₂ sym. stretch
1103	199.1	1070	1009	0	-1	-2	-1	CrO ₂ antisym. st.
1527	41.9	1481	1450	-6	^a	-372		NH ₂ bend
3536	136.7	3430	3322	-5	-6	-984		NH ₂ sym. stretch
3650	59	3540	3437	-11	-10	-954	-994	NH ₂ antisym. st.

computed	$\text{Cr}(\text{O})_2\text{NH}$			$\text{Cr}(\text{O})_2^{15}\text{NH}$		$\text{Cr}(\text{O})_2\text{ND}$		assignment
	intensity	scaled	expt.	comp. shift	expt. shift	comp. shift	expt. shift	
633	85	614	552	-3	-3	-138		Cr-N-H bend
751	92	728	744	-3	-18	-184		Cr-N-H bend
901	55	874		-23		-6		Cr=N stretch
1039	132	1008	1009	-1	-1	-2	-1	CrO ₂ sym. stretch
1093	249	1060		-1		-2		CrO ₂ antisym. st.
			1450		^a			
3422	46	3319	3322	-8	-6	-920		N-H stretch
			3437		-10		-994	

^a Band too broad to measure accurately.

Band assignments for the complex are generally straightforward, given the proximity of the product bands to corresponding parent absorptions. These assignments are collected in Table 1, for both the normal isotopic species and the labeled species. Of note is ν_2 , the symmetric deformation or "umbrella" mode of NH_3 . This mode has been shown many times to be extremely sensitive to complexation^{23,24} and to shift to higher energy upon complex formation. In hydrogen bonding interactions, this mode has been observed to shift 25–100 cm^{-1} to higher energy, while in a Lewis acid–base complex, shifts of up to 400 cm^{-1} to higher energy have been observed; shifts of 200 cm^{-1} are typical. In solid argon, the doublet at 1188 and 1196 cm^{-1} is readily assigned to ν_2 on the basis of the ^{15}N shift (4 cm^{-1}) which is identical to that of parent NH_3 and strong shift with deuteration. The shift of ν_2 , 218 cm^{-1} from the parent position of 974 cm^{-1} , demonstrates that CrCl_2O_2 is a moderately strong Lewis acid, although at room temperature in solution such complexes are themselves sufficiently reactive that they cannot be isolated.

Of interest also are the perturbations to ν_3 and ν_4 of NH_3 , the two doubly degenerate vibrational fundamentals, in the complex. In addition to shifting, each appears as a distinct doublet. The doublet structure (1589, 1600 and 3401, 3407 cm^{-1}) arises from the loss of the C_3 symmetry axis upon complexation to CrCl_2O_2 and the splitting of the degeneracy of these modes.

In addition, one new band was formed as a result of complexation, at 702 cm^{-1} , with a ^{15}N counterpart at 698 cm^{-1} . This band does not have its origins in a parent mode of either of the subunits in the complex. Rather, studies have shown that complexed NH_3 undergoes a rocking motion when complexed;²⁴ this motion has been observed²⁵ near 700 cm^{-1} for moderately strongly bound complexes of NH_3 . For comparison, this mode was observed¹⁵ at 692 cm^{-1} for the analogous complex $\text{OVCl}_3 \cdot \text{NH}_3$. This (and 5 lower frequency modes) arise from the loss of 3 translational and 3 rotational degrees of freedom upon complex formation. The others, including the Cr–N stretching mode, are expected to lie below the 400 cm^{-1} cutoff of the infrared spectrometer.

Photochemical Products. The 1:1 molecular complex is clearly very sensitive to ultraviolet irradiation, as bands due to this complex were destroyed by 1 h of irradiation with light of $\lambda > 300\text{ nm}$. Similar results were observed for a number of related complexes, including the $\text{OVCl}_3 \cdot \text{NH}_3$ complex and the $\text{CrCl}_2\text{O}_2 \cdot \text{O}(\text{H})\text{CH}_3$ complex. In each of these cases, it was shown conclusively that complex destruction occurred through HCl elimination, after absorption of a photon. The HCl produced in these systems, however, was trapped within the matrix cage with the second photoproduct ($\text{Cl}_2\text{V}(\text{O})\text{NH}_2$ and $\text{ClCr}(\text{O})_2\text{OCH}_3$, respectively). The HCl spectrum, then, was that of weakly hydrogen bonded HCl, with bands appearing near 2750 cm^{-1} shifted from isolated monomeric HCl which absorbs at 2863 and 2888 cm^{-1} in solid argon. Similar absorptions were seen in the present experiments, at 2733 and 2764 cm^{-1} in argon matrices (see Figure 3). These bands did not shift upon ^{15}N substitution but did shift to 1979 and 1983 cm^{-1} upon deuteration. This is precisely the isotopic dependence anticipated for HCl. In addition, the $\nu_{\text{H}}/\nu_{\text{D}}$ ratio of 2733/1979 = 1.38 is identical to that observed for both gas phase²⁴ and matrix isolated^{26,27} HCl, namely, 1.38. Given the isotopic behavior of these bands and the analogy to several well-established systems, the bands at 2733 and 2764 cm^{-1} are assigned to photoproduct HCl, arising from the decomposition of the initial 1:1 molecular complex. Further, the HCl that is produced is trapped within the same matrix cage, and weakly hydrogen bonded to the species responsible for the remainder of the set B bands.

As discussed below, species B contains a chloro, an oxo and an amide ligand, all of which are potential hydrogen bond acceptors. It is difficult to anticipate where the trapped HCl may interact, and indeed, a bifurcated or bridged structure might occur. The density functional calculations suggest that the nitrogen atom carries the greatest negative charge (−0.44 units), followed by the oxygen atoms (−0.17 units each) with the chlorine atom carrying a slight positive charge (+0.05 units). This suggests that the hydrogen bonding may take place at the amide group, but the evidence is limited.

Species B is clearly identified with the species resulting from an HCl elimination process from the molecular complex. In the previous studies of the $\text{OVCl}_3 + \text{CH}_3\text{SH}$, $\text{CrCl}_2\text{O}_2 + \text{CH}_3\text{OH}$

and $\text{OVCl}_3 + \text{CH}_3\text{OH}$ systems, only one HCl elimination product was possible. This was the product arising from the elimination of one HCl unit from the complex, yielding $\text{Cl}_2\text{V}(\text{O})\text{SCH}_3$, $\text{ClCr}(\text{O})_2\text{OCH}_3$ and $\text{Cl}_2\text{V}(\text{O})\text{OCH}_3$, respectively. However, in the present case, the possibility of the elimination of either one or two HCl units from the molecular complex is present, to yield $\text{ClCr}(\text{O})_2\text{NH}_2$ or $\text{Cr}(\text{O})_2\text{NH}$, respectively. The bands due to species B maintained a constant intensity ratio in all of the experiments, including different irradiation times and different sample concentrations. This suggests that only one product (other than HCl) is formed upon irradiation. The observation of two distinct, rather intense product bands in the N–H stretching region, the site-split doublet near 3307 and 3337 cm^{-1} and the triplet at 3437 cm^{-1} suggests strongly that the product contains two N–H bonds. This is further supported by the broad band near 1450 cm^{-1} . This region is often associated with the NH_2 bending mode in molecules containing this functionality; the breadth may also indicate that the HCl is hydrogen bonded to the amide group. Both of these observations suggest that the species responsible for the set B product bands is $\text{ClCr}(\text{O})_2\text{NH}_2$, weakly interact with HCl trapped in the same matrix cage. Certainly, no vibrational mode of $\text{Cr}(\text{O})_2\text{NH}$ is anticipated in the 1450 cm^{-1} region, and only one N–H stretch should be present.

The theoretical calculations also provide computed spectra and isotopic shifts for comparison to experiments. Table 4 compares the computed infrared band positions, intensities and isotopic shifts for both $\text{ClCr}(\text{O})_2\text{NH}_2$ and $\text{Cr}(\text{O})_2\text{NH}$ to the experimental band positions. The computed spectrum for $\text{Cr}(\text{O})_2\text{NH}$ contains only a single N–H stretching mode, and no bands in the region 1200–1600 cm^{-1} , supporting the argument above that $\text{Cr}(\text{O})_2\text{NH}$ cannot account for the experimental spectrum. Further, the Cr–N stretching mode for $\text{Cr}(\text{O})_2\text{NH}$ is predicted to lie between 875 and 900 cm^{-1} , far above the experimental band position of 744 cm^{-1} . In contrast, the Cr–N stretching mode for $\text{ClCr}(\text{O})_2\text{NH}_2$ is predicted near 750 cm^{-1} , with a ^{15}N shift of -15 cm^{-1} , in good agreement with the experimental shift of -18 cm^{-1} . Overall, the agreement between the experimental bands where observed and the computed spectrum and shifts for $\text{ClCr}(\text{O})_2\text{NH}_2$ is very good, and supports the identification of species B as $\text{ClCr}(\text{O})_2\text{NH}_2$. Band assignments are then given in Table 2.

Further Considerations. Several matrix isolation studies of the reaction mechanism of CrCl_2O_2 and OVCl_3 with small molecules all suggest that the first step in the reaction is the formation of a molecular complex,^{11–15} for those small molecules containing a heteroatom (N, O, P, S). This agrees with theoretical calculations as well.^{3,4} The second step in each system studied has been HCl elimination. In several cases, this

was observed to occur thermally, in a merged-jet system, while in other cases (including the present study), the reaction was photochemically induced. Like several previous systems, merged-jet experiments with CrCl_2O_2 and NH_3 led to complete reaction in the merged region, producing involatile products that deposited on the walls of the deposition system and did not survive transit to the cold window. Since a growth of bands due to HCl was not observed, formation of a involatile, stable 1:2 complex or higher aggregate is likely.

Acknowledgment. The National Science Foundation is gratefully acknowledged for support of this research, through Grant CHE 9877076.

References and Notes

- (1) Crans, D. C.; Chen, H.; Felty, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 4543.
- (2) Yajima, A.; Matsuzaki, R.; Saeki, Y. *Bull. Chem. Soc. Jap.* **1978**, *51*, 1098.
- (3) Deng, L.; Ziegler, T. *Organometallics* **1996**, *15*, 3011.
- (4) Deng, L.; Ziegler, T. *Organometallics* **1997**, *16*, 716.
- (5) Ziegler, T.; Li, J. *Organometallics* **1995**, *14*, 214.
- (6) Rappe, A. K.; Goddard, W. A., III. *Nature*, **1980**, *285*, 311.
- (7) Rappe, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 3287.
- (8) Craddock, S.; Hinchliffe, A. *Matrix Isolation*; Cambridge University Press: Cambridge, 1975.
- (9) Hallam, H. E. *Vibrational Spectroscopy of Trapped Species*; John Wiley: New York, 1973.
- (10) Andrews, L.; Moskovitz, M., Eds. In *Chemistry and Physics of Matrix Isolated Species*; Elsevier Science Publishers: Amsterdam, 1989.
- (11) Ault, B. S. *J. Am. Chem. Soc.* **1998**, *120*, 6105.
- (12) Ault, B. S. *J. Mol. Struct.* **2000**, *526*, 227.
- (13) Ault, B. S. *J. Phys. Chem. A* **1999**, *103*, 11474.
- (14) Ault, B. S. *J. Phys. Chem. A* **2000**, *104*, 11796.
- (15) Ault, B. S. *J. Phys. Chem. A* **2001**, *105*, 4758.
- (16) Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426.
- (17) Carpenter, J. D.; Ault, B. S. *J. Phys. Chem.* **1991**, *95*, 3502.
- (18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, M.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision E.1; Gaussian, Inc.: Pittsburgh, PA, 1995.
- (19) Varetti, E. L.; Muller, A. *Spectrochim. Acta* **1978**, *34A*, 895.
- (20) Abouaf-Marguin, L.; Jacox, M. E.; Milligan, D. E. *J. Mol. Spectrosc.* **1977**, *67*, 34.
- (21) Nelander, B. *Chem. Phys.* **1984**, *87*, 283.
- (22) Ault, B. S. *J. Mol. Struct.* **2000**, *526*, 97.
- (23) Ault, B. S. *Rev. Chem. Intermed.* **1988**, *9*, 233.
- (24) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley-Interscience: New York, 1997.
- (25) Ault, B. S. *Inorg. Chem.* **1981**, *20*, 2817.
- (26) Barnes, A. J.; Hallam, H. E.; Scrimshaw, G. F. *Trans. Faraday Soc.*, **1969**, *65*, 3150.
- (27) Maillard, D.; Schriver, A.; Perchard, J. P. *J. Chem. Phys.* **1979**, *71*, 505.