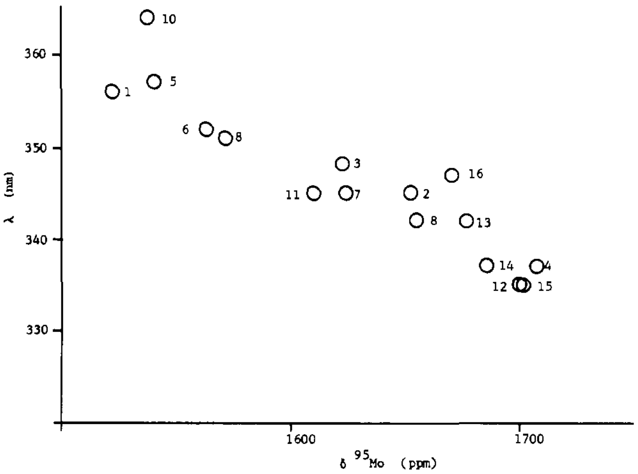

Figure 1. Plot of the ^{95}Mo NMR chemical shifts vs. the wavelengths of the highest frequency UV–vis charge-transfer bands for a series of *cis*-Mo(CO)$_4$(P-donor ligand)$_2$ complexes.

crease with the increasing electronegativity of the X group; i.e., $^1J_{\mathrm{MoP}}$ for X = O, Cl is greater than that for X = NH, S.

The peak half-heights ($\nu_{1/2}$) of the ^{95}Mo resonances of the bis(P-donor ligand)tetracarbonylmolybdenum(0) complexes in this study range from 40 to 150 Hz. These somewhat large line widths have been attributed to the relatively large field gradient present at the ^{95}Mo nucleus of *cis*-bis(P-donor ligand)tetracarbonylmolybdenum(0) complexes[11] and are also similar in magnitude to those previously reported for some (diphenylphosphinamide)- and (diphenylphosphinite)pentacarbonylmolybdenum(0) complexes.[12,13]

^{95}Mo Chemical Shift Correlations. The correlations observed between the ^{95}Mo chemical shifts and the other chemical shifts in these complexes are uniformly poor. These poor correlations were expected as earlier studies of Mo(CO)$_5$(PPh$_2$XR) (X = NH or O, R = alkyl;[12] X = O, R = para-substituted phenyl[13]) complexes have demonstrated that good correlations involving the ^{95}Mo chemical shifts are only observed when the steric and electronic changes in the P-donor ligands are carefully controlled. This is reflected in the improvement in the correlation between ^{95}Mo and ^{31}P chemical shifts when the data used for the correlation are reduced from those for all the complexes ($r = -0.53$) to those for the complexes containing monodentate ligands with similar cone angles (complexes **3–10**, $r = -0.88$).

Although poor correlations are observed between the chemical shifts of the ^{95}Mo resonances and all other resonances, a good correlation ($r = 0.93$) is observed between the chemical shifts of the ^{95}Mo resonances and the wavelength of the lowest frequency optical absorption maxima of the neutral complexes of monodentate ligands and of bidentate ligands that form six- or seven-membered rings, compounds **1–16**, as shown in Figure 1. This correlation is similar to those previously reported between the wavelength of the lowest frequency visible absorptions and the ^{59}Co NMR chemical shifts for two series of cobalt(III) complexes,[17,18] the ^{183}W NMR chemical shifts of a series of polytungstates,[19] and the ^{95}Mo NMR chemical shifts of a series of dioxomolybdenum(VI) Schiff base complexes.[8]

These correlations between the lowest frequency optical absorption maxima and heavy-metal NMR chemical shifts have been ascribed to the domination of heavy-metal shielding by the paramagnetic term of Ramsey's treatment of chemical shielding.[20–25] This is given approximately by eq 1, where ΔE is an average energy of electronic excitation from the ground

$$\sigma^P = -(2e^2h^2/3m^2c^2\Delta E)(\langle r^{-3}\rangle_{np}P_i + \langle r^{-3}\rangle_{nd}D_i) \quad (1)$$

state to states that are of the correct symmetry and are mixed in by the magnetic field, $\langle r^{-3}\rangle_{np}$ and $\langle r^{-3}\rangle_{nd}$ are radial expression terms representing the average inverse cubes of the distances of the relevant p and d electrons, and P_i and D_i are measures of the degree of electronic imbalance in the relevant p and d orbitals. Since ΔE can often be related to the wavelength of the lowest frequency visible absorption, a linear correlation should be observed between the chemical shifts and these wavelengths within a series of complexes as long as the other terms, $\langle r^{-3}\rangle_{np}$, $\langle r^{-3}\rangle_{nd}$, P_i, and D_i, remain approximately constant for the series.

Conclusions

From the study of the ^{95}Mo NMR spectra of a series of *cis*-Mo(CO)$_4$(PPh$_2$XR)$_2$ complexes, an explanation of the effect of changes in the XR groups on the ^{95}Mo chemical shifts has been proposed that involves π-donation from the filled p orbitals of the X group into the empty phosphorus 3d orbitals. This study has also demonstrated that although the chemical shifts of the ^{95}Mo resonances do not correlate with the chemical shifts of other resonances of the complexes, a good correlation is obtained with the wavelengths of the highest frequency UV–vis absorption band. This correlation can be related to the paramagnetic term of Ramsey's treatment of chemical shielding.

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Registry No. **1**, 42724-61-8; **2**, 55835-45-5; **3**, 66024-56-4; **4**, 65991-64-2; **5**, 65991-51-7; **6**, 86707-60-0; **7**, 65991-54-0; **8**, 65991-63-1; **9**, 65991-50-6; **10**, 86646-33-5; **11**, 65614-05-3; **12**, 65991-55-1; **13**, 65991-45-9; **14**, 65991-56-2; **15**, 65991-57-3; **16**, 73643-89-7.

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(17) Freeman, R.; Murray, G. R.; Richards, R. E. *Proc. R. Soc. London, Ser. A* **1957**, *242*, 455.
(18) Juranic, N.; Celap, M. B.; Vucelic, D.; Malinar, M. J.; Radiovojsa, P. N. *J. Magn. Reson.* **1975**, *35*, 319.
(19) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1982**, *104*, 5384.
(20) Ramsey, N. F. *Phys. Rev.* **1950**, *77*, 667.
(21) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699.
(22) Karplus, M.; Das, T. P. *J. Chem. Phys.* **1961**, *34*, 1683.
(23) Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803.
(24) Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803.
(25) Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* **1964**, *40*, 1714.

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Wavelength Independence of Phosphorescence Yields in $[\mathrm{Cr(en)_3}]^{3+}$

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There have been several reports in the literature that for particular chromium(III) complexes there is a wavelength dependence of the intersystem crossing yield on irradiation within a single absorption band. Such studies have been based on either measurements of the percentage of quenchable photoreaction or measurements of relative phosphorescence yields from the metastable doublet state,[2–4] and in one recent

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[2] N. A. P. Kane-Maguire, J. E. Phifer, and C. G. Toney, *Inorg. Chem.*, **15**, 593 (1976).
[3] D. Sandrini, M. T. Gandolfi, L. Moggi, and V. Balzani, *J. Am. Chem. Soc.*, **100**, 1463 (1978).

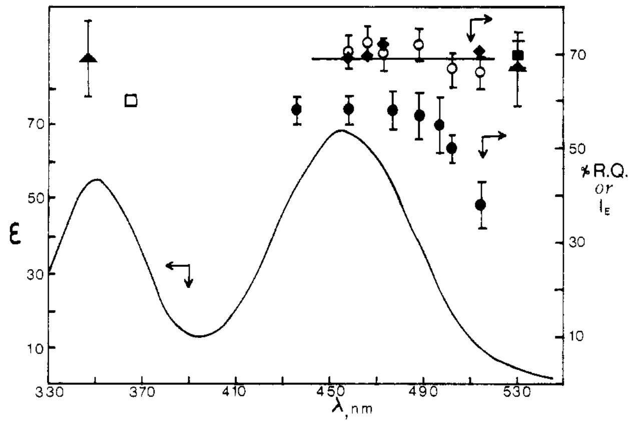

Figure 1. Relative emission yields and percentage quenchable (slow) reaction vs. wavelength and absorption spectrum of $[Cr(en)_3]^{3+}$: ○, relative emission yield (I_E), at 21 °C, for absorbance 0.340 ± 0.003 solutions of $[Cr(en)_3]^{3+}$ in 10^{-2} or 10^{-3} M $HClO_4$ (averages of four measurements); ◆, relative emission yield, same conditions, for $[Ru(bpy)_3]^{2+}$ in water (averages of six measurements); ■ and ▲, percentages of slow photoproduct formation (ref 9 and 10, respectively); ● and □, percentages of quenchable reaction (% RQ) (ref 2 and 11, respectively); —, absorption spectrum.

investigation both techniques were used.[4] The wavelength dependencies observed have been ascribed to competition between intersystem crossing and vibrational equilibration of the Franck–Condon excited state. This interpretation is supported by the observations of very fast rates for the rise time of phosphorescence,[6-8] recently found to exhibit medium dependence.[7,8]

It was of concern to us to note, therefore, that the observations on the wavelength dependence of $[Cr(en)_3]^{3+}$ intersystem crossing[2] were inconsistent with more recent figures for the fraction of quenchable (slow) reaction from two quite independent studies using different methods. Thus Fukuda et al.[9] found a fraction of slow reaction of 0.70 ± 0.03 for 530-nm excitation from studies of the time evolution of photoproduct using absorbance monitoring, while Waltz[10] and co-workers found 0.69 ± 0.08 for 347-nm and 0.67 ± 0.08 for 530-nm excitation using conductivity monitoring. These results conflict with the earlier values of 0.58 ± 0.03 at 436 nm and 0.38 ± 0.05 at 514.5 nm based on percent quenchable photoracemization;[2] here, evidence was also presented that the ratio of phosphorescence yield for 514.5–436-nm excitation was 0.63, consistent with the quenching result. The value of 0.58 from this work is concordant with an independent literature measurement of reaction quenching of 0.6.[11] In light of these disagreements and the limited extent of the phosphorescence data, we decided to undertake a more extensive study of the phosphorescence yield as a function of wavelength. We report here our results.

Absorbance-matched acidic aqueous solutions of $[Cr(en)_3]^{3+}$ were excited by the 457.9-, 465.8-, 472.7-, 488-, 501.7-, and 514.5-nm lines from an argon ion laser (Coherent Radiation CR-6) using a 4 cm path length flow cell. The excitation power was in the range 10 → 40 mW, and flow rates were adjusted to maximize the emission signal. Excitation powers were measured with a Coherent Radiation Model 210 power meter, calibrated against both ferrioxalate and Reineckate actinometers, and shown to be correct within 5% as per specifications. The emission signal was measured with a Ramanor HG2S monochromator, cooled RCA 31034 photomultiplier, and PAR 1140A photon-counting amplifier. The emission signals were found to be linear in excitation power over the range 10 → 50 mW, as previously reported.[12] All solutions were filtered through 3-μm Millipore filters (the same absorbance values were found for solutions filtered, more laboriously, through 0.22-μm filters).

As a calibration check, similar determinations were carried out on $[Ru(bpy)_3]^{2+}$; this ion has been reported to have a constant quantum yield for emission over the wavelength range of interest.[13] These calibration measurements revealed a serious potential source of error. The laser was found to show significant (about twofold) variations in beam diameter from wavelength to wavelength, altering markedly the fractional efficiency of emission signal collection at the monochromator entrance slit over the whole adjustment range of the entrance optics. Inclusion of a 1.0-mm aperture to hold the laser beam diameter constant led to wavelength-independent emission signals (±3%) from $[Ru(bpy)_3]^{2+}$ once the incident powers (mW) had been converted to photon numbers.

The emission signals per photon (arbitrary units) obtained for $[Cr(en)_3]^{3+}$ by using this arrangement are shown in Figure 1 together with their error bars and have been scaled to enable a simple comparison with all the literature data and our data for $Ru[(bpy)_3]^{2+}$, also shown. Except for a *possible* decrease of ≤7% toward 500 nm allowed by the experimental uncertainty, Figure 1 shows the intersystem crossing yield is independent of wavelength (solid line). As our emission data are completely consistent with the more recent percent slow reaction data,[10] we conclude that the weight of evidence now suggests that the intersystem crossing yield for $[Cr(en)_2]^{3+}$ does not vary significantly with wavelength over the range 347–530 nm.

This conclusion should not be taken as questioning all reports of wavelength dependence of photochemistry and phosphorescence yields in the red edges of absorption bands, a phenomenon reported for several systems.[3,4] Other observations of the effect have, however, been found further to the red edge of the band than earlier reported for $[Cr(en)_3]^{3+}$, even for the strong field complex $[Cr(bpy)_3]^{3+}$. Kane-Maguire et al.[2] claimed a wavelength dependence of yield extending very much deeper into the first ligand field quartet band than for other systems, implying a competition between intersystem crossing and vibrational relaxation over a large range of energies. Ir remains possible that some wavelength dependence of yield might be found for $[Cr(en)_3]^{3+}$ in the less accessible range from 540 to 650 nm. But our present observations of the potential artifacts convince us of the care required to obtain reliable relative emission yields using laser sources in such experiments. Studies of the quenching of the photoreaction over this range would be informative as they would not be influenced by such artifacts.

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Registry No. $[Cr(en)_3]^{3+}$, 15276-13-8.

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(4) Roger Sasseville and C. H. Langford, *J. Am. Chem. Soc.*, **101**, 5834 (1979); *Inorg. Chem.*, **19**, 2850 (1980).

(5) A. D. Kirk, D. E. Hoggard, G. B. Porter, M. G. Rockley, and M. W. Windsor, *Chem. Phys. Lett.*, **37**, 199 (1976).

(6) S. C. Pyke and M. W. Windsor, *J. Am. Chem. Soc.*, **100**, 6518 (1978).

(7) S. C. Pyke, M. Ogasawara, L. Kewan, and J. F. Endicott, *J. Phys. Chem.*, **82**, 302 (1978).

(8) K. L. Sala, R. W. Yip, C. H. Langford, and R. Lesage, Abstracts, 65th Chemical Institute of Canada Conference, Toronto, Canada, 1982, No. PH12-15.

(9) R. Fukuda, R. T. Walters, H. Macke, and A. W. Adamson, *J. Phys. Chem.*, **83**, 2097 (1979).

(10) W. L. Waltz, R. T. Walters, R. J. Woods, and J. Lilie, *Inorg. Chim. Acta*, **46**, L153 (1980).

(11) R. Ballardini, G. Varani, H. F. Wasgestian, L. Moggi, and V. Balzani, *J. Phys. Chem.*, **77**, 2947 (1973).

(12) A. D. Kirk and M. A. R. Scandola, *J. Phys. Chem.*, **86**, 4141 (1982).

(13) J. N. Demas and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 2481 (1971).