

Electronic Spectroscopy and Photophysics of d^4 Clusters^{*,†}

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The electronic structural analogies between $(d^4)_2 M_2 X_8^{4-}$ and $(d^4)_6 (M_6 X_8) X_6^{2-}$ ($M = Mo, W; X = Cl, Br, I$) clusters are outlined. Metal-localized δ -type orbitals play an important role in the ground state and the lowest excited states of each complex. All evidence suggests that the splitting between the emissive $\delta\delta^*$ -singlet and the $\delta\delta^*$ -triplet excited states of $M_2 X_8^{4-}$ and related species is greater than 1 eV, whereas the ~ 2 -eV emissive excited state of $(M_6 X_8) X_6^{2-}$ is a spin triplet. © 1985 Academic Press, Inc.

Introduction

The development of a detailed picture of the nature of metal-metal interactions in extended metallic arrays will ultimately depend upon a thorough understanding of the electronic structures of the cluster subunits of which they are composed. Experimental studies of the bonding in such discrete molecular clusters have largely utilized crystallographic methods in cataloging the intermetallic distances of varying bond orders, while theoretical investigations, namely calculations, have focused on determining the electron distributions in these systems. From this large body of work have arisen both detailed oxidation state/molecular structure correlations and successful electron counting schemes, especially for

the low-valent, π -acid-containing clusters of the late transition metals (*I*).

The study of the electronic structures of metal cluster compounds has been an active area of research in our laboratory over the last 15 years. Our general approach has been to probe the properties of the ground and lowest-lying electronic excited states of these systems by investigating their spectroscopic, photophysical, and photochemical behavior (2-6). One class of polynuclear complexes that has attracted our attention is the extensive series of high-symmetry clusters derived from square-planar d^4 -transition-metal monomers:

Electronic configuration	Example
$(d^4)_2$	$Re_2 Cl_8^{2-}, Mo_2 Cl_4 (PR_3)_4$
$(d^4)_3$	$Re_3 Cl_{12}^{3-}$
$(d^4)_4$	$Mo_4 Cl_8 (PR_3)_4$
$(d^4)_5$	$Mo_5 Cl_{13}^{3-}$
$(d^4)_6$	$Mo_6 Cl_{14}^{2-}, W_6 Cl_{14}^{2-}$

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In this paper we focus on the relationship between the electronic properties of the

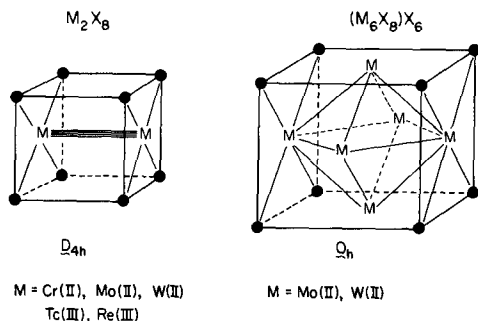


FIG. 1. Comparison of the generalized molecular structures of M_2X_8 and $(M_6X_8)X_6$ systems.

two sets of complexes which represent, with respect to both nuclearity and metal-metal bond order, the extremes of this series, namely the binuclear (quadruply bonded) and hexanuclear (singly bonded) species. While the overall geometries and stoichiometries of these two systems are quite different (Fig. 1), there are also obvious localized structural, and hence electronic, similarities with regard to both metal-ligand environment and trans-cube metal-metal interaction.

Binuclear d^4 Complexes

There is now a wealth of experimental evidence suggesting that the lowest-lying band in the electronic absorption spectra of these ($\sigma^2\pi^4\delta^2$) complexes (7) corresponds to the singlet $\delta \rightarrow \delta^*$ transition, as has been documented elsewhere (2, 8, 9). Typical absorption spectra show the relative ligand insensitivity of this transition (Fig. 2).

One important feature of the ${}^1(\delta \rightarrow \delta^*)$ absorption band is that its intensity is quite low ($\epsilon_{\text{max}} \sim 10^2\text{--}10^3 \text{ M}^{-1} \text{ cm}^{-1}$) for a fully allowed transition. This is in contrast to the situation found in other metal-localized transitions of binuclear complexes, e.g., $\text{Mn}_2(\text{CO})_{10}$ ($\epsilon_{\text{max}} {}^1(\sigma \rightarrow \sigma^*) \sim 10^4$) (10). From the work of Mulliken, it is known that the oscillator strength of a one-electron $N \rightarrow V$ transition is related to the square of the

overlap (11). Hence, the relatively low intensity of this transition is a consequence of the small orbital overlap (~ 0.1) of the d_{xy} functions that comprise the δ bond.

The energy of the ${}^1(\delta \rightarrow \delta^*)$ transition also provides information regarding the bonding in these systems. Specifically, it has been observed that the energy of this band is usually two to three times greater than the corresponding doublet ($\delta \rightarrow \delta^*$) transitions of related one-electron oxidized or reduced species (12, 13). If one adopts a valence-bond formalism to describe the wavefunctions of this system, which is appropriate in light of the above discussion of the δ overlap, then the δ^2 ground state is largely covalent, while the ${}^1(\delta\delta^*)$ excited state is ionic (14):

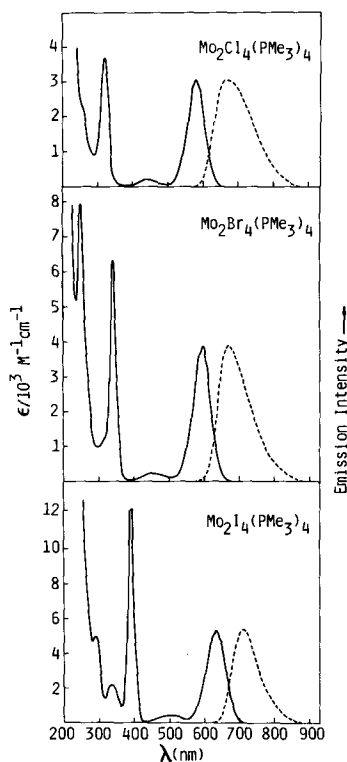
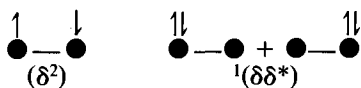
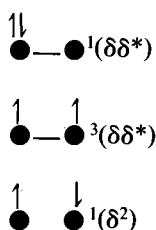


FIG. 2. Electronic absorption (—) and corrected emission (---) spectra of $\text{Mo}_2X_4(\text{PMe}_3)_4$ in 2-methylpentane solution at 300 K.



Thus, the large energy difference between the δ^2 and ${}^1(\delta\delta^*)$ states relative to that between ${}^2(\delta)$ and ${}^2(\delta^*)$ is due to the fact that the singlet excited state energy contains a substantial electron correlation term in addition to reflecting the splitting of δ and δ^* orbitals.

An important additional implication of this experimental evidence for the covalency of the δ bond is that the similarly covalent ${}^3(\delta\delta^*)$ excited state should be substantially lower in energy than the corresponding singlet; from simple theory, the ${}^2(\delta^*)$ energy would be an upper limit. While the vanishingly



small oscillator strength of the ${}^3(\delta \rightarrow \delta^*)$ transition has thus far discouraged direct spectroscopic observation of this state (a possible exception to this has recently been reported in (15)), evidence for a large-energy splitting of singlet and triplet excited states can be derived from emission spectroscopic and photophysical measurements of these systems. The luminescence lifetimes, quantum yields, and energies of the emission spectra of the $\text{Mo}_2\text{X}_4(\text{PMe}_3)_4$ series (Fig. 2) are set out in Table I (16). The close agreement of the observed radiative rate constants with those calculated from the oscillator strengths of each complex is consistent only with assignment of the emission to ${}^1(\delta^* \rightarrow \delta)$ fluorescence; no phosphorescence has been observed for these or any other emissive quadruply bonded systems. Furthermore, there is no

evidence for the occurrence of ${}^1(\delta\delta^*)$ to ${}^3(\delta\delta^*)$ intersystem crossing at an appreciable rate in either the decay of the emissive transient (14) or in the nonradiative rate constants. The latter, for the $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$ series, are displayed as a function of temperature in Fig. 3. Fitting the data to an Arrhenius-type expression of the form

$$k_{\text{nr}} = k_0 + k_1 \exp(-E_a/kT) \quad (1)$$

highlights the two nonradiative pathways of the emissive singlet state. At high temperature, all complexes display nonradiative behavior consistent with thermally activated decay via a potential surface crossing between the ${}^1(\delta\delta^*)$ and some higher energy electronic excited state ($E_a \sim 2500\text{--}3000 \text{ cm}^{-1}$). At low temperature these species undergo activationless nonradiative decay, indicative of direct internal conversion to the ground state. The fluctuation of this low-temperature rate with halide (Fig. 3) is consistent with the general sensitivity of this decay pathway to the energy gap between the ground state and emissive excited state (Table I).

A large singlet-triplet $\delta\delta^*$ excited state splitting also is obtained in *ab initio* calculations on $\text{Re}_2\text{Cl}_8^{2-}$, which place ${}^3(\delta\delta^*)$ very near the ground state ($\sim 0.4 \text{ eV}$) (17). The energy gap between the ground state and the ${}^3(\delta\delta^*)$ state of $\text{W}_2\text{Cl}_8^{4-}$ probably is somewhat larger than that of $\text{Re}_2\text{Cl}_8^{2-}$, judging from the higher energy of the $\delta\delta^*$ singlet state in the tungsten dimer. To complete the comparative energy level picture (Fig. 4), the placement of the $\text{Mo}_2\text{Cl}_8^{4-}$ $\delta\delta^*$ triplet state at roughly 0.6 eV is based on the results of a recent MC-SCF calculation (18).

Hexanuclear d^4 Complexes

All four d electrons on each metal in the $(\text{M}_6\text{X}_8)\text{X}_6^{2-}$ clusters are involved in metal-metal bonding. In these clusters the HOMO is built by overlapping d_{xy} functions on ad-

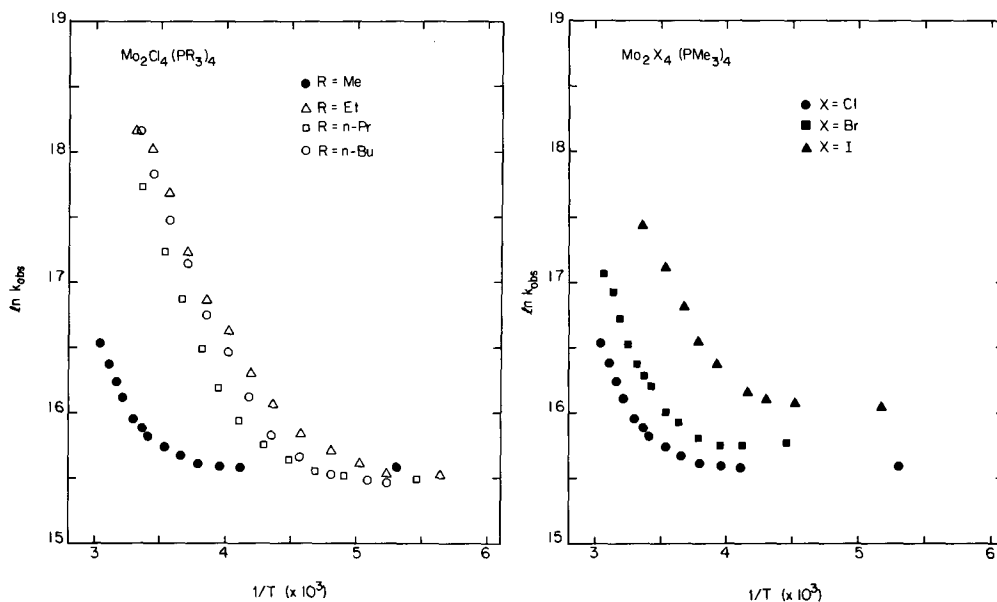


FIG. 3. Temperature dependence of $k_{\text{obs}}^{\text{em}}$ of $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$ in 2-methylpentane solution.

jacent metal atoms (Fig. 5). Because this "cis" overlap is much greater than the face-to-face δ overlap in the quadruply bonded dimers, the energy gap between the lowest triplet excited state and the ground state of an M_6 cluster is expected to be fairly large (~ 2 eV) (19, 20).

The $\text{Mo}_6\text{X}_{14}^{2-}$ cluster anions are yellow to

red in color; their electronic spectra are dominated by charge transfer transitions in the near ultraviolet region. The emission spectra of all of these clusters are in the red and near-infrared region (19, 20). In the Mo series, the intense bands in the near uv are red-shifted upon exchange of chloride ligands for bromides (or bromides for io-

TABLE I
SPECTROSCOPIC AND PHOTOPHYSICAL PARAMETERS FOR $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$ COMPLEXES IN 2-METHYLPENTANE SOLUTION

Compound	Absorption ($\delta^2 \rightarrow \delta^1\delta^{*1}$)			Emission ($\delta^1\delta^{*1} \rightarrow \delta^2$)					
	$\bar{\nu}_{\text{max}}$ (cm^{-1})	f		$\bar{\nu}_{\text{max}}$ (cm^{-1})	ϕ (300 K)	τ (nsec)		k_{rad} (10^6 sec^{-1})	$k_{\text{rad}}^{\text{calc}}$ (10^6 sec^{-1})
		300 K	77 K			300 K	77 K		
$\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$	17,090	0.024	0.025	14,880	0.259	135	171	1.92	5.3
$\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$	16,980	0.025	—	14,730	0.013	14	188	0.929	5.4
$\text{Mo}_2\text{Cl}_4(\text{PPr}_3)_4$	17,040	0.026	—	14,880	0.016	21	187	0.762	5.8
$\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$	17,040	0.026	0.027	14,810	0.013	14	189	0.929	5.9
$\text{Mo}_2\text{Br}_4(\text{PMe}_3)_4$	16,720	0.030	0.034	14,900	0.162	90	144	1.92	6.7
$\text{Mo}_2\text{I}_4(\text{PMe}_3)_4$	15,720	0.040	0.039	14,030	0.123	29	105	4.24	7.9

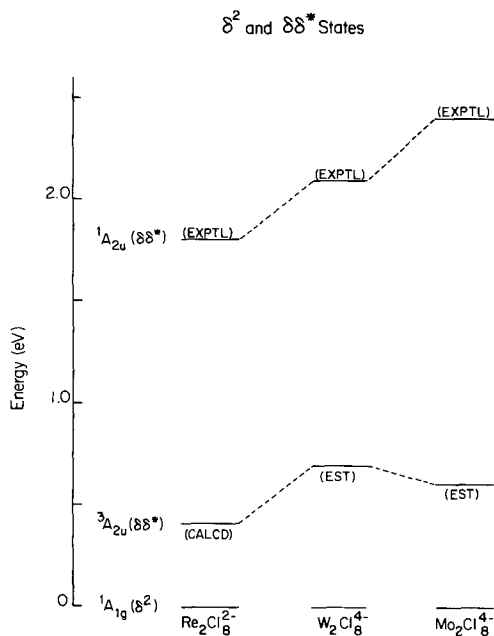


FIG. 4. Energies of $(\delta)^2$ and $(\delta\delta^*)$ states of $\text{Re}_2\text{Cl}_8^{2-}$, $\text{W}_2\text{Cl}_8^{4-}$, and $\text{Mo}_2\text{Cl}_8^{4-}$.

ides), clearly implying that these bands are due to ligand-to-metal charge transfer (LMCT) transitions. However, the emission spectra of these Mo clusters are insensitive to the halide ligand, suggesting that the emissive excited state is metal-localized, which is expected by analogy to the dimer photophysics. The emission bands

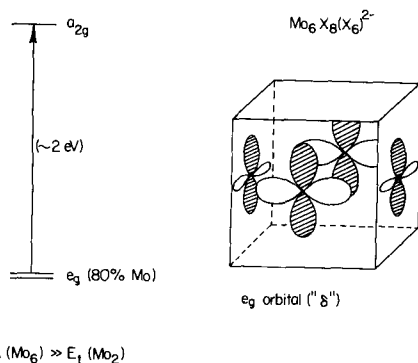


FIG. 5. HOMO-LUMO splitting for $(\text{Mo}_6\text{X}_8)\text{X}_6^{2-}$ clusters. The ground state is $(e_g)^4$.

TABLE II
PHOTOPHYSICAL PARAMETERS FOR MOLYBDENUM
AND TUNGSTEN CLUSTERS IN ACETONITRILE
SOLUTION AT 300 K

	τ (μsec)	ϕ_{em}	k_r (sec^{-1})	k_{nr} (sec^{-1})
$(\text{Bu}_4\text{N})_2\text{Mo}_6\text{Cl}_{14}$	180	0.19	1.1×10^3	4.5×10^3
$(\text{Bu}_4\text{N})_2\text{Mo}_6\text{Br}_{14}$	110	0.23	2.1×10^3	7.0×10^3
$(\text{Bu}_4\text{N})_2\text{Mo}_6\text{I}_{14}$	84	0.16	1.9×10^3	1.0×10^4
$(\text{Bu}_4\text{N})_2\text{W}_6\text{Cl}_{14}$	2	0.02	1.0×10^4	4.9×10^3
$(\text{Bu}_4\text{N})_2\text{W}_6\text{Br}_{14}$	15	0.12	8.0×10^3	5.9×10^4
$(\text{Bu}_4\text{N})_2\text{W}_6\text{I}_{14}$	30	0.39	1.3×10^4	2.0×10^4

observed for the Mo series are broad and structureless even at low temperature. The Stokes shifts of these clusters are large ($\sim 5000 \text{ cm}^{-1}$), which indicates that there is a large distortion of the molecular geometry in the excited state relative to the ground state. It is somewhat surprising, given that there are 24 electrons in the metal-bonding framework, that this excited state geometry should be significantly different from that of the ground state.

In an effort to understand the nature of this excited state in the Mo clusters, time-resolved emission experiments were done. The results for $\text{Mo}_6\text{X}_{14}^{2-}$ anions in acetonitrile solution at room temperature are given in Table II. The lifetimes of the excited states are extremely long for inorganic species. The calculated radiative (k_r) and non-radiative (k_{nr}) rate constants are both very small for this type of system. The low k_r for these clusters can be explained by the assignment of the radiative transition from the excited state back to ground state being forbidden by both symmetry and spin. Consistent with this explanation, at low temperature the absorption spectrum of $(\text{Bu}_4\text{N})_2\text{Mo}_6\text{Cl}_{14}$ can be resolved into several weak components in the origin region of the emission band. The relatively small nonradiative rate constants for these clusters are probably due to the general structural characteristics of the molecule. The excited state is metal-localized, with very little li-

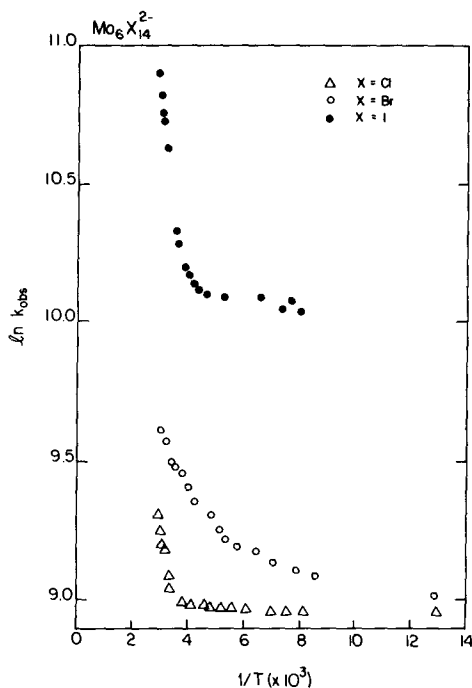


FIG. 6. Temperature dependence of k_{obs}^{em} in crystalline $(Bu_4N)_2Mo_6X_{14}$.

gand character. Because the metal orbitals are insulated by a ball of negative charge (the halides), the solvent cannot accept energy from the excited state very efficiently. Variable temperature lifetime data for solid samples of the $Mo_6X_{14}^{2-}$ clusters are presented as a plot of $\ln k_{obs}$ vs $1/T$ in Fig. 6. [Note that k_{obs} ($= 1/\tau$) is roughly k_{nr} , see Eq. (1), because variable-temperature quantum yield measurements on $Mo_6Cl_{12}(PR_3)_2$ systems—which display the same emission behavior as the $Mo_6Cl_{14}^{2-}$ cluster—show that the radiative rate shows no temperature dependence down to 77 K, Ref. (21).] The non-radiative rate shows a marked temperature dependence from which an activation energy of ~ 3000 cm^{-1} can be calculated for the $Mo_6Cl_{14}^{2-}$ and $Mo_6I_{14}^{2-}$ clusters. (It is not clear why the bromide analog displays anomalous behavior.) It is interesting that the E_a for the Mo_6 clusters is about the same

as that for the Mo_2 complexes. The chloride and bromide molybdenum clusters have approximately the same lifetime at low temperature (77 K), whereas the molybdenum iodide emission lifetime is significantly shorter. This type of behavior is also observed in the tungsten system and will be discussed shortly.

The absorption spectra of the $W_6Cl_{14}^{2-}$, $W_6Br_{14}^{2-}$, and $W_6I_{14}^{2-}$ anions are dominated by intense charge transfer transitions in the visible and near ultraviolet. The bands in the tungsten clusters are blue-shifted relative to those of the molybdenum species, thereby indicating once again that LMCT transitions are involved. All of the tungsten clusters exhibit luminescence in the red and near-infrared region of the spectrum, but the emission spectra are not isoenergetic (as they were in the molybdenum series). Surprisingly, the energy of the emitting excited state *increases* according to Cl (1.83) $\sim Br$ (1.85) $< I$ (2.05 eV) (21). This is, of course, the opposite trend from that expected when some charge transfer is mixed into the transition. The ordering of the energies of the tungsten halide emissions stays the same at low temperature, so the effect does not arise from thermal population of other higher energy excited states. The fact that these complexes follow an “inverse halide order” establishes conclusively that there is virtually no halide (charge transfer) character in the emitting excited state.

The lifetimes and emission quantum yields of the tungsten clusters in solution are unusual in that they increase with increasing size of the halide (Table II). However, the calculated radiative rate constants for all three clusters are very similar, indicating that the excited state is configured in the same way in each case. The radiative rates for the tungsten clusters are an order of magnitude greater than those of the corresponding molybdenum complexes. This could be a reflection of the greater spin-

TABLE III
ENERGY TRANSFER QUENCHING OF TUNGSTEN CLUSTERS IN ACETONITRILE SOLUTION AT 300 K

Cluster (E_i)	k_q ($M^{-1} \text{ sec}^{-1}$)			
	Azulene ^a ($E_t = 1.3 \text{ eV}$)	9,10-Dichloroanthracene ($E_t = 1.7$)	Anthracene ($E_t = 1.8$)	t-Stilbene ($E_t = 2.2$)
$W_6Cl_{14}^{2-}$ (1.83 eV)	1.1×10^9	8.7×10^8	1.0×10^7	$< 10^5$
$W_6Br_{14}^{2-}$ (1.85 eV)	1.2×10^9	8.1×10^8	1.1×10^8	$< 10^5$
$W_6I_{14}^{2-}$ (2.05 eV)	1.9×10^9	5.9×10^9	1.9×10^9	2.7×10^7

^a Quencher triplet energies are from Murov, S. L. "Handbook of Photochemistry," Dekker, New York, 1973.

orbit coupling of the third-row metal, since the excited state-to-ground state transition is spin forbidden (triplet to singlet). The trend in the nonradiative rate constants is the opposite seen for the molybdenum series and again quite surprising. In excited state decay processes in molecular systems such as these, small changes in vibrational energies may cause large changes in the behavior of the state (16). The tungsten chloride cluster's vibrational modes may couple better with a deactivation mode in the excited state than the vibrations in the tungsten iodide system. Time-resolved Raman spectroscopic studies now underway may shed some light on this aspect of the decay of these excited states.

Variable-temperature emission lifetime measurements confirm that the apparently anomalous lifetime of the tungsten chloride cluster at room temperature is not associated with charge transfer mixing (Fig. 7). Rather, it is due to the dominance of the nonradiative pathway for $W_6Cl_{14}^{2-}$ at higher temperatures. Upon cooling, the ordering of the lifetimes becomes the same as that observed in the Mo_6 series. As was observed for Mo_6 species, the chloride and bromide W_6 clusters possess very similar lifetimes at 77 K, whereas the iodide lifetime is significantly shorter.

The spin-triplet nature of the cluster emissive state has been confirmed through energy transfer experiments employing or-

ganic acceptors with well-established triplet excited state energies (Table III). Efficient quenching by the triplet organic acceptors is observed for all three clusters. As a control, $(Bu_4N)_2Re_2Cl_8$ also was examined, since it has a singlet excited state; as expected, $k_q(\text{azulene}) < 10^5 M^{-1} \text{ sec}^{-1}$. Quenching of the cluster luminescence occurs via an energy transfer mechanism, be-

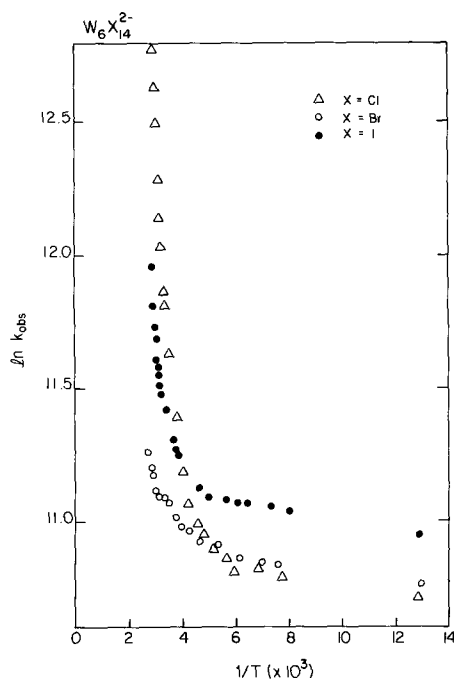
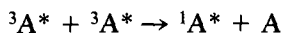


FIG. 7. Temperature dependence of k_{obs}^{em} in crystalline $(Bu_4N)_2W_6X_{14}$.

cause delayed fluorescence of the organic quencher was observed (22). This delayed fluorescence arises from triplet-triplet annihilation processes of the organic quencher,



The ${}^1A^*$ (singlet excited state of the acceptor) arising from this process has the same spectrum as if it were directly excited, but the lifetime of the emission approaches that of the triplet (${}^3A^*$), which is usually several orders of magnitude longer than the natural lifetime of the fluorescence. The general trend in the energies of the cluster excited states also can be probed by quenching experiments. This is especially clear with the tungsten clusters where, using anthracene as the quencher, the energy order appears to be $E(W_6Cl_{14}^{2-*}) < E(W_6Br_{14}^{2-*}) < E(W_6I_{14}^{2-*})$. It is gratifying that both the quenching and the spectroscopic experiments arrive at the same "inverse halide order" for the tungsten clusters. Our results also indicate clearly that even with third-row metals, the assignment of a spin to an excited state is reasonable and chemically relevant.

Acknowledgments

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