Table I. $C2/c$ Coordinates (x, y, z, and $U_{eq}{}^{a} \times 10^4$)

atom	x	y	z	U_{eq} or B, Å^2
Ga	0	398 (0.3)	2500	423 (1)
Cl	0	2221 (0.9)	2500	814 (3)
N11	2603 (2)	−555 (2)	3595 (1)	495 (5)
N12	2054 (2)	367 (2)	3158 (1)	482 (4)
N21	271 (2)	−1161 (2)	3985 (1)	481 (4)
N22	−606 (2)	−449 (2)	3474 (1)	465 (4)
C13	3101 (3)	1120 (3)	3217 (2)	577 (6)
C14	4320 (3)	688 (3)	3680 (2)	662 (8)
C15	3972 (3)	−361 (3)	3905 (2)	646 (7)
C23	−1789 (3)	−350 (3)	3843 (2)	604 (6)
C24	−1673 (3)	−996 (3)	4585 (2)	687 (7)
C25	−377 (3)	−1491 (2)	4655 (2)	608 (7)
B	1667 (3)	−1586 (2)	3677 (2)	542 (7)
HBA	2238 (28)	−2180 (24)	4212 (17)	6.5 (7)[b]
HBB	1338 (23)	−1999 (19)	3032 (15)	4.4 (5)[b]
H13	2884 (30)	1832 (25)	3006 (18)	6.3 (8)[b]
H14	5162 (30)	1049 (25)	3825 (18)	6.3 (7)[b]
H15	4468 (31)	−896 (26)	4228 (19)	6.8 (8)[b]
H23	−2538 (28)	115 (23)	3561 (17)	5.6 (7)[b]
H24	−2363 (31)	−1099 (25)	4931 (19)	6.6 (7)[b]
H25	140 (31)	−2003 (25)	5054 (20)	6.6 (8)[b]

[a] $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i{}^*a_j{}^*)(\vec{a}_i\cdot\vec{a}_j)]$. [b] Isotropic displacement parameter, B.

to Ga, suggesting that these B–N bonds have been slightly rehybridized to reflect the different Ga–N distances, without disturbing the pyrazolyl rings. Another interesting result is a splaying of the C–H bonds in the 3- and 5-positions of the pyrazolyl rings, the H–C–N angles being substantially smaller (118 (1)°) than H–C–C (133 (1)°). All C–H distances are equal to their average value (0.93 Å) within their esd's of 0.03 Å; B–H distances are 1.16 (3) and 1.11 (2) Å.

Supplementary Material Available: Tables SI–SIII, listing anisotropic U_{ij}'s for the heavy atoms and bond distances and angles (2 pages); a listing of observed and calculated F's for the $C2/c$ refinement (5 pages). Ordering information is given on any current masthead page.

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Origin of the Solvent Effect on the Photolysis of $Co(NH_3)_5Br^{2+}$ at 254 nm in a Water–Acetonitrile Solvent System

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Charge-transfer excitation of $[Co(NH_3)_5Br]^{2+}$ causes an intramolecular redox reaction in which an electron is transferred from an orbital centered on the bromine ligand to an orbital centered on the cobalt metal.[1] The primary photoproduct is formed via homolytic fission of the Co–Br bond, and this product consists of a Br radical and a Co(II) species.[2,3] The process may be described by the following equation

$$[Co(NH_3)_5Br]^{2+} \rightarrow \{Co^{II}(NH_3)_5\ Br^{\bullet}\} + \Delta \qquad (1)$$

where Δ is the amount of light energy absorbed in excess of that required for homolytic dissociation. Prior to separation, the Br radical with the Co(II) fragment is referred to as a cage species.

The Co portion of the cage species is labile and will undergo aquation in a stepwise fashion at rates in the microsecond time domain. The Br radical may either undergo primary recombination or escape from the solvent cage to form a solvent-separated radical pair. The competition between these two pathways for the bromine radical determines the overall quantum yield of Co(II), and the cage escape process can carry traces of the effects of initial excitation through the magnitude of Δ.

The competition is dependent upon the solvent used. As well, Endicott[4] discovered that there is a dependence of the product quantum yield on the excitation wavelength (energy). The quantum yield of Co(II) increased upon decreasing the excitation wavelength. However, there is a limit to this increase in water. For $\lambda \leq 333$ nm, the quantum yield remains constant. It is especially interesting that this limit may be removed by changing the solvent. For example, in 80% acetonitrile, the quantum yield of Co(II) approaches unity upon decreasing the excitation wavelength.[4] This phenomenon may be explained if the step involving competition between escape from the solvent cage and recombination follows a solvent-dependent step in which the system may be trapped in an unreactive state.[2,5]

Experimental Section

Materials. $[Co(NH_3)_5Br]Br_2$ was synthesized according to a published procedure.[6] $[Co(NH_3)_5Br](NO_3)_2$ was prepared by treating $[Co(NH_3)_5Br]Br_2$ with $AgNO_3$. The AgBr was filtered out and the product isolated by freeze-drying. $[Co(NH_3)_5Br](BPh_4)_2$ was precipitated by addition of $NaBPh_4$ to aqueous $[Co(NH_3)_5Br]Br_2$. The product was isolated by filtration. In all cases, the solvent was distilled water.

Photolysis Experiments. The light source was a Rayonet photochemical reactor with a low-pressure 253.7-nm lamp. The intensity of the light was measured by ferrioxalate actinometry.[7] Solutions of $[Co(NH_3)_5Br]^{2+}$, approximately 2.5×10^{-3} M, were irradiated to a conversion of less than 12% in all cases. The Co(II) formed was determined via spectrophotometric analysis of $Co(SCN)^{4-}$ in acetone at 620 nm.[8] An HP-8452A diode array spectrophotometer interfaced with an IBM-PC was used for all absorbance measurements. The quantum yield of Co(II) was calculated according to the method described in the literature.[9] Spectrophotometric grade acetone and acetonitrile were purchased from Aldrich and used as received.

Results and Discussion

The composition of an acetonitrile–water solvent system was systematically varied so as to study the effects of the reaction medium upon the quantum yield of Co(II) when $[Co(NH_3)_5Br]^{2+}$ was irradiated at 253.7 nm. Due to solubility problems, two salts of $[Co(NH_3)_5Br]^{2+}$ had to be used. These were the nitrate salt and the tetraphenylborate salt. The nitrate salt was chosen as it is readily soluble in polar solvents and because the nitrate anion does not absorb light significantly at 253.7 nm at the concentrations involved in the photolysis. Therefore it does not interfere with the reaction system and the photochemistry of the system may be attributed to only the cationic complex. Unfortunately, $[Co(NH_3)_5Br](NO_3)_2$ is insoluble in neat acetonitrile. To overcome this problem, the tetraphenylborate salt was used. The tetraphenylborate anion (in the form of the sodium salt) absorbs strongly at 253.7 nm and is found to fluoresce. The fluorescence was quenched in the presence of the Co complex, exhibiting a linear Stern–Volmer plot with a slope equal to 6650 M^{-1}. A stoichiometric concentration of the cation in a 2.5×10^{-3} M solution of $[Co(NH_3)_5Br](BPh_4)_2$ quenches greater than 99% of the emission. Thus, it can be inferred that the tetraphenylborate anion sensitizes the cobalt complex and, as with the nitrate salt, the photochemistry is due only to the cationic complex.

The change from the nitrate to the tetraphenylborate salt occurs in the region where the quantum yield is essentially constant. This

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Table I. Quantum Yields of Co(II) in Various CH_3CN-H_2O Mixtures

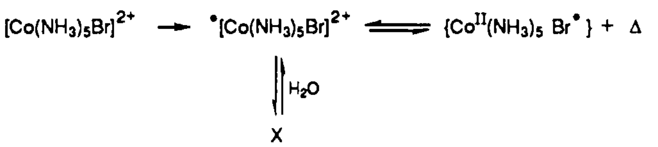
$\Phi(Co(II))^{a-c}$	$X(CH_3CN)$	η^d	$1/\epsilon^e$
0.28 (0.02)^5	0.0000	0.890	0.0127
0.37 (0.02)^{10}	0.0795	0.959	0.0147
0.34 (0.02)^5	0.1872	0.819	0.0172
0.43 (0.03)^6	0.3413	0.595	0.0207
0.48 (0.05)^5	0.5801	0.430	0.0241
0.39 (0.03)^7	0.8678	0.360	0.0267
0.47 (0.04)^5	0.9442	0.341	0.0274
0.90 (0.06)^9	1.0000	0.341	0.0278

[a] The number in parentheses refers to the standard deviation. [b] The superscript refers to the number of runs in each data set. [c] The literature value for $\Phi(Co(II))$ in water is 0.32 (4). [d] The viscosity data were obtained from ref 11. [e] The dielectric constant data were obtained from ref 11.

implies that it is not important which salt is used in the final interpretation of the data. In addition, it may be noted that the conclusions drawn regarding the solvent dependence are based predominantly on the data obtained with the tetraphenylborate salt, as major changes in the quantum yield of Co(II) happen only above an acetonitrile mole fraction of 0.9442.

The results of the photolysis experiments are listed in Table I. Note that the data for mole fractions of acetonitrile up to and including 0.5801 were obtained by using the nitrate salt; the data for mole fractions of acetonitrile greater than and including 0.8678 were obtained by using the tetraphenylborate salt. These results exhibit several interesting features: (1) It was found that there was little change in the quantum yield of Co(II) over a factor of 2 solvent viscosity, η, in the region $0.08 \leq X(CH_3CN) \leq 0.58$. Thus, arguments based on classical solvent dynamics do not offer viable explanations of the manner in which the quantum yield of Co(II) varies with solvent composition. (2) Similarly, the quantum yield of Co(II) does not change significantly over a factor of 2 change in the inverse dielectric constant between $1/\epsilon = 0.014$ and $1/\epsilon = 0.028$. This suggests that the solvent polarity cannot be used to provide a reasonable explanation of the behavior of $[Co(NH_3)_5Br]^{2+}$ in the acetonitrile–water solvent system. A large change in the quantum yield is, however, observed for a change of solvent in which both η and $1/\epsilon$ remain essentially constant. Consequently, we must formulate a new hypothesis for the origin of the solvent effect on the photochemical behavior of this complex.

Suppose that the role of water is the specific promotion of a quenching process leading to an unreactive state called X, since its precise character is unknown. Then the reaction scheme can be written



The wavelength dependence can lie in the probability of dissociation of the caged radicals, and the main solvent effect can lie in the competition between dissociation and trapping leading to X. In this model, if trapping is unimportant in acetonitrile, the quantum yield should *approach unity at high energy*, as is observed. It is, however, important to remember that the role of the solvent occurs very early in this process, specifically, faster than exchange between primary and secondary coordination spheres (~1 ns). That is, it occurs before the solvent can diffuse into the radical cage. Hence, it may be concluded that the solvent effects are not due simply to the intrusion of the solvent into the radical cage and the formation of a solvento adduct (i.e. the pentacoordinate Co species plus one solvent molecule).

If the quenching effect of water is molecular and dependent on a single water molecule, it will depend on the probability of a water molecule being in appropriate encounter with the complex at the time of excitation, since the existence of wavelength dependence implies initial steps that are fast in comparison to diffusional dissociation. This is an equilibrium process and proportional in simplest form to the activity of water, measured from the relative vapor pressure, $P/P°$.[10] In Figure 1, the dashed line shows the expectations for the simple model where the quantum yield decreases from the theoretical limit of 1 in acetonitrile to the experimentally well-defined limit of 0.32 in water,[4] proportionately to water activity. The line is not far from the experimental trend. The existing significant departure suggests that bulk solvent effects are not completely negligible. Nevertheless, the simple model appears capable of describing the principal effect.

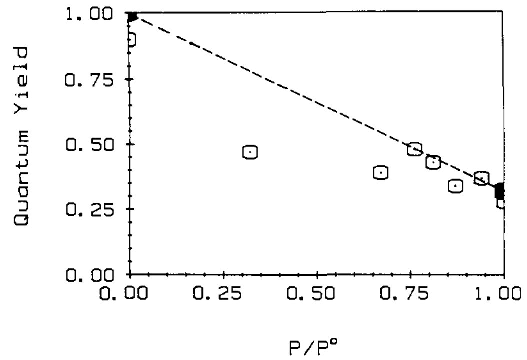


Figure 1. Quantum yield vs activity of water for $[Co(NH_3)_5Br]^{2+}$. The dashed line represents the theoretical curve. The activity of water is measured as $P/P°$, the vapor pressure over the mixture compared to the vapor pressure of pure water.

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Registry No. $[Co(NH_3)_5Br]^{2+}$, 14970-15-1; Co(II), 22541-53-3; H_2O, 7732-18-5; CH_3CN, 75-05-8.

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Synthesis, X-ray Crystal Structure, and Metal Ion Extraction from a Nitrogen–Sulfur "Pendant Arm" Encapsulated Complex of Cobalt(III)

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The synthesis of macrocyclic ligands that contain appended side chains incorporating potentially reactive donor functions has been of recent interest. The bifunctional nature of these ligands, with one site possessing a high affinity for the metal ion and a second site with a chemically reactive group suitable for further elaboration, has found many applications in the attachment of the ligands to polymers and biomolecules.[2-18] There are, however,

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