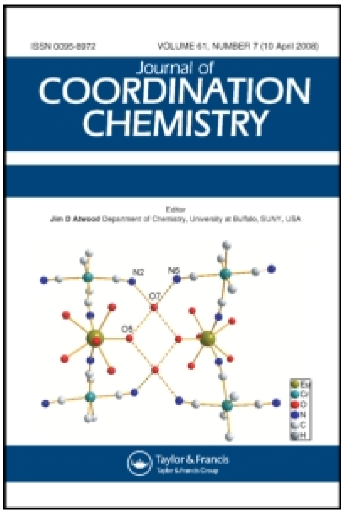

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LIQUID AMMONIA SOLUTIONS: XIII AMMONOLYSIS OF COORDINATED TRANSITION METAL CATIONS

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LIQUID AMMONIA SOLUTIONS: XIII AMMONOLYSIS OF COORDINATED TRANSITION METAL CATIONS

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KEY WORDS: Amines; Cobalt[III] amines; Rhodium[III] amines; Iridium[III] amines; Ammonia, liquid; Ammonolysis.

The nature of the species present in liquid ammonia solutions of $[\mathrm{Men_3}]\mathrm{I_3}$ (M = Co, Rh, Ir) was investigated spectroscopically and using computer resolution techniques. $[\mathrm{Coen_3}]\mathrm{I_3}$ behaves as a weak acid (pKa = 7) in pure, anhydrous ammonia. Deprotonation of the ligand gives a species with a charge transfer band at 280 nm. Two equivalents of $\mathrm{KNH_2}$ produce a trans-deprotonated species $[\mathrm{Coen(en{-}H_2)}]^+$. The rhodium complexes behave similarly to those of cobalt in the presence of $\mathrm{KNH_2}$, spectra of the iridium complexes and their mixtures with $\mathrm{KNH_2}$ in liquid ammonia were featureless.

INTRODUCTION

It might be expected that the coordination of amines by transition metal ions would enhance the acidity of N–H moieties (if present) in analogy to the hydrolysis processes which produce acid solutions when transition metal salts dissolve in water. Numerous observations on the ammonolysis of solvated cations in liquid ammonia have been summarized by Franklin.[1] It is well known that coordinated ethylenediamine molecules are sufficiently acidic to form stable complex ions; indeed, $[\mathrm{Au(en{-}H)(en)}]\mathrm{Br_2^2}$ was isolated from aqueous solution.[3] As expected deprotonation of coordinated amines occurs more readily in basic solvents because these have a tendency to enhance the acidity of dissolved species, compared to that which it exhibits in water. Thus, several deprotonated ethylenediamine complex ions containing osmium have been isolated from ethylenediamine solution[4] and liquid ammonia has been the solvent of choice for the isolation of similar complexes of cobalt, rhodium, iridium, platinum, palladium, and osmium.[5-13]

Our continuing interest in the nature of solution species in liquid ammonia led us to investigate the acidity of selected ethylenediamine metal complexes in this solvent. Previous reports[14,15] from this laboratory have established the spectroscopic parameters for $\mathrm{NH_2^-}$, the basic analog of $\mathrm{OH^-}$ in water, which gave us a method of following the concentration of this ion in equilibrium processes.

EXPERIMENTAL

Spectrophotometric measurements were made in a portable thermostated absorption cell which could be attached to an ammonia gas handling/vacuum system and in which liquid ammonia solutions of known concentrations could be prepared. Known amounts of solute (i.e., $\mathrm{KNH_2}$ and/or metal complexes) could be introduced into the cell without exposing the solution to the atmosphere. Measurements were made at –75° after thermal and chemical equilibria had been attained. A detailed description of the apparatus and general procedure is available.[14]

Chemicals

Refrigeration grade ammonia was stored in 10 liter cylinders over sodium metal prior to use. This ammonia was then distilled into the gas handling system, and condensed over sodium before it was redistilled for use in the preparation of the solutions to be investigated.

Potassium amide was prepared by allowing reagent grade, redistilled potassium to react with ammonia at the boiling point of the solution in the presence of solid iron oxide as a catalyst. The solution was filtered at its boiling point using standard techniques.[16] The filtrate was evaporated and cooled to promote the crystallization of the product, which was isolated by filtration. The solid was dried *in vacuo* and stored in a dry box until used.

$[Coen_3]I_3$ was prepared in 80% yield using a modification[17] for the reported preparation of the corresponding chloride.[18]

Anal. Calcd. for $[Coen_3]I_3$: C, 11.62; N, 13.58; H, 3.90; I, 61.40. Found: C, 11.68; N, 13.57; H, 3.80; I, 60.00.

$[Co(NH_3)_6]I_3$ was prepared using an adaptation of the procedure reported for the preparation of the corresponding bromide.[19]

Anal. Calcd. for $[Co(NH_3)_6]I_3$: I, 70.4. Found: I, 70.2. $[Rhen_3]I_3$ [20-22] and $[Iren_3]I_3$ [23,24] was prepared by standard methods.

Anal. Calcd. for $[Rhen_3]I_3$: C, 10.8; N, 12.7; H, 3.65. Found: C, 10.8; N, 12.7; H, 3.63.

Anal. Calcd. for $[Iren_3]I_3$: C, 9.60; H, 3.20. Found: C, 9.57; H. 3.40.

Procedure

All substances that were to be used in spectrophotometric determinations were recrystallized from liquid ammonia, a practice which in our experience[14,15] is useful in removing adsorbed water. The recrystallized compounds were stored in a helium-filled dry box, the atmosphere of which was equilibrated with the liquid Na–K entectic. The dry box contained a Cahn microbalance which was used to weigh samples for preparing the solutions to be investigated. Solutes were weighed in the dry box and introduced into the spectrophotometer dewar using the winch assembly described previously.[14]

After the spectrophotometer Dewar had been assembled and evacuated for several hours, it was rinsed with anhydrous liquid ammonia, and condensed from the vapor state, several times. The rinse liquid ammonia was siphoned from the Dewar, and about 125 ml of a KNH_2 solution prepared in the apparatus. The apparatus was allowed to equilibrate with the KNH_2 solution for several hours, a process which insured that adsorbed water was removed from the walls,[15] the spent solution was siphoned from the Dewar, the Dewar was rinsed several times with liquid ammonia again, and evacuated for several hours at room temperature. After this process the cell was considered ready for the spectroscopic investigations reported here.

Spectra were recorded for solutions prepared in the following manner. About 100 ml of KNH_2

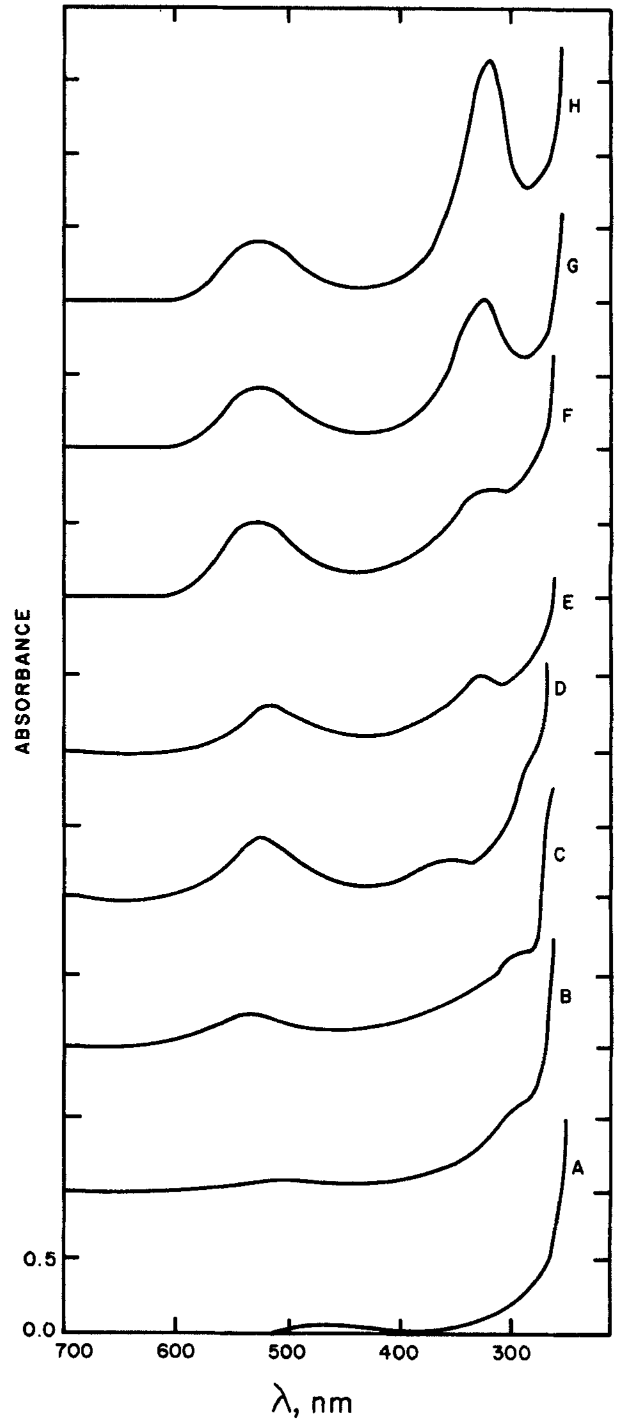

FIGURE 1 Spectra of $(Coen_3)I_3$ in liquid ammonia solutions −75°: A 5×10^{-4} M $(Coen_3)I_3$. The following curves were obtained for solutions containing the indicated mole ratio $[KNH_2]/[(Coen_3)I_3]$ at a solute concentration of 10^{-4} M: B, 1.9/1; C, 2.4/1; D, 3.5/1; E, 4.5/1; F, 5.5/1; G, 6.4/1; H, 8.8/1.

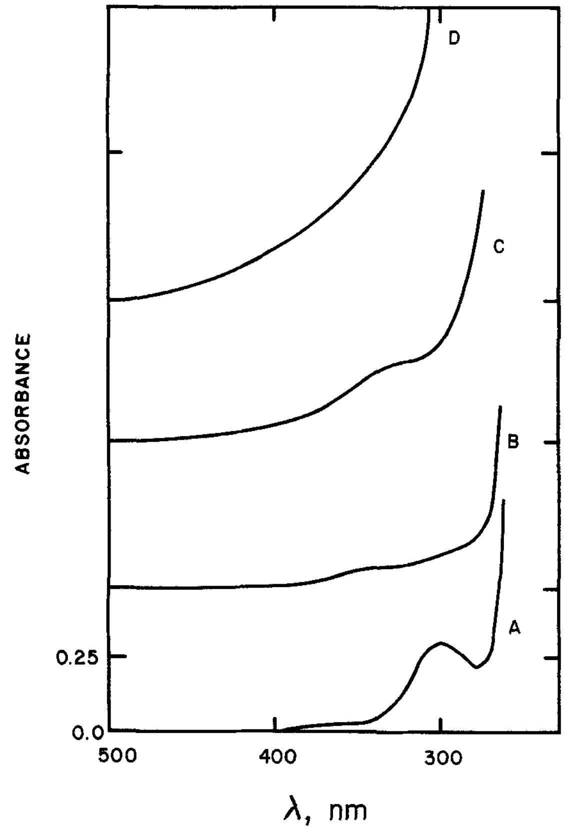

FIGURE 2 Spectra of (Rhen$_3$)I$_3$ in liquid ammonia solutions at −75°: A 5.5 x 10^{-4} M(Rhen$_3$)I$_3$. The following curves were obtained for solutions containing the indicated mole ratio [KNH$_2$]/[(Rhen$_3$)I$_3$] at a solute concentration of 10^{-4} M: B, 1/1; C, 2.2/1; D, 5/1.

solution was prepared using the winch assembly. The concentration of the KNH$_2$ solution, determined from the liquid ammonia used and the weight of KNH$_2$ introduced, could be verified by measuring the intensity of the ctts band for NH$_2^-$ which appears at 330 nm.[15] This band was useful in monitoring whether the solution had reached thermal equilibrium and/or the atmosphere had leaked into the apparatus. Only about 50% of the runs were useful by these standards. After establishing the concentration of amide ion, the appropriate amount of the coordination compound was introduced into this solution, and the spectrum recorded in the range 700–260 nm using a Cary Model 14 spectrophotometer. The spectrum was monitored until both chemical and thermal equilibria were attained. Spectra are reported at −75° using pure liquid ammonia as reference. Using such techniques, it was possible to record the spectra of pure complexes, and their mixtures with known amounts of KNH$_2$. Figures 1–3 are examples of the spectra so determined. The spectral data were digitized and subject to curve resolution techniques using program RESOL as described elsewhere.[25] In brief, each band in the spectrum can be described as a combination of Gaussian and Lorentzian functions. RESOL performs a least squares analysis of a series of non-linear equations using an iteration scheme which calculates corrections to estimated parameters using an expanded Taylor's series. The program iterates until either (a) the difference between the experimental envelope and the calculated spectrum reaches a preassigned value (usuably set at less than the experimental error) or (b) a predetermined number of iteration cycles has been attained. Input information consists of estimated positions of the spectral bands, their widths at half heights, and the digitized experimental spectrum. The output consists of the best calculated parameters (position, intensity, width at half height, and fraction Gaussian character) for all bands, the experimental envelope, the calculated envelope, and a point by point display of the difference between the calculated spectrum and experimental spectrum. It is understood that the band parameters discussed here are those obtained from RESOL. The spectra of solutions containing excess NH$_2^-$ are reported with the band associated with this species subtracted; a process which is easily accommodated within RESOL since the band parameters for NH$_2^-$ are well described.[15]

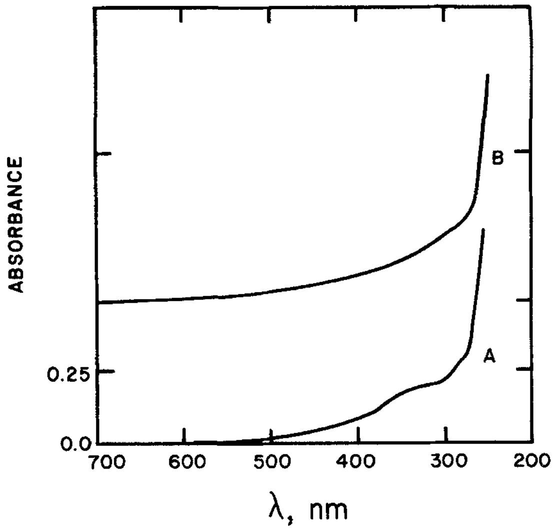

FIGURE 3 Spectra of (Iren$_3$)I$_3$ in liquid ammonia solutions at −75°: A, 7.0 x 10^{-4} M (Iren$_3$)I$_3$; B, [KNH$_2$]/[(Iren$_3$)I$_3$] = 2.6/1 at a solute concentration of 10^{-4} M.

RESULTS AND DISCUSSION

The spectra of these solutions provide information on possible ionization processes occurring and on the nature of the species present in solution. For convenience we discuss the former processes first for each of the metal complexes, $[\mathrm{Men_3}]^{3+}\mathrm{I_3}$ (M = Co, Rh, Ir).

Cobalt System of Compounds

The spectrum of $\mathrm{Coen_3I_3}$ in liquid ammonia (Fig. 1) exhibits features in the low energy range [bands at 467 nm ($\epsilon = 90$) and 338 nm ($\epsilon = \sim 90$] which are virtually identical to those observed in aqueous solution. The higher energy band of the two, appears as a shoulder on another more intense band (288 nm) which is not present in aqueous solution.

The 288 nm band itself is a shoulder of the ccts band attributed to $\mathrm{I^-}$.[26] The intensity of the 280 nm band increases regularly with increasing concentration of $\mathrm{KNH_2}$, the maximum in intensity being observed at one equivalent of $\mathrm{KNH_2}$. The intensity of the 280 nm band is unaffected by the addition of KI indicating that it is not associated with a Co–I containing species which could arise by displacement of en ligands, a process which is unlikely on thermodynamic arguments. The 280 nm band, however, disappears completely on the addition of an ammonium salt. These observations strongly suggest that the 280 nm band arises from a deprotonated species such as $[\mathrm{Coen_2(en{-}H)}]^{2+}$ and that the deprotonation of $[\mathrm{Coen_3}]^{3+}$ occurs readily in pure liquid ammonia (Eq. 1).

$$[\mathrm{Coen_3}]^{3+} + \mathrm{NH_3} \rightleftharpoons [\mathrm{Coen_2(en{-}H)}]^{2+} + \mathrm{NH_4^+} \qquad (1)$$

Other arguments are presented (vide infra) to support the assignment of the 280 nm band to a deprotonated species. The spectroscopic method reported previously[14] for equilibrium systems described by Eq. 2 was applied to solution of $[\mathrm{Coen_3}]^{3+}$ in liquid ammonia

$$\mathrm{HA} + \mathrm{NH_3} \underset{}{\overset{\mathrm{Ki}}{\rightleftharpoons}} \mathrm{NH_4{}^+}, \quad \mathrm{A^-} \overset{\mathrm{K_a}}{\rightleftharpoons} \mathrm{NH_4{}^+} + \mathrm{A^-} \qquad (2)$$

by following the intensity of the 280 nm band as a function of dilution. This analysis gives an ionization constant (K_i) for $[\mathrm{Coen_3}]^{3+}$ of $(2.3 \pm 0.3) \times 10^{-1}$ and a dissociation constant for the ion-pair (K_d) of $(5.2 \pm 2.0) \times 10^{-7}$ at -75°C; the pKa of $[\mathrm{Coen_3}]^{2+}$ is ~7, which should be compared with a value of ~12.5 reported for aqueous solutions.[27,28] The enhanced acidity of the complex ion would be expected since liquid ammonia is a markedly more basic solvent than is water.

Solutions containing $[\mathrm{Coen_3}]^{3+}$ and $\mathrm{NH_2^-}$ in a mole ratio of 2:1 or greater exhibit an additional band at 546 nm. Arguments presented later suggest that the spectrum of a solution containing a mole ratio of 2:1 is consistent with the removal of two protons from different ligands.

$$[\mathrm{Coen_3}]^{3+} + 2\mathrm{NH_2^-} \rightarrow \mathrm{Coen(en{-}H)_2^+} + 2\mathrm{NH_3} \qquad (3)$$

Unfortunately we were unable to obtain sufficient quantitative data to establish the second ionization constant for $[\mathrm{Coen_3}]^{2+}$. At concentrations of the parent complex ion above $\sim 2 \times 10^{-4}$ M and more than ~2 equivalents of $\mathrm{KNH_2}$ present, a finely divided precipitate invariably formed within the time required to attain equilibrium. Thus, the spectra of these solutions provided useful information only on the nature of the species present. It has been suggested[5] that beyond 3 equivalents of $\mathrm{KNH_2}$, displacement of ethylene diamine ligands begins to occur. In our work, $\mathrm{NH_2^-}$ was not detected in solution spectroscopically before 3 equivalents of $\mathrm{NH_2^-}$ had been added.

Since the spectrum of $[\mathrm{Coen_3}]^{3+}$ in liquid ammonia exhibits bands at 467 nm and 338 nm with the same low intensity ($\epsilon = \sim 90$) as appear in water,[28] the assignments of these bands to d–d transitions appears reasonable. The assignments correspond to transitions from the ${}^1A_{1g}$ ground state to the ${}^1T_{1g}$ and ${}^1T_{2g}$ exited states. The Tanabe–Sugano theory[29] for a pure 3d-configuration suggests that the low energy band (467 nm) corresponds to the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition and the 338 nm band to a ${}^1A_{1g} \rightarrow {}^1T_{2g}$. The remaining possible transition, viz. ${}^1A_{1g} \rightarrow {}^3T_{1g}$ and ${}^1A_{1g} \rightarrow {}^3T_{2g}$, should be very weak and would probably not be observed in liquid ammonia solutions because of the limited solubility of the complexes. The markedly more intense band at 280 nm which is present in solution and increases in intensity upon the addition of $\mathrm{KNH_2}$, appears to be best described as a charge transfer (from ligand to metal) band. The deprotonated amine group of the ethylene diamine ligand formed in the ionization of $[\mathrm{Coen_3}]^{3+}$ (Eq. 1) carries an extra lone pair which could be involved in the charge transfer process. A similar change in spectral features occurs when $\mathrm{Cl^-}$ in the species trans-$[\mathrm{Coen_2Cl_2}]$ is replaced by $\mathrm{NH_3}$ in liquid ammonia solution. Initially the trans-dichloro species shows a very intense band at 310 nm, but after several hours, when presumably the chloro ligands have been replaced by $\mathrm{NH_3}$, the spectrum exhibits only two very weak bands at 460 nm and 335 nm. Thus complexes containing NH_3 ligands, which carry neither negative charge or uncoordinated electron pairs, show no intense bands in the charge transfer region, whereas those containing Cl^- ligand do show such features.

The spectrum of $[Coen_3]^{3+}$ in pure liquid ammonia should also contain contributions from the monodeprotonated species $[Coen_2(en–H)]^{2+}$. The spectrum of a solution containing equivalent amounts of KNH_2 and $[Coen_3]I_3$ should be that of the monodeprotonated species $[Coen_2(en–H)]^{2+}$; this spectrum could be resolved into bands at 510 nm ($\epsilon = -3.5 \times 10^2$), 389 nm ($\epsilon = 3.5 \times 10^2$), and 288 nm ($\epsilon = 4.5 \times 10^3$).. The last band indicated, is obviously the ctts band observed in solutions of $[Coen_3]^{3+}$ in pure liquid ammonia, and the other two bands are the corresponding d–d transitions for the deprotonated species. The increase in intensity of the d–d transition bands is ascribed to the breakdown of the Laporte selection rule forbidding transitions which involve the redistribution of electrons in a single quantum shell of a complex exhibiting a center of symmetry. Deprotonation causes a change in the metal ligand interaction which, in turn, places the metal ion in a position that lacks a center of symmetry. This allows the previously forbidden transitions to occur. The change in position of the two d–d bands to lower energy can be associated with a change in ligand field strength. However it does not appear reasonable to deduce that a deprotonated amine should be a weaker field ligand than the corresponding amine. The metal ion in the parent complex has a set of non-bonding (t_{2g}) d orbitals that are capable of interacting with the p orbitals, which are stable and occupied, of the deprotonated ligand atoms and would be expected to have a large effect on the metal t_{2g} orbitals. The net effect is to make the occupied t_{2g} metal orbitals antibonding and raised in energy, leading to a decrease in ligand field splitting.

The spectrum of the product formed when $[Coen_3]^{3+}$ is treated with two equivalents of KNH_2 suggests that the deprotonated species carries the charged nitrogen ligands in trans positions. The experimental spectrum (Figure 1) contains obvious bands at the high 285 nm, $\epsilon = 5.2 \times 10^3$) and low (546 nm, $\epsilon = 7.7 \times 10^2$) energy regions. The intermediate region is best resolved into two bands at 426 nm ($\epsilon = 5.3 \times 10^2$) and 389 nm ($\epsilon = 4.7 \times 10^2$) rather than the one apparent band at 396 nm. If these were only a single band at 396 nm contributing to the observed spectrum, its width at half height (7179 cm^{-1}) is considerably greater than that observed for other d–d transitions. On the other hand, the widths of half-height for a two band resolution for this region (426 nm, $W_{h/2}$ = 5760 cm^{-1}, 389 nm, $W_{h/2}$ = 3951 cm^{-1}) give results which are more consistent with line shapes in other d–d transition spectra. Thus, we favor the two band interpretation for this region of the spectrum. A theoretical treatment[30] of cis and trans isomers of hexacoordinated complexes from the point of view of crystal field theory indicates that the superposition of a crystal field of lower symmetry on an octahedral complex splits the $^1T_{1g}$ state and that the $^1T_{2g}$ state would not be split sufficiently to be observed. The $^1T_{1g}$ state in a trans complex shows a greater splitting than is observed for the cis-complex. Thus the presence of 3 bands assigned to d–d transitions indicates that the deprotonated species $[Coen(en–H)_2]^+$ carry ethyleneamide groups (^-NHR) in trans-positions. In other words deprotonation has occurred on two different ethylenediamine molecules.

The Rhodium and Iridium Systems of Compounds

We were less fortunate in the study of $[Rhen_3]I_3$ dissolved in liquid ammonia because this substance is not very soluble. A well defined band (Figure 2) observed at 300 mm (ϵ = ~250) corresponds to the band at 302 nm reported[31,32] in water and apparently arises from the first ($^1A_{1g} \rightarrow {}^1T_{1g}$) d–d transition. The second band observed in aqueous solutions at 253 nm is obscured by the I^- ctts band and the solvent cut off. Attempts to study deprotonated rhodium-containing species were foiled by the fact that the ctts band for NH_2^- obscured the 300 nm region (Figure 2). The deprotonated rhodium complex $[Rhen_2(en–H)]^{2+}$ gives rise to a band at 340 nm appearing on a shoulder of a band, the center of which is below 280 nm. The latter, unfortunately, coincides with the ctts amide band, making it virtually impossible to use RESOL. The shift of ~40 nm of the first d–d band is less than that observed in the corresponding cobalt complexes and suggest less π-interaction between the deprotonated amine and the larger Rh^{3+} ion. Increasing the number of equivalents of KNH_2 did not produce spectra with resolvable features. Precipitates occurred in solutions containing 2.5–3.5 equivalents of KNH_2 in 1×10^{-4} M solutions of $[Rhen_3]I_3$.

Although aqueous solutions of $[Iren_3]I_3$ exhibit a weak band at 301 nm,[31] the spectra of this compound in ammonia or in the presence of KNH_2 are essentially featureless (Figure 3).

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