which is responsible for the canting of the spins.[11]

A similar canting behavior was observed for the deuterated salt also. Between 3.7 and 4.3 K, $\chi_a(D)$ was found to be constant. Below this temperature, it dropped off sharply to a constant value of 0.055 ± 0.002 emu/mol at the lowest temperatures. Both the drop off rate and the size of the region of constant χ are smaller here and appear to be consistent with Losee's conclusion of being due to larger demagnetizing effects. The value of the constant susceptibilities also agrees favorably with Losee's value of 0.056 emu/mol for $\chi_a(H)$.

Between 4.3 and 22 K, the data were fitted to eq 7 by varying simultaneously g_a and the constant D/J. Good fits within 10% of the measured susceptibilities were obtained for $g_a = 3.23 \pm 0.05$ and $|D/J| = 0.65 \pm 0.2$. Whereas this value of $|D/J|$ is the same as obtained by Losee for $\chi_a(H)$, g_a is somewhat larger than the earlier value of 2.95 ± 0.05.

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Registry No. $[(CH_3)_3NH]CoCl_3\cdot 2H_2O$, 60294-92-0; $[(CH_3)_3ND]CoCl_3\cdot 2D_2O$, 60294-94-2.

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Preparation and Photochemistry of Azidopentacyanorhodate(III) and -iridate(III)

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The potassium salts of the complex ions $[Rh(CN)_5N_3]^{3-}$ and $[Ir(CN)_5N_3]^{3-}$ have been prepared and characterized. Their electronic spectra show weak ($\epsilon \sim 230$) bands near 3.2 μm^{-1}, which are assigned to N_3^--localized electronic transitions. The photochemistry associated with these bands appears to be nearly exclusively simple aquation, with high quantum yields ($\Phi = 0.42$ for the rhodium complex and 0.60 for the iridium complex). The marked contrast between these results and those obtained by other workers for the analogous amine complexes is discussed.

Introduction

A series of recent papers by Basolo and co-workers[1] has established a novel photochemical reaction of the complexes $M(NH_3)_5N_3^{2+}$, M = Rh and Ir, yielding intermediates, presumed to be coordinated nitrenes, $M(NH_3)_5N^{2+}$, which undergo reactions with nucleophiles to give characteristic products. An unresolved problem arising from this work is the nature of the reactive excited state. Basolo and co-workers[1] have argued that the reaction could not be associated with metal-centered ligand field excited states and suggested that it arose from states, postulated to be the lowest excited states available to the complexes, in which excitation is localized in the azide ligand. Unfortunately, the observed low-energy absorption bands of the complexes could be plausibly assigned to ligand field transitions,[1] and the ligand-localized transition could only be assumed to be weak and obscured by the other, stronger, absorption bands.

Our continuing interest in high-energy photochemical products led us to attempt the investigation of analogous azidopentacyano complexes. Previous work with other pentacyano derivatives[2,3] had shown that both ligand field and charge-transfer type electronic transitions are shifted to higher energy relative to pentaammine analogues. Consequently we anticipate that weak, ligand-localized transitions might be *directly* observable.

Experimental Section

Preparation of $K_3[Rh(CN)_5N_3]\cdot H_2O$ and $K_3[Ir(CN)_5N_3]\cdot H_2O$. Solutions of $K_2[Rh(CN)_5OH_2]$ or $K_2[Ir(CN)_5OH_2]$ were prepared by 254-nm photolysis of aqueous (adjusted to pH 1 with concentrated $HClO_4$) solutions of $K_3[Rh(CN)_6]$ or $K_3[Ir(CN)_6]$, as described by Geoffroy et al.[2] Our preparations employed ~200 ml of $\sim 10^{-3}$ M solution.

The volume of a solution prepared as described above was reduced to 10 ml under reduced pressure at 40 °C. The pH was then brought to 6 with concentrated aqueous KOH and ~1 g of KN_3 was added. After standing for 1–2 days, the solution was filtered and 250 ml of acetone was added to give an off-white precipitate. Operations from this point on were conducted with minimal exposure to light. The precipitate was extracted with 50 ml of warm methanol, and the resulting solution was filtered. Acetone (100 ml) and ether (35 ml) were added, precipitating about half of the dissolved material. The precipitate was filtered off and the mother liquor, containing mainly potassium azide, was discarded.

The above recrystallization procedure was repeated (usually two or three times) until the infrared spectrum (KBr pellet) of the white product showed no trace of the sharp bands of KN_3 at 650 cm^{-1} and 644 cm^{-1}. The infrared spectra indicated the presence of crystal water (moderately sharp bands at 3640, 3560, and 1605 cm^{-1} for both compounds), and a monohydrate formulation fits the analytical data reasonably well. Anal. Calcd for $K_3[Rh(CN)_5N_3]\cdot H_2O$: Rh, 25.08; C, 14.63; H, 0.49; N, 27,31; C:N, 0.536. Found: Rh, 25.23; C, 14.41; H, 1.03; N, 27.00; C:N, 0.532. Calcd for $K_3[Ir(CN)_5N_3]\cdot H_2O$: Ir, 38.47; C, 12.02; H, 0.40; N, 22.63; C:N, 0.536. Found: Ir, 39.65; C, 12.18; H, 0.58; N, 22.60; C:N, 0.539.

Strong infrared bands, in addition to those previously mentioned, were observed for the rhodium complex at 2135, 2072, and 1297 cm^{-1} and for the iridium complex at 2130, 2080, and 1295 cm^{-1}. These are assigned, for both complexes, to $\nu(CN)$, $\nu_{as}(N_3)$, and $\nu_s(N_3)$, in order.

Irradiation Procedures. Three-milliliter samples were irradiated using a merry-go-round,[4] employing filters to isolate the group of lines near 313 nm in the spectrum of a medium-pressure mercury lamp.

Table I. Electronic Spectra of $[M(CN)_5N_3]^{3-}$ Complexes in Aqueous Solution at 300 K

M	Assignment	λ_{max}, nm	$\bar{\nu}_{max}$, μm^{-1}	ϵ
Co[a]	$d_{xy,yz} \rightarrow d_{z^2}$	383	2.61	743
	$\pi_g(N_3^-) \rightarrow d_{z^2}$	281	3.56	8 580
	b	220	4.55	11 000 sh
Rh	$\pi_g(N_3^-) \rightarrow \pi_u(N_3^-)$	325	3.08	235 sh
	$d_{xz,yz} \rightarrow d_{z^2}$	272	3.68	3 230
	$\pi_g(N_3^-) \rightarrow d_{z^2}$	244	4.10	4 990
	b	205	4.88	12 200
Ir	$\pi_g(N_3^-) \rightarrow \pi_u(N_3^-)$	297	3.37	225
	$d_{xz,yz} \rightarrow d_{z^2}$ and/or $\pi_g(N_3^-) \rightarrow d_{z^2}$	244	4.10	2 280

[a] Reference 8. [b] See text for discussion of these bands.

Light intensities, measured using ferrioxalate actinometry,[5] were of the order of 10^{-7} einstein min^{-1}. The complexes were thermally inert under the photolysis conditions. Disappearance of the azide complexes was monitored by following the decrease in absorbance at wavelengths from 340 to 320 nm, where products do not absorb, or, in experiments where only relative disappearance rates were desired, at the maxima of the intense bands in the region. Considerable qualitative and product analysis work was also done using only Pyrex filters ($\lambda \geq 300$ nm) in order to obtain higher light intensities.

Azide ion,[1,6] NH_2Cl,[1] and NH_2OH[7] products were determined by literature methods. Solutions were generally photolyzed under an argon atmosphere in order to eliminate possible complications resulting from reaction of oxygen with intermediates or products. The azide determinations were carefully calibrated for the differing chloride and hydrogen ion concentrations used in various experiments.

Physical Measurements. Infrared spectra were recorded with a Perkin-Elmer Model 337 Grating infrared spectrophotometer. Ultraviolet and visible spectra were recorded on a Cary 14 spectrophotometer.

Results and Discussion

The title complexes were prepared by the photochemical route of Geoffroy et al.[2] Consistent with these authors' comments for their related products, the potassium salts were initially obtained in very impure form. Furthermore, in our hands, chromatographic methods were notably unsuccessful in purification of the compounds, presumably because of partial decomposition on the columns. However, we found that the salts were fairly soluble in methanol, in which several of the impurities (notably $KHCO_3$, $KClO_4$, and $K_3[M(CN)_6]$) were insoluble, and standard recrystallization techniques allowed efficient separation from a persistent KN_3 impurity.

Electronic Spectra. The electronic spectra of the potassium salts of the complexes are shown in Figure 1 and summarized in Table I; also set out in Table I are spectral data for the $[Co(CN)_5N_3]^{3-}$ ion, from ref 8.

The assignments given for the rhodium and iridium complexes derive from comparison to the analogous cobalt complex, following correlations established in ref 2 and 3. The lowest energy singlet–singlet ligand field band ($^1A_1 \rightarrow {}^1E$, $d_{xz,yz} \rightarrow d_{z^2}$) of $[Co(CN)_5X]^{3-}$ complexes is generally blue shifted by ~1.1 μm^{-1} for the analogous $[Rh(CN)_5X]^{3-}$ complexes, while ligand-to-metal charge-transfer (LMCT) bands are blue shifted by ~0.7 μm^{-1}. Thus, the 3.68-μm^{-1} band of $[Rh(CN)_5N_3]^{3-}$ is assigned to the $^1A_1 \rightarrow {}^1E$ ligand field transition, and the 4.10-μm^{-1} band is assigned to LMCT to the empty d_{z^2} metal orbital from a C_s symmetry (the complex ion symmetry) orbital component which derives from the π_g (internally nonbonding) orbital of free N_3^-, the highest filled ligand orbital.[9]

Singlet–singlet ligand field and charge-transfer bands are generally blue shifted by ~0.5 μm^{-1} in $[Ir(CN)_5X]^{3-}$ complexes relative to the bands in $[Rh(CN)_5X]^{3-}$.[2] Therefore, the 4.10-μm^{-1} band of $[Ir(CN)_5N_3]^{3-}$ is assigned to the $^1A_1 \rightarrow {}^1E$ ligand field transition of the complex. No charge-transfer band is evident near 4.6 μm^{-1}, although the high-energy tail of the 4.10-μm^{-1} band indicates the presence of at least one more band near 4.3 μm^{-1}. Thus, the expected LMCT band appears to be "missing". Also, there are no maxima at $\bar{\nu} > 4.6$ μm^{-1}, although absorption is rising rapidly in this region. Apparently the band observed at 4.55 μm^{-1} for the cobalt complex[8] and at 4.88 μm^{-1} for the rhodium complex is shifted to still higher energy (and/or weakened) for the iridium complex. This suggests that the transition responsible for these bands is charge transfer rather than intraligand, the original assignment for the cobalt complex.[8] Possible charge-transfer assignments include LMCT from the azide π_g orbital to the empty metal $d_{x^2-y^2}$ orbital (as has been suggested for analogous thiocyanate complexes[3]), LMCT from the bonding azide π_u orbital[9] to the metal d_{z^2} orbital, and metal-to-azide charge transfer. The apparent absence of the lowest energy LMCT band deserves some discussion.

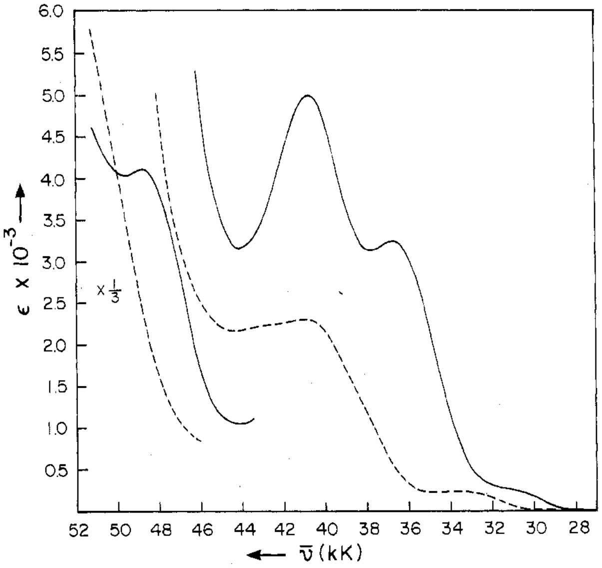


Figure 1. Electronic spectra in aqueous solutions of $[Rh(CN)_5N_3]^{3-}$ (–) and $[Ir(CN)_5N_3]^{3-}$ (- - -).

The low-energy ligand field and LMCT transitions under discussion have the same terminal orbital (the metal d_{z^2}) and originate in orbitals (metal $d_{xz,yz}$ and azide π_g, respectively) which are directly involved in a π-bonding interaction. Thus, extensive mixing of the two transitions can be expected. This is consistent with the relatively high intensity of the ligand field band of $[Rh(CN)_5N_3]^{3-}$, since the two transitions are rather close together. Even the spectrum of the cobalt complex, where the separation is greater, shows higher intensity in the ligand field transition than is common with $[Co(CN)_5L]^{3-}$ complexes.

This mixing accounts for some of the apparent weakening of the LMCT band of the rhodium complex relative to that of the cobalt complex, as the intensity has been "redistributed". However, the sum integrated intensity of the LMCT and ligand field bands is still considerably lower than for the cobalt complex, and the apparent further loss of total intensity for the iridium complex is evidently an extension of a trend. A similar trend is apparent in the electronic spectra of the amine analogues of these complexes.[10] It seems that the azide (π_g) $\rightarrow$ M(d_{z^2}) transition becomes increasingly weaker for the heavier metal ion complexes. This is conceivably due to a radial mismatch of the heavier metal d orbitals with the compact filled pπ orbital of nitrogen; similar explanations have been invoked for the basicity trends of heavy heteroatom-substituted amines.[11]

Finally, we turn to the weak near-uv bands observed for the two complexes. For iridium complexes, singlet–triplet ligand field bands are usually observed 0.4–0.5 μm^{-1} to lower energy

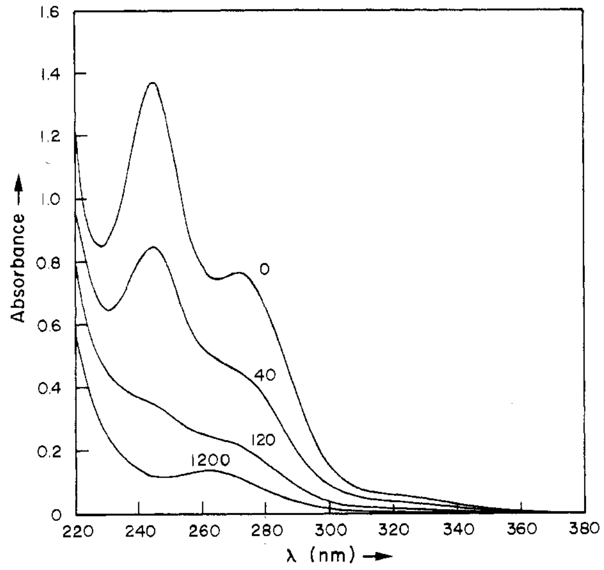


Figure 2. Photolysis of 2.25 × 10^{-4} M aqueous $[Rh(CN)_5N_3]^{3-}$ with 313-nm light; the numbers beside the curves refer to photolysis times, in minutes; the lowest curve is essentially an infinity-time spectrum.

of the singlet–singlet ligand field band, with about one-fourth of the intensity of the singlet–singlet transition.[2] Thus, the 3.37-μm^{-1} band of $[Ir(CN)_5N_3]^{3-}$ could conceivably be the $^1A_1 \rightarrow {}^3E$ ligand field transition, if the singlet–triplet splitting were exceptionally large. However, the band of $[Rh(CN)_5N_3]^{3-}$ at 3.08 μm^{-1} is equally intense, whereas Geoffroy et al.[2] noted no example of a resolved singlet–triplet ligand field band for $[Rh(CN)_5X]^{3-}$ complexes. The band of the rhodium complex is of much too low energy[2,3] to be a singlet–singlet ligand field transition.

We believe that these bands are azide-localized $\pi \rightarrow \pi^*$ transitions and that the $^1A_1 \rightarrow {}^3E$ ligand field transition of $[Ir(CN)_5N_3]^{3-}$ is unresolved near 3.7 μm^{-1}. Alkyl azides [12-14] have weak ($\epsilon \simeq 25$) bands near 287 nm which have been assigned to a transition between components of the azide π_g and π_u orbitals, which are the highest energy filled and lowest energy empty orbitals of free N_3^-.[15] The bands of the metal complexes are probably a singular transition, both red shifted and intensified because of π interaction with the metal. The smaller red shift for the iridium complex reflects less π interaction consistent with previous discussion. This transition is that invoked by Basolo et al.[1] in their discussion of the photochemical reactions of the analogous ammine complexes.

Photochemistry. Our photochemical investigations were limited to 313-nm irradiation, as we were only interested in reactions deriving from the lowest energy absorption bands, believed to be azide-localized electronic transitions.

Irradiation of aqueous solutions of the complexes leads to efficient photoreaction. The spectral changes resulting upon irradiation of $[Rh(CN)_5N_3]^{3-}$ solutions are illustrated in Figure 2. The final spectrum in Figure 2 corresponds to quantitative conversion to $[Rh(CN)_5OH_2]^{2-}$ (ϵ 605 at 265 nm),[2] within experimental error (~5%). The observed spectrum deviates from the spectrum of the aquo complex at shorter wavelengths because of the presence of N_3^- in the product solution (vide infra).[3] Additional proof for the identity of the photoproduct was obtained by incubation with KI. The complex $[Rh(CN)_5I]^{3-}$ (λ_{max} 313 nm, ϵ 1500)[2] was formed quantitatively, within experimental error.

Spectral changes for irradiated solutions of $[Ir(CN)_5N_3{}^{3-}$ are less informative because the major bands of the aquo product are obscured by N_3^- absorption. However, the final absorbance at 270 nm agreed within experimental error with that expected for quantitative formation of $[Ir(CN)_5OH_2]^{2-}$ (ϵ 180 at 270 nm).[2]

The absence of any absorption in the photolyzed solutions to the red of the $[M(CN)_5OH_2]^{2-}$ bands indicates that disubstituted metal complexes are not significant products. (The lowest ligand field band of $[Rh(CN)_4(OH_2)_2]^-$ has a maximum near 330 nm.[2b]) Such products might have been anticipated either if cyanide aquation were a significant process of if a nitrene intermediate were to react by migration of CN from metal to ligated nitrogen giving a structure such as M=NCN.

Disappearance quantum yields were obtained for concentrated ($C \geq 10^{-2}$ M) solutions of the complexes in pH 5.5 acetate buffer (ionic strength 0.2), and determinations followed only the first few percent of reaction, in order to avoid possible complications from secondary photoreactions. The values obtained at 25 °C were 0.42 ± 0.02 for $[Rh(CN)_5N_3]^{3-}$ and 0.60 ± 0.05 for $[Ir(CN)_5N_3]^{3-}$. The disappearance quantum yields were found to be insensitive to ionic strength (0–1.0 M $NaClO_4$ or sodium acetate), chloride ion (NaCl concentrations from 0 to 2 M), the presence or absence of O_2 in the solutions, and pH in the range 2–12. Both this behavior and the high quantum yields are similar to those reported[1b] for $[Ir(NH_3)_5N_3]^{2+}$.

Chloramine and related compounds[1] were sought in solutions irradiated under conditions of high chloride ion concentration (0.1–2.0 M) and acidity (0.01–0.1 M HCl). We found only very small yields amounting to conversion of 1–2% of the photolyzed complexes to chloramine. That no products capable of oxidizing I^- were formed in the absence of chloride ion suggeests that the observed product may actually by NH_2Cl. However, it is certainly not a major product, and because of the small yield, no additional evidence confirming its identity could be obtained.

On the assumption that a presumed metal nitrene intermediate in this system might have different reactivity than in the system studied by Basolo et al.[1] or that a "free" nitrene (plus a metal nitrogen complex) might be a primary product,[16] irradiated solutions were analyzed for hydroxylamine,[7] a likely product from a "reactive" nitrene in aqueous solution. Under conditions similar to those used in the NH_2Cl determinations, none could be found within our error limits. This indicates that conversions were 0.5% or less.

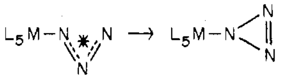
The only significant photoproduct, other than the metal–aquo complex, proves to be N_3^-. For solutions of the title complexes ~10^{-3} M, photolyzed to less than 10% conversion, greater than 90% yields of N_3^- could be obtained, and yields extrapolate to 100 ± 5% at $t = 0$. Thus, in the absence of free N_3^-, the quantum yield for N_3^- production appears to equal the disappearance quantum yield of the complexes. For longer irradiation times, we found that apparent azide yields were low, presumably as a result of secondary reactions.[17] It is clear, however, that the primary photochemical process is simply aquation.

Conclusions

Our results are surprising. We have indeed, as we originally hoped, observed weak, near-uv absorption bands for our complexes, which can be reasonably assigned to electronic transitions localized in the azide ligand. However, irradiation of the complexes in those bands does *not* generate nitrene-derived products but instead leads to azide ion release. The surprising contrast to the results of Basolo and co-workers cannot be rationalized simply by reassigning the low-energy transitions in the pentacyano azides to a ligand field transition, because low-energy irradiation of the analogous ammine complexes,[1] in absorption bands which *are* reasonably assigned to ligand field transitions, gives only nitrene-derived products. There is clearly a large change in reaction mode, regardless of electronic spectral assignments, and we therefore feel no compulsion to doubt our present assignments.

One possible explanation of the photochemical results involves the differences in bonding characteristics between cyanide and ammine ligands. The stability of the coordinated nitrene intermediate of Basolo et al.[1] was explained by invoking π-back-bonding interactions of the nitrene with the metal center. Conceivably, the π-back-bonding capacity of the cyanide ligands of the title complexes considerably reduces the ability of the metal center to π bond to a nascent nitrene. Thus, an alternative reaction pathway (elimination of azide ion) might become preferred. However, this explanation provides no simple rationale for the *high* quantum yields for azide ion release observed for our complexes. It is unsettling that both the calculations of Zink[16] and intuition do not suggest any large reduction in M–N(azide) bonding in either ligand-localized or MLCT excited states of the complexes. If the excited state has a long lifetime of course, it could give the observed high product yields even if it were not highly reactive.

One interesting possibility is that the excited states of the complexes decay to high-energy isomers which are actually responsible for the observed dissociation reactions. One such possibility would be a tris(azacyclopropene) structure produced by relaxation of the strongly bent[13,16] ligand-localized excited state



Such a bizarre species might dissociate with loss of cyclic N_3^- or lose N_2 to give the nitrene complexes when activated by sufficient π-donor activity of the central metal atom. Reaction of either the cyclic complex or the cyclic anion with azide ion or NH_3 could be responsible for falloff in quantum yields as photolysis proceeds.[17]

Irrespective of the merits of any rationalizations, our observations warn against overreliance on attractive simple theories relating the changes of electron distribution on excitation to the ultimate selection of decay paths by excited states. Specifically, we have shown that the photochemisty of a particular ligand bound to a particular metal ion can be not only just modified but also completely changed by variation of the nature of other ligands which do not themselves undergo permanent changes in the photoprocess.

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Registry No. $K_3[Rh(CN)_5N_3]$, 60305-96-6; $K_3[Ir(CN)_5N_3]$, 60305-97-7; $K_3[Rh(CN)_6]$, 20792-40-9; $K_3[Ir(CN)_6]$, 20792-41-0.

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