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Infrared Spectra of the Argon-Matrix Isolated Alkali Halide Salt/Ammonia Complexes. Spectrum of the NH_3M^+ Cation

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Abstract: The reaction products of alkali halide and cyanide salt molecules with NH_3 in argon matrices have been investigated and characterized by infrared spectroscopy. Four product bands were detected and assigned to two N-H stretching modes, an NH_3 symmetric deformation mode, and an NH_3 rocking mode in the complex. Analysis of the cation and anion dependences of these bands, and comparison to transition metal ammine complexes, has led to a proposed structure of the form $NH_3M^+ \cdot X^-$, with the interaction involving the attraction of the alkali metal cation to the nitrogen lone pair, while a hydrogen bonding interaction is *not* indicated.

Introduction

Recently, a study was reported in which the argon matrix-isolated complexes of alkali metal halide salt molecules with H_2O were studied,¹ to investigate the interactions between alkali metal cations and Lewis bases. It is of interest to extend these studies to other Lewis bases, and in particular NH_3 , to more completely characterize this interaction. Also, Devlin and co-workers have carried out several studies in this area,²⁻⁴ first through the investigation of alkali nitrate and chlorate ion pairs in glassy NH_3 , and secondly through the investigation of the interaction of the ion pairs with NH_3 in argon matrices, at 3-20% NH_3 in Ar. They conclude that in each case the interaction is through the lone pair on the NH_3 molecule to the alkali metal cation, and that the interaction is consistently stronger for NH_3 than H_2O . Finally, transition metal ammine complexes are available as models for these complexes.⁵⁻⁷

Consequently, a number of reactions were carried out in argon matrices, to thoroughly characterize the 1:1 reaction product.

Experimental Section

The apparatus used for the present studies is identical with that used previously,¹ NH_3 (Matheson), ND_3 (Merck), and $^{15}NH_3$ (Merck,

95.2% ^{15}N) were all condensed into a stainless steel finger at 77 K, and volatile impurities pumped off. Argon, without further purification, was used as matrix gas in all experiments.

The alkali halide and cyanide salts employed were NaCl (Mallinckrodt, analytical reagent), KCl (Allied, reagent), KBr (Fisher), KCN (Fisher), RbCl (Fairmount), CsCl (Fisher), CsF (Alfa), CsBr (Orion), and CsI (Harshaw). These salts were loaded in a stainless steel Knudsen cell and heated to generate a pressure of about 1μ for deposition into Ar/ NH_3 matrices. Operating temperatures follow: NaCl, 600 °C; KCl, 550 °C; KBr, 525 °C; KCN, 550 °C; RbCl, 525 °C; CsCl, 500 °C; CsBr, 500 °C; CsF, 500 °C. Matrix samples were deposited onto a CsI cold window for 20-30 h at between 14 and 16 K, before final spectra were recorded.

Results

Before the reaction products of the salt molecules with NH_3 were investigated, the argon matrix spectra of NH_3 and its isotopic counterparts were recorded. The spectra were complex, owing to both dimerization and inversion structure, so that multiple bands were observed in the region of the NH_3 fundamentals, especially for ν_2 . The spectra obtained here, and shown in Figure 1, agree well with literature spectra of NH_3 in argon.^{8,9} Similar spectra were recorded for samples of Ar/ $^{15}NH_3 = 250$ and Ar/ $ND_3 = 250$, with band positions again in agreement with reported literature values. The spectra also

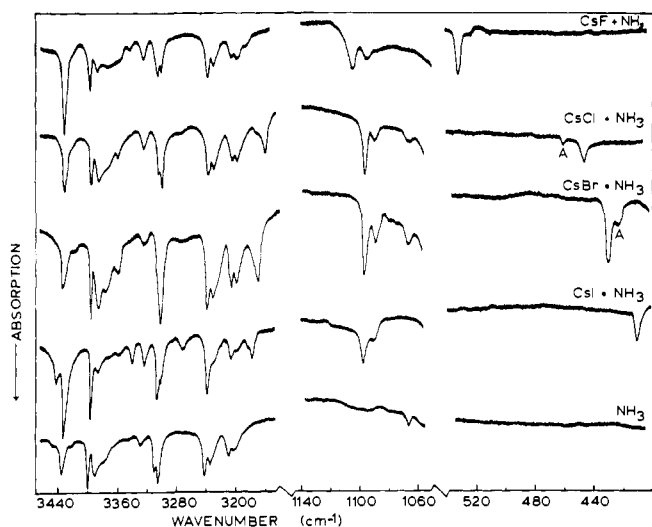


Figure 1. Infrared spectra of the reaction products of the cesium halides with Ar/NH₃. The band designated by the letter A in several scans is due to the reaction product of the salt molecule with impurity H₂O.

showed only a small amount of ND₂H, indicating a high D/H ratio.

CsCl + NH₃. CsCl molecules were deposited with samples of Ar/NH₃ in several different experiments, employing different reactant concentrations. In each experiment, with M/R values from 200 to 500, four new bands (at 447, 1096, 3167, and 3366 cm⁻¹) grew in which could not be attributed to the precursor molecules. These bands maintained a constant intensity ratio in the various experiments, and were relatively sharp, although the 1096-cm⁻¹ band had a satellite band at 1089 cm⁻¹. In each of the experiments described in this paper, H₂O was present as a minor impurity, with M/R ~ 3000, from H₂O adsorbed on the walls of the vacuum vessel, or any number of other sources. Consequently, bands due to the salt/H₂O complex which have been assigned previously⁵ were detected. Since they are well characterized, they will not be discussed further in this paper, other than to be designated by the letter "A" in Figures 1-3.

CsBr + NH₃. In a similar set of experiments, CsBr molecules were deposited with samples of Ar/NH₃, yielding four product bands at 430, 1096, 3176, and 3365 cm⁻¹ only slightly shifted from the above bands in the CsCl reactions. Similar bands shapes and intensities to those reported above were observed.

CsI + NH₃. CsI molecules were also deposited into a matrix containing Ar and NH₃, at M/R = 250, yielding four product bands at 411, 1098, 3186, and 3369 cm⁻¹, and showing the

same relative intensities and band shapes as were observed in the experiments with CsCl and CsBr.

CsF + NH₃. One reaction involving CsF with NH₃ in an argon matrix at M/R = 250 was investigated and while the overall yield was low, product bands were observed at 534 and 1105 cm⁻¹. All of the spectra of the cesium halides with NH₃ are presented in the five traces of Figure 1, while band positions and intensities are listed in Table I.

RbCl + NH₃. The reaction of RbCl with Ar/NH₃ = 250 was investigated in one experiment, and product bands were observed at 452 and 1104 cm⁻¹, with relatively low intensity.

KCl + NH₃. The reaction of KCl with Ar/NH₃ was investigated in several experiments, including isotopic NH₃ molecules. Each time KCl was deposited with Ar/NH₃ = 250, five intense product bands were observed, at 234, 460, 1108, 3180, and 3371 cm⁻¹. The latter four bands are in close proximity to bands observed in the above reactions, while the first band has no direct analogue in the other experiments. (See Table I.) When KCl was deposited with a sample of Ar/ND₃ = 250, with a D/H ratio of 6, product bands were detected at 222, 347, 849, 2327, and 2500 cm⁻¹, each shifted a substantial amount from the analogous bands observed in the NH₃ experiment. The shift (ν_H/ν_D) ratios are 1.05, 1.33, 1.31, 1.37, and 1.35, the latter four being indicative of primarily hydrogen motion, while the first band indicates a mode which is not primarily hydrogenic in character. Two weaker product bands were observed in this experiment, a doublet at 919 and 907 cm⁻¹ and a single band at 2403 cm⁻¹, which are apparently due to reaction of KCl with trace residual NHD₂ in the ND₃ sample.

KCl was also deposited with a sample of Ar/¹⁵NH₃ = 250 in one experiment. Product bands, shifted slightly, were observed at 232, 458, 1103, 3177, and 3365 cm⁻¹. The relative intensities also matched those observed in the prior experiments with the normal isotope of nitrogen. Also, since enrichment of the ¹⁵NH₃ was not complete, product bands due to the reaction product of KCl with ¹⁴NH₃ were also clearly observed, as were the bands due to the parent ¹⁴NH₃. These spectra are shown in Figure 2.

KBr + NH₃. KBr was also vaporized and codeposited with Ar/NH₃ = 250. Five product bands were observed, in close analogy to the KCl experiments described above, at 223, 444, 1100, 3189, and 3370 cm⁻¹, as shown in Figure 2. Slight KCl impurity was present but at very low levels that did not affect the KBr reaction products.

KCN + NH₃. One experiment was conducted in which KCN was vaporized and deposited with Ar/NH₃ = 250. Five product bands were detected in high yield, analogous to the KCl experiment, at 224, 460, 1121, 3160, and 3370 cm⁻¹. Unfortunately, the KCN samples employed contained a small amount of KCl impurity, as indicated by a weak band at 247

Table I. Band Positions^a and Intensities^b of the Reaction Products of Alkali Halide and Cyanide Salts with NH₃ in Argon Matrices

salt	ν_1^f	ν_2	ν_3	ν_4	ν_5	ν_6
CsCl	3167 (0.07)	1096 (0.15)		3366 (0.02)		447 (0.04)
CsBr	3176 (0.10)	1096 (0.17)		3365 (0.04)		430 (0.12)
CsI	3186 (0.04)	1098 (0.08)		3369 (0.02)		411 (0.07)
CsF		1105 (0.06)				534 (0.09)
RbCl		1104 (0.07)				452 (0.02)
KCl	3180 (0.10)	1108 (0.36)	234 (0.10)	3371 (0.04)		460 (0.23)
KCl ^c	3177 (0.09)	1103 (0.25)	232 (0.06)	3365 (0.03)		458 (0.15)
KCl ^d	2327 (0.08)	849 (0.23)	222 (0.06)	2500 (0.04)		347 (0.13)
KBr	3489 (0.11)	1110 (0.24)	222 (0.09)	3370 (0.05)		444 (0.14)
KCN	3160 (0.13)	1121 (0.33)	224 (0.05)	3370 (0.03)		460 (0.10)
NaCl		1116 (0.11)				
NaCl ^e		1111 (0.30)				

^a Band positions in cm⁻¹. ^b Optical densities given parenthetically. ^c KCl + ¹⁵NH₃. ^d KCl + ND₃. ^e NaCl + ¹⁵NH₃. ^f Band designations taken from ref 7.

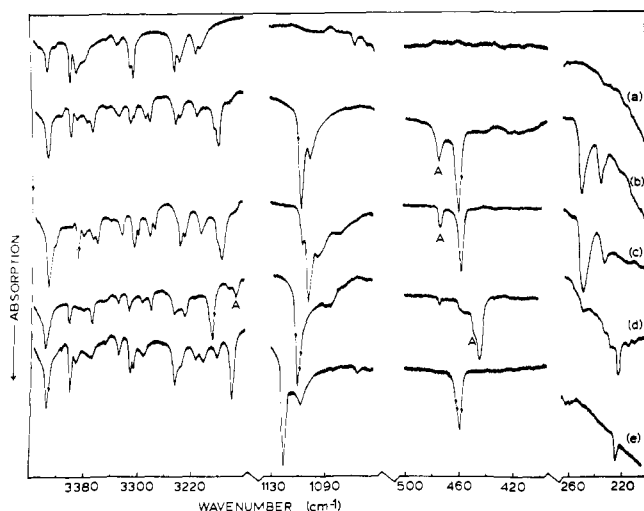


Figure 2. Infrared spectra of potassium salts with Ar/NH₃ and Ar/¹⁵NH₃. Trace (a) shows the spectrum of NH₃ isolated in argon with no salt molecules present, while trace (b) shows the analogous scan with KCl codeposited with the NH₃. Trace (c) shows the effect of ¹⁵N substitution, with KCl as a reaction partner, while trace (d) shows the effect of substitution of KBr for KCl, with NH₃, while trace (e) shows the effect of the substitution of KCN for KCl.

cm⁻¹ due to monomeric KCl. The product bands due to KCl + NH₃ were also clearly detected, at 1108 and 3180 cm⁻¹, but they do not detract from the intense bands due to the KCN reaction product.

NaCl + NH₃. NaCl was deposited with Ar/NH₃ and its isotopic counterparts in several experiments. In each case, three bands due to the parent NaCl molecules and (NaCl)₂ were detected, at 335, 275, and 229 cm⁻¹, as well as one major product band in the reaction with NH₃, an intense band at 1116 cm⁻¹. No other product bands were observed in the spectrum, and in particular, no product bands were detected between 200 and 400 cm⁻¹, although a band at 469 cm⁻¹ due to the reaction product of NaCl and H₂O was observed. NaCl was deposited with a Ar/¹⁵NH₃ = 250 in one experiment, and the product band at 1116 shifted to 1111 cm⁻¹.

Discussion

Codepositing alkali halide salt molecules with NH₃ in argon matrices led to several bands which must be assigned to a reaction product. In most experiments, four product bands were observed: two in the region 3100–3400 cm⁻¹, one near 1100 cm⁻¹, and one between 400 and 500 cm⁻¹. In the several experiments performed with CsCl and NH₃, over a range of concentrations, the intensities of the four bands maintained the same relative ratios, indicating that all four bands can be ascribed to the same product species. The experiments also demonstrate that these four bands persist at high dilution, indicative of a 1:1 reaction product. In addition, in those experiments in which K⁺ was the alkali metal cation, a fifth band was observed below 250 cm⁻¹, with distinct deuterium and ¹⁵N counterparts. It is reasonable to assign this product band to the same product to which the other four bands have been assigned. Certainly, it would be difficult to postulate a second product, which has only a single detectable absorption and this coming below 250 cm⁻¹. Thus this low-energy band is associated with the 1:1 reaction complex.

As a prototype for analysis the reaction product of KCl with NH₃ may be considered, as the product bands were relatively intense, and considerable isotopic data are available. The upper four bands showed a small ¹⁵N shift, on the order of a few wavenumbers, while all four also showed a strong deuterium shift, indicative of primarily hydrogenic vibrations. The fifth band, below 250 cm⁻¹, showed a small deuterium shift (shift

POSSIBLE STRUCTURES OF NH₃-SALT COMPLEXES

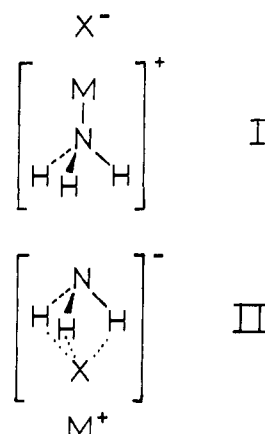


Figure 3. Two of the most probable structures for the 1:1 reaction product of an MX salt molecule with NH₃ in the argon matrix.

ratio of 1.05), indicating that the vibration responsible for this band is primarily not hydrogenic. The two bands between 3100 and 3400 cm⁻¹ are in the region associated with N–H stretching vibrations, and are readily assigned as such in view of their hydrogenic character. While there are several possible geometries for a 1:1 reaction complex, at least two N–H stretching modes are anticipated. If the complex preserves C_{3v} geometry, two N–H stretches are anticipated, while if the geometry of the complex is reduced to C_{2v} or lower, then three such bands are anticipated. Regardless, the bands between 3100 and 3400 cm⁻¹ may be assigned to two N–H stretching modes.

The product band near 1100 cm⁻¹ is also a hydrogenic vibration, and lies about 130 cm⁻¹ above the symmetric deformation mode ν_2 of NH₃. The reaction complex, regardless of geometry, should have an analogous band, so the band near 1100 cm⁻¹ is assigned to this symmetric deformation. The ¹⁵N shift for this product band, 5 cm⁻¹, is exactly the same shift observed for ν_2 of NH₃, lending further support for this assignment. A shift to higher energy is anticipated for this mode owing to an increase in the barrier to inversion of NH₃ in the complex. This shift has been shown to be proportional to the strength of the interaction. Finally, ν_2 of NH₃ is the most intense band in the NH₃ spectrum, and likewise, the band near 1100 cm⁻¹ was the most intense product band observed.

The fourth product band, at 460 cm⁻¹, for KCl–NH₃ is also a hydrogenic vibration, but does not have any direct analogue in the parent NH₃ spectrum. To understand the origin of this product band, the different possible geometries of the reaction complex must be considered.

Two possible structures are those that preserve C_{3v} symmetry, either a metal cation bound species NH₃M⁺ or a symmetrically hydrogen-bonded species NH₃X⁻. These two possibilities are depicted as structures I and II in Figure 3, respectively. A third structure, which preserves C_{3v} geometry, is a composite of I and II, but, it seems highly unlikely that the major centers of positive and negative charge, the metal cation and the halide anion, could be separated by the distance that would be required in this arrangement, in an isolated ion pair.

Possible structures which do not preserve the C_{3v} symmetry of the complex might be considered, such as a partial hydrogen bonding, partial metal cation attachment structure. However,

energetically these structures seem unlikely, so structures I and II remain as most probable for the reaction complex.

The cation and anion dependence of the vibrational band will help in the structure determination. The symmetric deformation mode of the NH_3 unit in the complex, assigned above to the band near 1100 cm^{-1} , should be relatively sensitive to the metal cation, if the structure is I, and should be sensitive to the anion, if the structure is II. The cation dependence of the 1100-cm^{-1} band is clear from Table I, with a systematic decrease in frequency of this mode from Na^+ to Cs^+ , with Cl^- as the halide anion. This trend is anticipated since the smaller alkali metal cations will bind more strongly, shifting the vibrational frequency upward. On the other hand, the halide dependence of this vibrational mode is minimal at best, as seen from the cesium halide sequence. This result points to structure I.

The N-H stretching frequencies of the complex provide structural information since a hydrogen-bonding interaction (structure II) is expected to cause a large shift in the N-H stretching frequency, on the order of many hundreds of wavenumbers,¹⁰ while a metal cation bound to the nitrogen should not shift the vibrational frequencies significantly. The interaction of a halide anion with NH_3 has been studied under conditions where metal cation complexation to the nitrogen cannot occur,¹¹⁻¹² so that the interaction is strictly one of hydrogen bonding. A major feature of the IR spectra of these complexes is a broad band, near 2100 cm^{-1} , which has been assigned to the N-H-Cl stretching mode in the hydrogen-bonded complex, in agreement with the expected large shift. A counterpart band in this present set of experiments was not observed, which supports structure I.

Assuming structure I, a more complex picture of the vibrational modes expected can be obtained. Figure 4 shows that the four vibrational modes of the XY_3 species correlate with four of the six modes of the XY_3Z species, while the XY_3Z species should have two additional vibrational modes, a stretching vibration of Z against the central atom X, and an XY_3 rocking mode. These two modes account for the two remaining bands of the KCl-NH_3 reaction complex. The XY_3 rock is nearly a pure hydrogen motion, which fits the 460-cm^{-1} band observed for this complex. The K-N stretching motion should show very little deuterium shift, and the shift of the 234 cm^{-1} band to 222 cm^{-1} , a ratio of 1.05, is clearly not a hydrogenic motion, consistent with assignment to the K-N stretch.

Comparison of the spectral data obtained here to the transition metal ammine complexes is informative as well. In these complexes, the N-H stretching frequencies lie in the region $3100\text{-}3400\text{ cm}^{-1}$, in good agreement with the values obtained here. Secondly, the symmetric deformation mode in the ammine complexes is shifted up a considerable amount from the 970-cm^{-1} position of ν_2 in NH_3 , similar to the present results. It has been noted that the magnitude of this shift⁵⁻⁷ is proportional to the strength of the interaction of the transition metal cation with the NH_3 ligand. Thus it is not surprising that the shifts observed here are smaller, and the trend is observed in the correct direction, from Na^+ to Cs^+ .

The NH_3 rocking mode has been detected in these transition metal ammine complexes, between 620 and 800 cm^{-1} , depending on the metal cation. Also this vibrational band is quite sensitive to the strength of the interaction, so that the weaker interaction with the alkali metal cations should lead to a rocking frequency lower than 600 cm^{-1} , and the band observed in each experiment between 400 and 500 cm^{-1} is a suitable candidate. This band, in the transition metal complexes, was somewhat sensitive to the anion, even though it is clear that the binding is through the transition metal cation. The rocking mode observed here is also somewhat sensitive to the anion as anticipated. The analogy to the transition metal ammine

Vibrational Correlations for the T_d and C_{3v} Point Groups

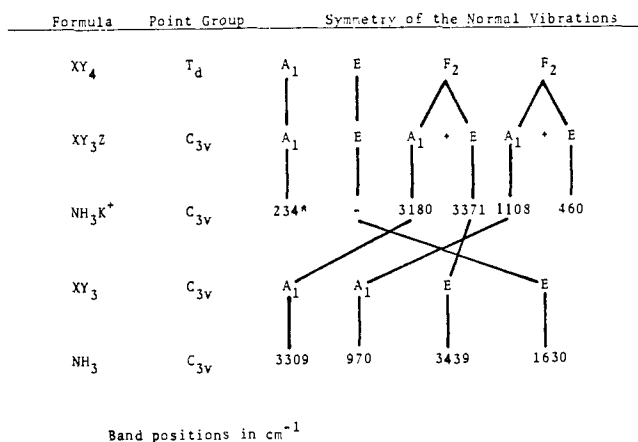


Figure 4. Diagram of the correlation between the normal vibrations of molecules of T_d and C_{3v} symmetry, with frequencies assigned for NH_3 and the NH_3K^+ species.

complexes does provide a model consistent with a metal cation bound species.

The band at 234 cm^{-1} in the $\text{KCl} + \text{NH}_3$ experiment is a good candidate for the metal-nitrogen stretching mode, based on its low deuterium shift, 1.05. This is precisely the predicted shift for a K atom vibrating against NH_3 (and ND_3), and it is in the correct spectral region for such a band. Similar bands were observed near 224 cm^{-1} , when KCN and KBr were employed, supporting this assignment. In the transition metal ammine complexes, this mode lies below 500 cm^{-1} , and is very sensitive to the strength of the interaction.⁶ Since the alkali metal cation- NH_3 interaction is weaker, frequencies below 300 cm^{-1} are anticipated. Also, this vibrational mode was very weak in the transition metal ammine complexes, which may account for the difficulty in locating this mode in the present studies, and in the previously reported studies of salt reactions with H_2O . While the evidence supports this assignment of the 234-cm^{-1} band, the assignment is not completed definitive owing to the difficulty in purging the infrared spectrometer, and subsequent interference from atmospheric H_2O . An analogous band was not observed, despite careful searching, for the Na^+ complex, where the band might be expected above 200 cm^{-1} , the cutoff of the infrared spectrometer, perhaps owing to interference from $(\text{NaCl})_2$.

The band positions and assignments for the NH_3K^+ cation, under C_{3v} geometry, have been included in Figure 4. Five of the six normal vibrations of the cation have been observed, with only the degenerate deformation mode missing. The studies of the transition metal ammine complexes have shown that this mode is very insensitive to complexation, and shifts only 10 cm^{-1} from the parent NH_3 band in the strongly bound $\text{Co}(\text{NH}_3)_6^{3+}$ complex. In the present experiments, with an excess of NH_3 , it is unlikely that this band could be observed.

One point which is not completely understood is the lack of observation of the NH_3 rocking mode in the NaCl-NH_3 complex, even though the symmetric deformation mode at 1116 cm^{-1} was quite intense. Table I shows that this band should lie near $465\text{-}470\text{ cm}^{-1}$, and indeed a band was observed at 469 cm^{-1} . Unfortunately, this is the precise location of one of the bands of the $\text{NaCl}\cdot\text{H}_2\text{O}$ complex,¹ and since residual H_2O is always present, it is impossible to make a clear-cut assignment.

Devlin and co-workers carried out extensive studies of the interactions of alkali nitrate and chlorate salts with NH_3 , and determined that the binding is through the metal cation to the nitrogen lone pair, in agreement with the results here. Devlin

and co-workers did not observe the bands detected in the present studies, however, most of which are bands due to the NH_3 entity in the complex. Their studies were conducted either in glassy NH_3 matrices, or in highly concentrated Ar/NH_3 samples, at 3–20% NH_3 . In their experiments, the regions near the NH_3 fundamentals probably blacked out, making detection of bands in the 3100–3400- and 1100- cm^{-1} regions very difficult. Instead, these workers monitored the intensity and splitting of the nitrate or chlorate anion bands as a measure of the interaction. While their experiments and the present experiments were quite different, overall there seems to be good qualitative agreement with the results of Devlin on the nature of the interaction.

Conclusions

The spectra of the reaction products of NH_3 and alkali halide salts have been recorded in dilute argon matrices. These spectra and the available isotopic data point to a 1:1 complex in which the species maintains a C_{3v} geometry, and in which the metal cation is bound to the lone pair on the nitrogen. Using the transition metal ammine complexes as a model, all of the observed product bands can be assigned to anticipated normal vibrations, with the band locations appropriate for a weaker

interaction between NH_3 and the alkali metal cations than between NH_3 and transition metal cations.

Acknowledgments. The author gratefully acknowledges support of this research through Grant 8305 from the Research Corporation, and the University of Cincinnati Research Council.

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Isotropic Shifts in a Series of Cobalt Bis(salicylaldehyde)ethylenediimine Derivatives

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Abstract: The isotropic shifts in Me_2SO for a number of ligand substituted Co(salen) complexes have been determined. The isotropic shifts in the series as a whole exhibit two interesting and unusual aspects. Substitutions at the periphery of the ligand cause dramatic changes (as large as 400 ppm) in the resonance positions of certain protons in the ligand. In addition non-Curie-law temperature-dependent behavior is observed for some of the complexes. Both the drastic changes in resonance positions throughout the series and the unusual temperature dependence can be explained with a simple model which allows for two electronic states to contribute significantly to the observed isotropic shifts. It appears as if there are at least one doublet and one quartet state contributing to the isotropic shifts in this series. In view of the fact that both a doublet and quartet state contribute to the observed shifts it is unlikely that a detailed analysis of the spin delocalization mechanism(s) can be made.

The properties of low-spin cobalt(II) complexes have received considerable attention in the past several years. This is due to a variety of factors including the ability of certain of these systems to bind oxygen¹ as well as the fact that vitamin B_{12} is a low-spin cobalt(II) system.² Of particular interest has been the electronic structures of these complexes. A detailed understanding of the electronic structures of these low-spin d^7 systems should lead to better insight into the ability of some of the complexes to undergo reversible oxygen binding.

An impressive arsenal of experimental and theoretical techniques has been employed to study the electronic properties of low-spin cobalt(II) complexes. Experimental methods which have been used include magnetic measurements,³ ESR spectroscopy,⁴ electronic absorption spectroscopy,^{4a,5,8c} photoelectron spectroscopy,⁶ and NMR spectroscopy.⁷ A number of theoretical calculations,⁸ notably the recent article by Hitchman,^{8c} have addressed the nature of the electronic structures in these low-spin cobalt(II) systems. It is clear that in five-coordinate adducts of low-spin cobalt(II), a ground state with the unpaired electron in d_{z^2} (2A_1 in C_{2v} symmetry of ${}^1A_{1g}$

in D_{4h} symmetry) is most common and perhaps universal. The question of the electronic state in the four-coordinate configuration has, however, been a point of debate. Several lines of work have been interpreted as indicating the unpaired electron to be in d_{z^2} . Other work has been interpreted as indicating that the unpaired electron resides in d_{yz} (2A_2 in C_{2v} symmetry; see Figure 1 for definition of axes). Hitchman's recent analysis of the electronic structure of Co(salen) in the four-coordinate configuration shows the 2A_2 (d_{yz}) state to be about 1100 cm^{-1} lower in energy than the 2A_1 (d_{z^2}) state.^{8c}

It is noteworthy, however, that virtually all of the interesting chemistry of low-spin cobalt(II) systems has been carried out in solution.² The attempts to study electronic properties of these complexes in solution have in general been more qualitative and have not led to unambiguous interpretation.

Of the experimental work which has been carried out in solution on these complexes, NMR spectroscopy has been used to a rather limited extent but has provided interesting information.⁷ In this article we wish to report an NMR study of a substantial series of Co(salen) complexes in Me_2SO solution.