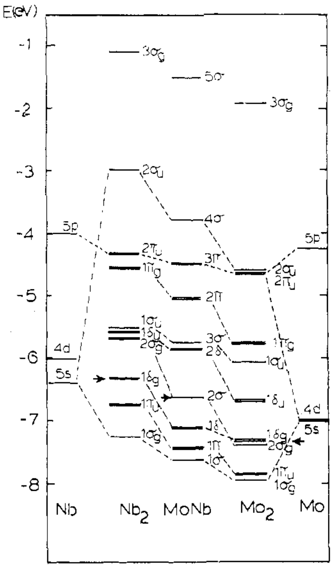

Figure 2. EHMO schemes for Mo_2, MoNb, and Nb_2 calculated at the minimum-energy geometries of 2.40, 2.30, and 2.20 Å, respectively (see text). Arrows indicate HOMO'S.

of trinuclear and higher clusters to be negligible. Therefore with a fair degree of confidence one can associate the new absorptions centered around 570 nm with the bimetallic molecule MoNb. Support for this proposal stems from comparisons with the optical spectra of the CrMo molecule which also shows a well-resolved, low-energy absorption (with similar splittings) located essentially midway between those of the respective parent diatomic absorptions,[3] a situation analogous to that discovered for a wide range of bimetallic cluster complexes.[10] Such an averaging effect for the transition energies of MoNb relative to Mo_2 and Nb_2 is not unreasonable for closely related atomic components having similar electronic configurations (Nb, $4d^45s^1$; Mo, $4d^55s^1$) and comparable valence orbital ionization potentials (Table I). One should note that an averaging effect of the bond dissociation energies of Mo_2, MoNb, and Nb_2 has recently been observed mass spectrometrically,[8] which is understandable since the ionic contribution to the Mo–Nb bond strength is calculated to be less than 1 kcal mol^{-1} from Pauling's formula[11] based on the electronegativity difference between Nb and Mo.

For some additional insight into the electronic architecture of MoNb, a series of EHMO calculations was performed on MoNb by employing input parameters which had been spectroscopically optimized with respect to the parent diatomics, Mo_2 and Nb_2 (Table I). The resulting energy-level schemes for Mo_2, MoNb, and Nb_2 calculated at the minimum-energy geometries are illustrated in Figure 2. One should note here that the modified EHMO parameters listed in Table I give rise to a d-orbital splitting which more closely resembles that found in related SCF–Xα–SW calculations.[3] On the basis of these ground-state, low-spin energy level diagrams, one can determine a set of optical assignments which are internally consistent with the absolute energy values as well as the spectral trends observed for Mo_2, MoNb, and Nb_2 (Table II). However, because of the changes in electronic configuration involving formally 10-, 11-, and 12-valence-electron diatomics, the spectral correlations are not as straightforward as those derived for the related 12-valence electron Cr_2, CrMo, and Mo_2 series of molecules.[3]

Table II. Calculated and Observed Optical Transitions for Nb_2, MoNb, and Mo_2 in Solid Argon

molecule	assignt[a]	calcd transtn energy, cm^{-1}	obsd transtn energy	
			cm^{-1}	nm
Nb_2	$1\sigma_g \rightarrow 1\sigma_u$	13 967	14 992	667
			15 290	654
	$1\sigma_g \rightarrow 2\pi_u$	23 690	23 809	420
	$1\sigma_g \rightarrow 2\sigma_u$	34 370	35 714	280
MoNb[b]	$1\sigma \rightarrow 3\sigma$	15 302	16 949	590
	$2\sigma \rightarrow 3\pi$	17 210	17 605	568
	$1\pi \rightarrow 2\pi$	19 175	17 921	558
	$1\sigma \rightarrow 2\pi$	20 970	18 148	551
	$2\sigma \rightarrow 4\sigma$	22 858		
Mo_2	$2\sigma_g \rightarrow 2\sigma_u$	22 419	19 305	518
	$1\sigma_g \rightarrow 2\sigma_u$	26 945	32 467	308
	$1\pi_u \rightarrow 3\sigma_g$	48 001	43 103	232

[a] Note that, with the modified EH parameters used in these calculations, the assignments of the optical bands of Nb_2 and Mo_2 differ from those reported previously.[3] [b] Note that the electric dipole allowed $1\delta \rightarrow 2\pi$ transition of MoNb, although falling within the spectroscopic range of interest (calculated 16 487 cm^{-1}), is expected to have a low oscillator strength and is therefore not assigned.

On a final note, it is interesting that the potential energy calculations of the present study support the concept that these refractory metal diatomic molecules are likely to have high bond orders and bond strengths as seen from the computed bond dissociation energies of 171, 72, and 123 kcal mol^{-1} for Mo_2, MoNb, and Nb_2, respectively. These values can be compared with those obtained mass spectrometrically by Gupta et al., that is, 96.5 ± 5, 108 ± 6, and 122 ± 2.4 kcal mol^{-1}, respectively. Thus, the EHMO calculations of the present study are unable to reproduce either the experimental trend in bond energies or the absolute values of the bond energies of these refractory molecules, although the experimental order $D(Nb_2) > D(MoNb) > D(Mo_2)$ is somewhat unexpected for molecules which are purported to have multiple bond orders of 5, $5^1/_2$, and 6, respectively.[3,8] SCF–Xα–SW and/or ab initio studies of these heavy-metal diatomics would seem warranted to illuminate this puzzling aspect of the work.

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Registry No. Nb_2, 12596-70-2; Mo_2, 12596-54-2; MoNb, 68777-39-9.

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(10) H. B. Abrahamson, C. C. Frazier, D. S. Ginley, H. B. Gray, J. Lilienthal, D. R. Tyler, and M. S. Wrighton, *Inorg. Chem.*, **16**, 1554 (1977).

(11) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, NY, 1960.

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Wavelength Dependence of Photohydrolysis and Luminescence Quantum Yields of Tris(bipyridine)chromium(III) Ion

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The photohydrolysis of $Cr(bpy)_3^{3+}$ (bpy = bipyridine) in basic media to give $Cr(bpy)_2(OH)_2^+$ has been assigned as a reaction from the ^2E (approximate O_h microsymmetry) state which is luminescent and relatively long-lived (τ = 63 μs in deaerated solution).[1] This is the only photosubstitution re-

Table I. Wavelength Dependence of Photohydrolysis and Luminescence Yields

λ, nm	pH	$10^3[\mathrm{Cr(bpy)_3}^{3+}]$, mol·dm^{-3}	10^8(intensity),[a] einsteins·s^{-1}	ϕ_R (±0.01)	luminescence[b] I_{488}/I_λ
488.0					(1.00)
514.5	9.2	5.45	2.20	0.12 (2)[c]	0.93 ± 0.16
514.5	9.2	9.97	6.12	0.11 (2)	
580.0	9.2	26.22	5.03	0.11 (1)	0.85 ± 0.10
580.0	9.2	26.22	3.44	0.09 (1)	
590.0					2.9 ± 0.03
600.0					4.2 ± 0.05
610.0	9.2	20.18	5.27	0.02_3 (2)	>4.2

[a] Intensity determined by Reneckate actinometry for absorbance matched solutions. [b] Intensities recorded relative to the $\mathrm{ClO_4}^-$ normal mode (A band is most intense) so that ϕ_{ISC} is the controlling variable for the relative intensity of 727-nm luminescence. $[\mathrm{Cr(bpy)_3}^{3+}] = 1.60 \times 10^{-2}$ mol·dm^{-3}. [c] Numbers in parentheses indicate number of runs.

action of a Cr(III) complex at present for which an argument exists to exclude the $^4T_{2g}$ excited state as an origin of reactivity. The exclusivity of the argument rests in large part on the report that the intersystem crossing yield (ϕ_{ISC}), $^4T_{2g} \rightarrow {}^2E$, is essentially unity (≥0.94).[2] If ^4T always goes to ^2E, it cannot have an alternative fate. However, intersystem crossing between quartets and doublets of Cr(III) complexes is subject to subtle wavelength dependence. Kane-Maguire and his colleagues[3] first observed a decline of the yield for doublet population in the long-wavelength tail of the quartet band of $\mathrm{Cr(en)_3}^{3+}$ (en = ethylenediamine). This was attributed to population of the quartet at an energy below a "crossing point" between quartet and doublet surfaces. Balzani and colleagues[4] observed a similar phenomenon with *trans*-$[\mathrm{Cr(en)_2(NCS)_2}]^+$ and used it to demonstrate unambiguously that both substitution reactions (NCS loss and chelate (en) ring opening) of this complex originated from the $^4T_{2g}$ state for neither showed a decrease in quantum yield (ϕ) at wavelengths beyond crossover.

If such a "crossover" wavelength exists beyond which ϕ_{ISC} for $\mathrm{Cr(bpy)_3}^{3+}$ falls below unity, irradiation in this region can provide a rigorous test of the assignment of reaction to a ^2E origin. As well, accumulation of data on the generality of the "crossover" phenomenon is of interest.

Experimental Section

Materials were obtained in the conventional manner.[1] Solutions were prepared at pH 9.2 by using $\mathrm{NH_3/NH_4Cl}$ buffers. Ionic strengths were adjusted to 1.0 with NaCl. Light intensities were measured by using Reineckate actinometry.[5] The actinometer solutions were absorbance matched to samples. Luminescence studies were done on absorbance-matched solutions except in the long-wavelength extreme. Relative luminescence quantum yields were accurately determined by using the $\mathrm{ClO_4}^-$ A_1 Raman normal mode as an internal standard for intensity at each wavelength on a spectrometer system designed for sensitive high-resolution light scattering.[6]

Illumination was carried out with a Coherent Radiation CR-4 Ar-ion laser (λ = 488.0, 514.5 nm) and a Coherent Radiation 590 dye laser pumped with the Ar-ion laser (580, 590, 600, 610 nm). Product monitoring was as described by Serpone et al.[7] The temperature was 25 °C.

Results and Discussion

Reaction quantum yields (ϕ_R) are reported from 488.0 to 610.0 nm in Table I. They are in satisfactory agreement with earlier reports at overlapping wavelengths. Intensities of luminescence at 727 nm (^2E phosphorescence) were monitored. These are expressed relative to the luminescence intensity at 488.0 nm and represent *variation* of ϕ_{ISC} since they are normalized to Raman intensity (with the ν^4 dependence included), absorbance at irradiation wavelength, and phototube sensitivity.

Two things are apparent. First $\mathrm{Cr(bpy)_3}^{3+}$ does display a crossover wavelength near 590 nm where ϕ_{ISC} decreases as indicated by the relative decrease in 727-nm emission at the normalized excitation wavelength absorbance based on $\mathrm{ClO_4}$-Raman intensity. The unit quantum yield for ISC reported earlier is valid only for quartet excitation well above the 0–0 band. Thus the rate of ISC must be fast enough to be competitive with vibrational relaxation within the quartet manifold. On the other hand, there is no evidence here to parallel observations on *trans*-$[\mathrm{Cr(en)_2(NCS)_2}]^+$. The reaction quantum yield declines across the crossover wavelength. In the long-wavelength tail of the quartet band the main fate of quartets is relaxation to the ground state without either ISC or reaction.

A puzzle noted earlier[2] remains. $\mathrm{Cr(phen)_3}^{3+}$ (phen = phenanthroline) appears to have a lower ϕ_{ISC} and undergoes photoracemization reaction from the quartet.[8] $\mathrm{Cr(bpy)_3}^{3+}$ has ϕ_{ISC} near unity at the band maximum and, as the present results confirm, no propensity to undergo ligand substitution from the quartet. The significance of this change for such a small structure variation is unclear.

Registry No. $\mathrm{Cr(bpy)_3}^{3+}$, 15276-15-0; $\mathrm{Cr(bpy)_2(OH)_2}^+$, 47514-01-2.

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(1) M. Maestri, F. Bolletta, L. Moggi, V. Balzani, M. S. Henry, and M. Z. Hoffman, *J. Am. Chem. Soc.*, **100**, 2694 (1978).

(2) F. Bolletta, M. Maestri, and V. Balzani, *J. Phys. Chem.*, **80**, 2499 (1976).

(3) N. A. P. Kane-Maguire, J. E. Phifer, and G. G. Loney, *Inorg. Chem.*, **15**, 593 (1976).

(4) D. Sandrini, M. T. Gandolfi, A. Surio, and V. Balzani, *J. Am. Chem. Soc.*, **99**, 4523 (1977), and references therein.

(5) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).

(6) L. V. Haley and J. A. Koningstein, *J. Raman Spectrosc.*, **5**, 305 (1976).

(7) M. A. Jamieson, N. Serpone, M. S. Henry, and M. Z. Hoffman, *Inorg. Chem.*, **18**, 214 (1979).

(8) R. L. Sasseville and C. H. Langford, *J. Am. Chem. Soc.*, **101**, 5834 (1979).