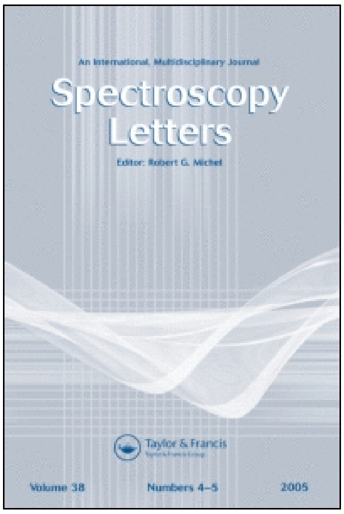

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THE INTERACTION OF GASEOUS AMMONIA WITH SOME TRANSITION METAL SALTS

KEY WORDS: chemisorption, infrared cell, transition metal salts, amines, gas-solid interactions

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ABSTRACT

Several transition metal salts, as solids, were exposed to gaseous ammonia at room temperature in a cell designed to allow measurement of infrared energy absorption at various pressures. For those salts which did form compounds with the ammonia, the new absorption bands are discussed in reference to spectra of amine complexes of known composition.

INTRODUCTION

A technique recently described by Guilbault, Scheide, and Das[1] indicates a means by which the interaction of a gaseous substance with a solid substrate can be investigated. A reaction cell was designed to permit the passage of infrared radiation through a thin layer of a given salt, before, during and after exposure to a gas at chosen pressures. This method was applied to studying the response of several transition metal salts at room temperature to gaseous ammonia. The salts themselves are, with few exceptions, transparent to infrared radiation between 4,000 and 600 cm^{-1}, whereas amine complexes have been shown to absorb energy in 4 regions of this energy span (e.g., ref. 2,3,4 and 5). The bands formed during the gas-solid reaction time in this study were therefore assigned by analogy to those designations shown to be consistent for compounds of known composition.

EXPERIMENTAL

Vacuum System

A dynamic vacuum was applied to the reaction cells by means of a two-stage Cenco fore pump and a Cenco water-cooled ultrahigh vacuum oil diffusion pump, both separated from the working area by a cold finger trap cooled in liquid nitrogen. A subsidiary branch connected at one of the four taps to the vacuum line, yet separated from this main line by a stop cock, was used for reactions requiring more than 6 hours. This freed the main line for the preparation of other samples.

Reagents

Ammonia was condensed directly from a Matheson Company, Inc. cylinder into a reservoir vessel. To limit atmospheric contamination the vessel was flushed by admitting the ammonia stream through the first stopcock into the vessel cooled by a dry ice-acetone bath. The flow rate exceeded the condensation rate, indicated by bubbles from a tube venting the reservoir through the second stopcock into a beaker of chloroform. After a small amount of ammonia had condensed, it was boiled away by removing the cold bath briefly. After repeating this step, a third condensation of the gas was deaerated by repeated freezing and thawing under a dynamic vacuum. This ammonia was then stored and used with the reservoir immersed in a dry ice-acetone bath.

GASEOUS AMMONIA AND TRANSITION METAL SALTS

Commercially made reagent grade salts, anhydrous when possible, were used without further purification.

PROCEDURE

The metal salts were ground with mortar and pestle under chloroform. The resulting suspension was dropped as uniformly as possible onto one of the KBr discs used as a window of the reaction cell. The cell (Type A, described by Guilbault, Scheide and Das[1]) was quickly assembled before the chloroform dried completely, and a vacuum was applied to remove the remaining chloroform and any other volatile contaminants. A baseline spectrum was traced when a pressure of 2×10^{-5}mm was reached. The cell was then re-evacuated, and connected to the system. The ammonia vapors were then passed from the reservoir into the cell for several hours. A Beckman model IR-7 double beam spectrophotometer was used to scan from 4000 to 650 cm^{-1}. A Perkin-Elmer model 337 double beam spectrophotometer was used from 1000 cm^{-1} to 400 cm^{-1}.

RESULTS

The compounds whose interactions with infrared radiation were noted before and after exposure to gaseous ammonia are listed below. The have been summarily categorized into four groups.

The first group includes those 16 compounds which neither appeared to react, nor gave rise to new absorptions in the infrared region scanned to indicate that reaction had occurred. The compounds tested were $TiCl_3$, VCl_3, $CrCl_2$, $CrCl_3$, FeF_2, $FeCl_2$, FeF_3, $Fe(NO_3)_3$, $Fe(ClO_4)_3$, CuCl, $CdCl_2$, $CdBr_2$, $HgCl_2$, AgCl, $AgNO_3$. Gold (III) iodide appeared to partially decompose to gold (I) iodide during sample preparation. However, the solid did not show any reaction with ammonia.

A second group consists of $MnCl_2$ and HgI_2. The appearance of both of these solids changed as ammonia was admitted to the reaction cell. The pale pink $MnCl_2$ changed subtly to a more bulky white substance. The transition in HgI_2 was a striking loss of the bright orange-red color, leaving an off-white solid. The orange-red color returned with the application of a vacuum less than 10^{-4}mm. Although these visually obvious changes occurred, no effect on the samples' absorption of infrared radiation was observed. Since the transition is so readily reversible perhaps the weak forces of physisorption alter the energy levels of absorbed ammonia molecules so slightly that the higher number of free ammonia molecules disguise this response with their own absorptions. However, this situation does raise the possibility that some of those compounds listed above as non-reactive did indeed react, undetected. The unchanged appearance of many of the compounds which did react lends credence to this possibility.

The last two groups include those compounds which did undergo chemisorption reactions with the gaseous ammonia, as indicated by the formation of bonds which caused two or more absorptions within the infrared region scanned, (See Figure 1 and Table 1). In 4 cases the broad absorption bands from the bonds formed in complexation remained unchanged during the evacuation of excess ammonia vapor. In the remaining 7 of the 11 compounds which gave infrared absorption bands, shifts of some of these bands were noted.

TABLE 1

Compounds Which Showed Reaction With Gaseous Ammonia
Listed in Order of Increasing Rocking Frequency, ρ_r, in cm^{-1}

Compound	ρ_r	δ_s	δ_d	ν_{N-H}
CdI_2	<630	1208	1590	3240,3330
FeI_2	(635)*590	(1170) 1252	(1605) 1595	3160,3240,3350
$CoCl_2$	(655) ---	(1155) 1235	(1590) 1595	--------
$FeBr_3$	<630	(1150) 1165, 1230	--------	--------
$Ni(ClO_4)_2$	(677) 670	(1190) 1265	--------	--------
$NiCl_2$	674	1175	1600	3340
$ZnCl_2$	(710) 680	(1230,1270) 1250	(1615) 1605	3150,3200,3300
ZnI_2	690	1245	--------	3300
$FeCl_3$	690,840	1222,1262	1600	3150,3200,3230,3300
$HgBr_2$	(695) ---	(1252) ----	--------	3145,3210,3290
$CuCl_2$	(732) 707	(1230) 1265	--------	3160,3210,3300

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* Numbers in parenthesis represent absorption maxima before evacuation of excess ammonia. Other absorptions listed were present to 10^{-5}mm.

DISCUSSION

The reaction products were found to absorb infrared energy in four ranges between 600 and 4000 cm^{-1} which were assigned as follows:

600 - 835	rocking
1150 - 1265	symmetric deformation
1590 - 1620	degenerate deformation
3150 - 3400	N-H stretch

These assignments have been made and tested by several researchers[2,3] The N-H stretching bands and the degenerate deformation bands were not evident for every compound. Since the rocking frequency should be most sensitive to any change in the metal atom, the position of this band was used in ordering the parent compounds listed in Table 1.

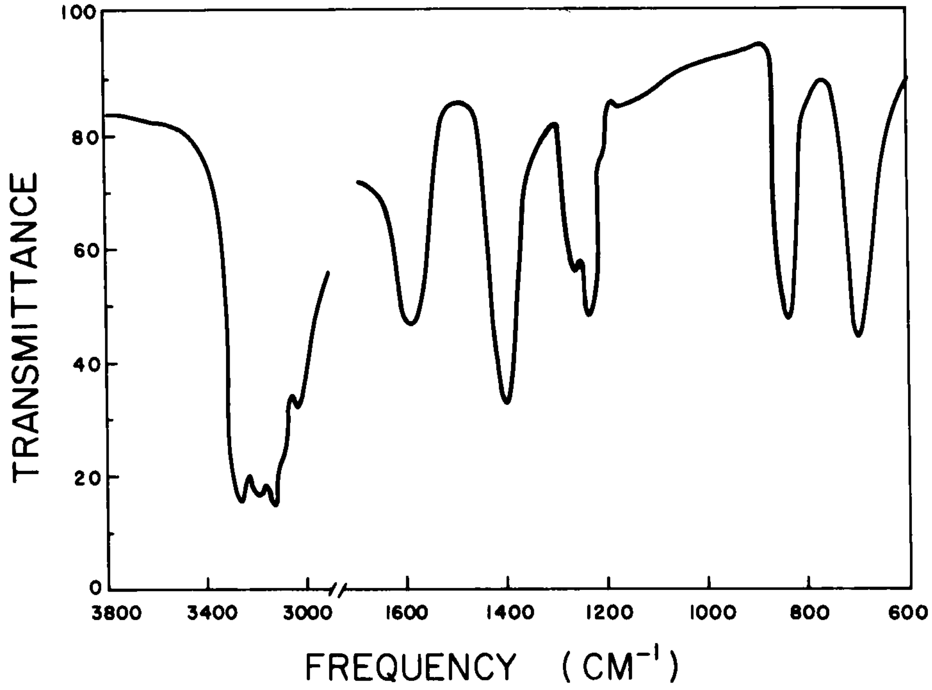

FIG. 1

Infrared Spectrum of $FeCl_3$ After Interaction With Ammonia

The exact compositions of the products were not determined, so comparisons made and trends projected must be treated with caution. Nevertheless, it is interesting to note that the metal-ammonia rocking frequencies observed for the reaction products of the dichlorides of cobalt, nickel, copper, and zinc do follow the Irving-Williams stability series: $Co < Ni < Cu > Zn$. This is also the order which the stability constants for the metal-ammonia complexes in solution follow. It is also striking that with a decrease in pressure, the rocking frequencies which shifted always moved to a lower energy level, whereas the symmetric deformation bands shifted to a higher energy level. It is not unreasonable to hypothesize that the decrease in availability of ammonia has caused the formation of a compound with a lesser stoichiometric proportion of ammonia molecules per metal atom. However, without further information, such as metal-halogen or metal-nitrogen stretching bands and x-ray data, which will give clues to the stereochemical environment of the metal atom at each pressure, it is difficult to pinpoint the reasons for these shifts. Svatos et al[4], found that with decreasing cationic charge in a series of octahedral Co(III) ammine complexes, both rocking and symmetric deformation frequencies decreased. The opposing trends in this study are at variance with this observation, but the stereochemistry of the compounds listed here may be changing, in addition to the decreasing ammonia-metal-ratio. The conclusions drawn by Clark and Williams[5] indicate that a shift from a metal hexammine to a substituted or polymeric ammine complex would cause a decrease in the energy level of the symmetric deformation band. This is coincident with the conclusion drawn by the Svatos et al[4] data, but contrary to the values observed under the conditions imposed in this study.

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