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.

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

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[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.

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

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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.

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