ion may be the ionization product of the proposed exchange intermediate II.

There are several advantages for the use of difluoroborane in the study of the reactions of borane. (1) The relative abundance of difluoroborane at equilibrium is high compared to that of borane in the dissociation of diborane. (2) The gas-phase reactions in the diborane system involve the formation of triborane.[12] (3) The pyrolysis of diborane produces the higher boron hydrides. In isotopic studies, this may lead to confusing side products. Pyrolysis products of difluoroborane are not observed in this study.

Acknowledgment. We are grateful for support of this work by the National Science Foundation (Grant No. CHE76-02477).

Registry No. DBF_2, 13709-79-0; B_5H_9, 19624-22-7; 1-$CH_3B_5H_8$, 19495-55-7; 2-$CH_3B_5H_8$, 23753-74-4.

---

[12] T. P. Fehlner in "Boron Hydride Chemistry", E. L. Muetterties, Ed., Academic Press, New York, 1975, and references therein.

Contribution from the Department of Chemistry,
University of California, Santa Barbara, California 93106

Long-Wavelength Excitation of Hexacyanocobaltate(III), $Co(CN)_6^{3-}$, in Aqueous Solution. Questions Regarding Intersystem-Crossing Efficiencies

Masato Nishazawa and Peter C. Ford*

Received June 26, 1980

The photochemistry and spectroscopy of the $Co(CN)_6^{3-}$ ion have been extensively investigated.[1] Comparison of the photochemical properties of this ion and monosubstituted derivatives $Co(CN)_5X^{(2+n)-}$ (where X^{n-} is an anion or neutral) to those of analogous pentaamminecobalt(III) derivatives $Co(NH_3)_5X^{(3-n)+}$ indicates very different behaviors.[1] Irradiation of the pentacyano derivatives in the wavelength region of the LF bands results in ligand photosubstitution, generally replacement of X^{n-} or CN^- by solvent. Quantum yields are moderately large (~0.1–0.4 mol/einstein) and essentially independent of irradiation wavelength (λ_{irr}) in the LF region. For example $Co(CN)_6^{3-}$ in aqueous solution undergoes CN^- photoaquation (eq 1) with a wavelength-independent Φ_{CN} =

$$Co(CN)_6^{3-} + H_2O \xrightarrow{h\nu} Co(CN)_5(H_2O)^{2-} + CN^- \tag{1}$$

0.31 when irradiated at wavelengths (254–365 nm) corresponding to spin-allowed LF absorptions.[2] In contrast, for the pentaammine derivatives photosolvation quantum yields are much smaller and are sharply λ_{irr} dependent, photoaquation of NH_3 from $Co(NH_3)_6^{3+}$ occurring with $\Phi_{NH_3} = 5.4 \times 10^{-3}$ and 3.1×10^{-4} at λ_{irr} = 365 and 472 nm, respectively.[3] An attractive rationalization of these photoreactivity differences is the interpretation that the lowest excited state (ES) of the pentacyano complexes has triplet character while that of the pentaammine series has quintet character.[4] This argument is consistent with the greater ligand field strength of CN^- and with parallels in the LF photoreactivity patterns of the pentacyanocobalt(III) species with other strong-field d^6 complexes such as the pentaammine complexes of Rh(III), Ir(III), and Ru(II) which have been concluded to undergo ligand labilization primarily from lowest energy triplet LF states.[5–7]

Table I. Photoaquation Quantum Yields for $Co(CN)_6^{3-}$ as a Function of Irradiation Wavelength[a]

λ_{irr}, nm	Φ_{CN^-}, mol/einstein	ref
254	0.31 ± 0.01	2
313	0.31 ± 0.01	2
365	0.31 ± 0.01	2
405	0.29 ± 0.02	this work
436	0.34 ± 0.05	this work

[a] In aqueous pH 2 solution, at 25 °C.

There is one major difference between the accepted models for the LF photochemistries of $Co(CN)_5X^{(2+n)-}$ and the heavier metal complexes. The latter complexes are generally viewed to undergo rapid internal conversion/intersystem crossing from initially populated single LF states to the lowest energy LF ES (a triplet) with unitary or near unitary efficiency. This property is reflected in the λ_{irr} quantum yields (including, in some cases, direct singlet to triplet excitations)[5a,b] and in the coincidence of limiting quantum yields obtained by triplet sensitization with values derived by direct singlet to singlet excitation.[7] In contrast, triplet sensitization experiments for $Co(CN)_6^{3-}$ have been interpreted as indicating that CN^- labilization from the lowest triplet state occurs with a very high yield (Φ(limiting) $\cong$ 0.8) and that intersystem crossing from initially excited singlets is relatively inefficient ($\Phi_{isc} \cong 0.4$).[8] Recently, two spectroscopic studies[9] have identified an absorption band for the $Co(CN)_6^{3-}$ ion at ~390 nm which has been assigned a singlet to triplet ($^3T_{1g} \leftarrow {}^1A_{1g}$) transition. Furthermore, plots of log ϵ vs. energy for the room-temperature aqueous solution spectrum of $K_3Co(CN)_6$ demonstrate the presence of a shoulder (ϵ = 0.38 M^{-1} cm^{-1}) at ~24.600 cm^{-1} (406 nm) which may be assigned to this spectral feature.[10] The present study examines the intersystem crossing efficiencies by measuring quantum yields for excitation in these spectral regions representing direct triplet excitation.

Experimental Section

The salt $K_3Co(CN)_6$ was prepared by the published method[11] and recrystallized twice from hot water. The photolysis apparatus has been described before[12] and consisted of a high-pressure mercury-lamp light source with λ_{irr} isolated with mercury-line interference filters. Light intensities were determined by ferrioxalate actinometry. The electronic spectrum of $K_3Co(CN)_6$ in dilute (pH 2) aqueous solution gave extinction coefficients of 2.0, 0.38, and 0.080 M^{-1} cm^{-1} at the wavelengths 380, 405, and 436 nm, respectively. In comparison, the spectrum of $Co(CN)_5(H_2O)^{2-}$, obtained in situ by exhaustive photolysis, gave the respective ϵ's of 260 (λ_{max}), 164, and 37 M^{-1} cm^{-1} at these wavelengths. Solution concentrations used for long-wavelength photolysis were 0.06 (λ_{irr} = 405 nm, initial absorbance at 405 nm $\cong$ 0.05, 2-cm cell) and 0.12 M (λ_{irr} = 436 nm, initial absorbance at 436 nm $\cong$ 0.02, 2-cm cell). Product yields were calculated for very small percent conversion to products (~0.5%) by monitoring absorbance

---

[1] Zinato, E. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; Chapter 4.

[2] (a) Moggi, L.; Bolleta, F.; Balzani, V.; Scandola, F. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2589. (b) Nakamura, K.; Jin, K.; Tazawa, A.; Kanno, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3486.

[3] (a) Manfrin, M. F.; Variani, G.; Moggi, L.; Balzani, V. *Mol. Photochem.* **1969**, *1*, 387. (b) Pribush, R. A.; Poon, C. K.; Bruce, C. M.; Adamson, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 3027.

[4] (a) Wilson, R. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 4085. (b) Langford, C. H.; Vuick, C. P. J. *Ibid.* **1976**, *98*, 5409.

[5] (a) Zanella, A. W.; Ford, K. H.; Ford, P. C. *Inorg. Chem.* **1978**, *17*, 1051. (b) Talebinasab-Sarvari, M.; Zanella, A. W.; Ford, P. C. *Ibid.* **1980**, *19*, 1835. (c) Matsubara, T; Ford, P. C. *Ibid.* **1978**, *17*, 1747.

[6] Bergkamp, M. A.; Brannon, J.; Magde, D.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 4549.

[7] Kelly, T. L.; Endicott, J. *J. Phys. Chem.* **1972**, *76*, 1937.

[8] Scandola, M. A.; Scandola, F. *J. Am. Chem. Soc.* **1972**, *94*, 1805.

[9] (a) Miskowski, V. M.; Gray, H. B.; Wilson, R. B.; Solomon, E. I. *Inorg. Chem.* **1979**, *18*, 1410. (b) Viaene, L.; D'Olieslager, J.; Ceulemans, A.; Vanquickenborne, L. G. *J. Am. Chem. Soc.* **1979**, *101*, 1405.

[10] This spectral feature has also been reported by: Fujita, J.; Shimura, Y. *Bull Chem. Soc. Jpn.* **1963**, *36*, 128

[11] Bigelow, J. H. *Inorg. Synth.* **1946**, *2*, 213.

[12] Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213.

0020-1669/81/1320-0294$01.00/0

changes (0.2–0.3 absorbance unit) at 380 nm ($\Delta\epsilon$ = 258 M^{-1} cm^{-1}). On the assumption that eq 1 is the sole photoreaction (consistent with spectral changes), the optical density at λ_{irr} due to $Co(CN)_6^{3-}$ could be calculated, and this value could be used to determine light absorbed by the starting material. This was done for 6–9 points during each photolysis run, and the incremental Φ_1 values so calculated were essentially constant over the small extent (0.5%) the photoreaction was allowed to proceed.

Results and Discussion

Quantum yields for CN^- labilization (Φ_{CN^-}) as determined for 405- or 436-nm excitation are within experimental uncertainties of the λ_{irr} independent value of 0.31 mol/einstein measured previously at shorter wavelengths (Table I). Given the assignment of this spectral region as including substantial triplet absorption,[9,10,13] we conclude that intersystem crossing for this ion must occur with near unitary efficiency. A similar conclusion was made for spectroscopic studies under considerably different conditions.[14] The source of the discrepancy of this conclusion with that drawn from the biacetyl sensitization studies is not obvious; however, the latter conclusion was based upon results requiring major corrections needed because the product $Co(CN)_5H_2O^{2-}$ is a particularly efficient triplet quencher.[8]

In conclusion, the present results provide strong evidence that, like a number of heavier metal d^6 complexes, the LF photochemistry of $Co(CN)_6^{3-}$ in aqueous solution is characterized by efficient interconversion to the lowest energy ligand field excited state, the $^3T_{1g}$ state, from which reaction (ligand labilization) or nonradiative deactivation to ground state occurs.

Acknowledgment. This research was supported by the National Science Foundation.

Registry No. $K_3Co(CN)_6$, 38883-79-3; $Co(CN)_5(H_2O)^{2-}$, 14842-83-2.

---

(13) With regard to the 405-nm exictation, the extent of triplet absorption may be estimated from the proposed relationship $\epsilon(^3T_{1g} \rightarrow {}^1A_{1g} \cong 10^{-3}\cdot\epsilon(^1T_{1g} \leftarrow {}^1A_{1g})$.[9a] If the shoulder found at 405 nm represents the spin-forbidden absorption,[10] then the extinction coefficient of this band at 405 nm would be ~0.2 M^{-1} cm^{-1} given the value of 200 M^{-1} cm^{-1} for the singlet absorption centered at 311 nm. Thus, irradiation at 405 nm would correspond to direct triplet excitation for at least 50% of the light absorbed.

(14) Conti, C.; Castelli, F.; Forster, L. S. *J. Phys. Chem.* **1979**, *83*, 2371.

Contribution from the Departments of Chemistry,
University of Houston, Houston, Texas 77004,
and Duke University, Durham, North Carolina 27706

Absolute Configurations and Axial Rotational Strengths of $M(en)_3(NO_3)_2$ Single Crystals

Ivan Bernal* and Richard A. Palmer*

Received June 11, 1980

Despite the fact that tris(ethylenediamines) of divalent cations have been known since 1893 when Werner reported the synthesis of the Ni(II) salts,[1] the absolute configurations of these substances have not been determined until recently, when we reported the results of our study of $Ni(en)_3(NO_3)_2$. A tentative assignment, based on optical measurements, was presented by Palmer and Yang[3] which was later[2] shown to be correct since the structure and absolute configuration (Bijvoet method[4]) were carried out on the same single crystals used for the optical work. Thus, it was possible to associate the absolute configuration with the signs of the rotational strengths (at least for the allowed transition) even for this labile complex.

Table I. Absolute Configuration and Rotational Strengths of $Zn(M)(en)_3(NO_3)_2$ Single Crystals[a]

M(II)	$\bar{\nu}_{max}$, μm^{-1}	excited state	$10^{40}R^d$
Ni	1.12	$^3E(^3T_{2g})$	+18.6
	1.72	$^3E(^3T_{1g})$	+0.41
	2.91	$^3E(^3T_{1g})$	+0.11
Co	1.00	$^4E(^4T_{2g})$	+5.58
	2.06	$^4E(^4T_{1g})$	+2.75
Cu	1.46	$^2E(^2T_{2g})$	+15.7
Mn	1.98	$(^4T_{2g}(G))$	+0.007
	2.37	$(^4E_g{}^4A_{1g}(G))$	+0.008
	2.65	$(^4T_{2g}(D))$	+0.006
Ru	2.60	$^1E(^1T_{1g})$	*b*
Zn	3.25	$^1A_1{}''$ *c*	−0.17

[a] Chirality of $M(en)_3^{2+}$: $\Lambda(\delta\delta\delta)$. [b] $\Delta\epsilon$ = +3.3. [c] NO_3^-. [d] 300 K.

For the purposes of many studies of the kinetic type, it may be convenient for the general scientific public to know the relationship between the absolute configuration of the $M^{II}(en)_3$ salts and their chiroptical properties. Thus, by the use of single-crystal-doping techniques, it was possible to obtain these data, as follows. Single crystals of $Zn(en)_3(NO_3)_2$ doped with Ni were used to determine the absolute configuration of the Zn host via the known absolute configuration of the Ni derivative.[2] A single crystal used for the optical measurements was then subjected, separately, to the Bijvoet test, and the consistency of the method was ensured.

The X-ray results are also consistent with the observation[3] that the sign of the CD band associated with the n → π* transition of NO_3^- in the axial spectrum is invariably opposite to that of the ligand field bands of each of the transition-metal ions used as dopants (Ni(II), Co(II), Cu(II), Mn(II), and Ru(II)). Therefore, by two independent determinations (the optical connection via the NO_3^- n → π*, the sign of $A_1 \rightarrow E$ transition in $Ru(en)_3^{2+}$, and the isoelectroic relationship between Ru(II) and Co(III)[3] and the X-ray results reported here and previously[2]) it is possible to put forth the data given in Table I.

Registry No. $Ni(en)_3(NO_3)_2$, 55524-15-7; $Co(en)_3(NO_3)_2$, 55524-17-9; $Cu(en)_3(NO_3)_2$, 75520-40-0; $Mn(en)_3(NO_3)_2$, 75475-74-0; $Ru(en)_3(NO_3)_2$, 75458-64-9; $Zn(en)_3(NO_3)_2$, 55555-48-1.

---

* Addresses for correspondence: I.B., University of Houston; R.A.P., Duke University.

(1) A. Werner, *Z. Anorg. Chem.*, **21**, 229 (1893).

(2) J. D. Korp, I. Bernal, R. A. Palmer, and J. C. Robinson, *Acta Crystallogr., Sect. B*, in press.

(3) R. A. Palmer and M. C.-L. Yang, *Chem. Phys. Lett.*, **31**, 492 (1975); *J. Am. Chem. Soc.*, **100**, 3780 (1978).

(4) J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature (London)*, **168**, 271 (1951).

0020-1669/81/1320-0295$01.00/0