Photoreduction of $Co(NH_3)_5N_3^{2+}$ at 2537 Å. Photolabilization of an Ammonia Ligand[1]

Sir:

It has been reported[2] that irradiation of the ligand-to-metal charge-transfer region of aqueous $Co(NH_3)_4N_3^{2+}$ leads to 100% photoreduction (*i.e.*, Co^{2+}). We can now report compelling evidence that $Co(NH_3)_5OH_2N_3^{2+}$ is actually the predominant initial product of this reaction and that this latter complex is itself subsequently photolyzed.

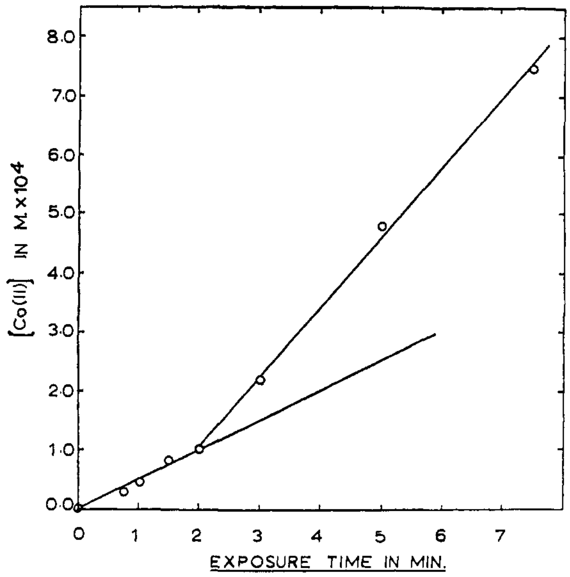

Figure 1. Co(II) production in the 2537-Å photolysis of $Co(NH_3)_5N_3^{2+}$: $[Co(NH_3)_5N_3]^{2+} = 9.88 \times 10^{-4}$ *M*; $[H^+] = 0.1$ *M*; $I_a = 3.3 \times 10^{-4}$ einstein l.$^{-1}$ min^{-1}; $I_0 = 5.5 \times 10^{-4}$ einstein l.$^{-1}$ min^{-1}.

Some evidence has been reported recently[3] which suggests that $Co(NH_3)_4OH_2Cl^{2+}$ is formed as a product in the uv irradiation of $Co(NH_3)_5Cl^{2+}$, and the photolabilization of a Cr^{III}–ammine bond seems to be fairly commonplace;[4] however, this kind of process has not heretofore been established as the dominant reaction path in the photochemistry of cobalt(III).

Table I. Spectral and Photochemical Data

Complex	λ_{max} (log ϵ), nm	$\epsilon_{254} \times 10^{-3}$, l. mole^{-1} cm^{-1}	$\varphi_{Co(II)}$ Initial	$\varphi_{Co(II)}$ Intermediate	$\varphi_{Co^{III}-N_3^-}$ apparent
$Co(NH_3)_5N_3^{2+}$	301 (3.89)	0.63	0.17	0.36	0.17 → 0.7
$Co(NH_3)_4(OH_2)N_3^{2+}$ (equilibrium mixture)	308 (3.91)	1.35	0.27	0.34	0.25 → 0.35

We have irradiated acidic solutions of $Co(NH_3)_5N_3^{2+}$[5] at 2537 Å under a nitrogen atmosphere using mercury resonance lamps of various intensities (10^{-3}–10^{-5} einstein l.$^{-1}$ min^{-1}). The quantum yield of cobalt(II) was determined spectrophotometrically[6] in comparison to uranyl- and ferrioxalate actinometry.[7] At the higher values of I_a, the rate of formation of Co^{2+} was not zero to first order (depending on whether 100% or less light was transmitted) in substrate concentration as is generally observed,[8] but rather $\varphi_{Co(II)}$ was very often found to increase with time. Typical kinetic behavior in this region of I_a is shown in Figure 1 where a distinct increase in the rate of cobalt(II) production is exhibited after 20–25% of reaction; this corresponds to a change of $\varphi_{Co(II)}$ from an initial value of 0.17 to a value greater than 0.35 (I_a decreases only about 20% over about 75% of reaction in this case).

A careful examination of the cobalt(II) yields and the spectra of irradiated solutions in a very large number of experiments has revealed a number of unexpected kinetic features: (1) the value of $\varphi_{Co(II)}$ and the appearance of the break in the kinetics curve appeared to be dependent on the rate at which light was absorbed; *i.e.*, at high I_a, $\varphi_{Co(II)} \simeq 0.2$ initially, becoming 0.3–0.6 after 20–25% of reaction while, at low I_a, $\varphi_{Co(II)}$ approached an apparent limit of ~0.6 with no break in the curve;[9] (2) in some experiments at very high I_a, the value of $\varphi_{Co(II)}$ appears to depend on the ratio of irradiation to dark time during the exposure and sample removal; (3) the apparent change in $[Co(NH_3)_5N_3^{2+}]$ as measured at its charge-transfer band maximum (301 nm) was considerably larger than that calculated at 254 nm, but disappearance of $[Co(NH_3)_5N_3^{2+}]$ (as determined by the absorbance change at 301 nm) was found to be stoichiometric in the appearance of Co^{2+} as a photolysis product; (4) the value of $\varphi_{Co(II)}$ was found to be very insensitive ($\Delta\phi \leq 10\%$) to the presence of potential radical scavengers, such as H^+, NO_2^-, NO_3^-, N_3^-, H_2O_2, O_2, I^-, Br^-, or $Co(NH_3)_6^{3+}$ in the solution during irradiation; (5) the yield of N_2 (*in vacuo*) relative to Co^{2+} was found to be independent of the period of irradiation.

These observations imply the formation of a species from the photolysis which is very similar to $Co(NH_3)_5N_3^{2+}$ both with respect to its near-ultraviolet and visible absorption spectra and the qualitative features of its photochemistry. Since both the photochemistry and absorption spectra of $Co(NH_3)_5N_3^{2+}$ are uniquely characteristic of the presence of the Co^{III}–N_3^- bond, the product species must be an azide complex of cobalt(III). Since the equilibrium mixture of $Co(NH_3)_4OH_2N_3^{2+}$

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[1] This work was supported by the National Science Foundation (Grant GP 7048) and was presented in part before the Division of Physical Chemistry, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

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[6] D. Katakis and A. O. Allen, *J. Phys. Chem.*, **68**, 1357 (1964).

[7] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 783.

[8] J. F. Endicott and M. Z. Hoffman, *J. Am. Chem. Soc.*, **87**, 3348 (1965).

[9] These observations are consistent with a significant absorption by $Co(NH_3)_4OH_2N_3^{2+}$ after ~25% of reaction (high I_a) and a photostationary state in $[Co(NH_3)_4OH_2N_3^{2+}]$. Note that ϵ_{254} for $Co(NH_3)_4OH_2N_3^{2+}$ is about twice ϵ_{254} of $Co(NH_3)_5N_3^{2+}$ (Table I). A detailed kinetic analysis will be presented elsewhere.[10]

[10] L. S. Beres, J. F. Endicott, M. Z. Hoffman, and R. W. McQuigg, manuscript in preparation.

meets all the requirements listed above,[11] we have also investigated the photochemistry of this material. Pertinent spectral and photochemical data for $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_4OH_2N_3^{2+}$ are compared in Table I.

After a sample of $Co(NH_3)_5N_3^{2+}$ was irradiated in the cell holder of a Cary 14 spectrophotometer for 1 min, the absorbance of the solution at 254 nm slowly decreased over the course of about 5 min. This transient absorbance exhibited a half-life for the decay of ≥ 40 sec. This is comparable to the half-life of the *trans* → *cis* isomerization of $Co(NH_3)_4OH_2N_3^{2+}$ reported by Haim.[11] The lifetime of this transient (which is presumably due to *trans*-$Co(NH_3)_4OH_2N_3^{2+}$) compared to the time required for photolysis and sampling at high I_a is such that the solution containing $Co(NH_3)_4OH_2N_3^{2+}$ will approach equilibrium only as the ratio of irradiation to dark time becomes very large.

Our observations, summarized above, of the photochemistry of $Co(NH_3)_5N_3^{2+}$, a cobalt(III) complex containing a strongly "reducing" ligand, show quite clearly that the photolabilization of a coordinated ammine has at least as great a quantum yield as photoreduction and that both of these processes are far more important than the formation of $Co(NH_3)_5OH_2^{3+}$. These observations are certainly at odds with a "radical-pair" model[2] for the photochemistry of coordination complexes of cobalt(III). Studies still in progress suggest that similar photolabilization occurs in the 2537-Å irradiation of *cis*-$Co(NH_3)_4(N_3)_2^+$ but not for *trans*-$Co(NH_3)_4(N_3)_2^+$.[10]

Acknowledgment. The authors wish to thank Mr. Laszlo S. Beres for many early studies on this system.

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A Nickel(II)-Catalyzed Synthesis of a Triarsine from a Diarsine

Sir:

Some years ago, one of us[1] reported the isolation of a compound which was considered to have the formula $[Ni(diars)_3](ClO_4)_2$ (diars = *o*-phenylenebis(dimethylarsine)), I, and in 1966 we described[2] an improved method of preparation. The compound was of interest in that it was diamagnetic although believed to be[1,2] an octahedral trisbidentate complex.

However, X-ray diffraction studies, which will be reported in detail elsewhere by P. J. Pauling, show that the substance which was isolated is *o*-phenylenebis(dimethylarsine)[bis(*o*-dimethylarsinophenyl)methylarsine]nickel(II) perchlorate. The compound contains *five* arsenic atoms arranged about the nickel at the corners of an almost regular tetragonal pyramid (Figure 1). We have now shown that the original compound can be prepared directly from the diarsine (I) and the triarsine (II) with nickel(II) perchlorate hexahydrate. Thus, when equal volumes of 0.1 *M* solutions of each of these three compounds in ethanol–ether were mixed, a deep maroon color developed and crystals were deposited within 30 min at room temperature. In this way a quantitative yield was obtained of a substance which had an X-ray powder pattern identical with that of the original material. As further evidence for this formulation it is possible, after breaking down the original complex with sodium cyanide solution, to isolate the triarsine (II) from the reaction mixture.

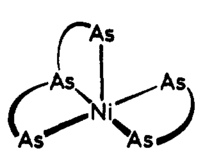
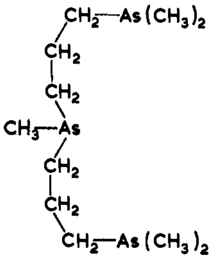


Figure 1. A diagramatic drawing of the coordination polyhedron in $[Ni(diars)(triars)](ClO_4)_2$. Crystals are monoclinic, space group $P2_1/c$; $a = 18.41$, $b = 20.21$, $c = 12.61$ Å, $\beta = 125.80°$, $Z = 4$ formula units per unit cell. At the present stage of least-squares refinement, the residual $R = 0.18$. The basal plane Ni–As distances are 2.26, 2.27, 2.30, and 2.32 Å. The apical Ni–As distance is 2.39 Å. The site below the square plane appears to be unoccupied.

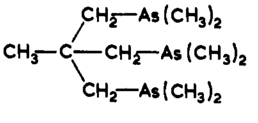
A reexamination of the proton magnetic resonance spectra of the original and the new complex in hexadeuteriodimethyl sulfoxide shows, in addition to the two previously reported peaks, now shifted to τ 8.23 and 8.41, three smaller, broader peaks at τ 6.53, 7.32, and 7.80. These peaks, which are of equal area and together constitute about one-third of the area of the strong peaks, were obscured by the solvent in dimethylformamide.

Thus we have discovered a new reaction whereby, in boiling diethylene glycol, *o*-phenylenebis(dimethylarsine) is converted in some 20% yield to the triarsine, bis(*o*-dimethylarsinophenyl)methylarsine. Phillips[3] reported the preparation of the so-called "tris complex" in some 40% yield by heating an ethanolic solution of $[Ni(diars)_2Cl_2]$ in a sealed tube at 200° but was unable to isolate the complex from the reaction mixture. It is of interest to note[4] that the reaction products from the sealed tubes always smelt more strongly than diarsine. This is probably due to the presence of $As(CH_3)_3$ formed in the disproportionation. This reaction requires the presence of the nickel(II) salt since, if a solution of the diarsine in diethylene glycol is refluxed for the same period of time, subsequent addition of nickel(II) chloride to the cooled solution does not yield the requisite product.

These results still leave unsolved the puzzle of the structures of the diamagnetic nickel(II) complexes of the type $[Ni(triars)_2](ClO_4)_2$, with the terdentate arsines, II, III, and IV. These all have spectra very similar to



III



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[3] D. J. Phillips, Ph.D. Thesis, University of London, 1958.

[4] D. J. Phillips, private communication.