The Photophysical Behavior of Mixed Transition Metal–Uranyl Complexes with Polyketonate Ligands. The Vibronically Isolated Uranyl Chromophore[†]

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Abstract

The uranyl excited-state lifetimes and luminescence spectra have been examined for a series of bis-triketonate and bis-tetraketonate uranyl–transition metal complexes at low temperatures. The energies of the vibronic components of the uranyl luminescence were found to be dependent on the complexing ligand, but they did not depend significantly on the neighboring transition metal (Cu, Co, Fe, Ni, Zn, Pd). The band shape was sometimes markedly dependent on the metal. Emission quantum yields varied over a 100-fold range. Emission lifetimes varied by less than a factor of three, despite the fact that most of the transition metals are potential quenchers, and despite the existence of a low energy ligand-to-metal charge-transfer excited state in the tetraketonate complexes. The vibronic isolation of the uranyl excited state from other molecular excited states in these complexes is attributed to a large nuclear reorganizational barrier for entry into or escape from the potential energy surface of the electronically excited uranyl moiety. Population of the uranyl excited state results in an increase in the U–O bond length, and the U–O nuclear motions are not activated by other low energy electronic excited states of the polyketonate complexes.

Introduction

Mixed metal polynuclear complexes have attracted considerable attention owing to their potential for exhibiting unique chemical properties distinctly different from those of related mononuclear complexes [1–4]. One of the major photochemical interests in such systems is based on the likelihood that there exist complexes with weakly coupled metal centers in which irradiations will result in the intramolecular separation of charge and the generation of transient species with the potential for facile multi-equivalent redox behavior. The generation of transient species with the appropriate properties depends on a critical balance between effective communication among high energy electronic excited states and the vibronic trapping of low energy intervalence (*i.e.*, metal-to-metal charge transfer) excited states. It is useful to use donors with relatively well understood excited state properties in exploratory studies of the photochemical behavior of such polynuclear complexes.

The convenient availability of a series of mixed metal polyketonate complexes containing the uranyl moiety [3], and the well-understood excited state properties of UO_2^{2+} [5–14] have led us to examine the photophysical behavior of transition metal–uranyl polyketonates. Since electron transfer is often a facile mechanism for quenching electronically excited UO_2^{2+} [7, 9, 14, 15], these complexes seemed likely candidates in which to examine photo-induced, intramolecular charge-separation processes. Contrary to this expectation, we have found the uranyl moiety to be vibronically isolated (at 77 K) in these molecules.

Experimental

Materials

Bis-acetylacetonatodioxouranium(IV), $UO_2(acac)_2 \cdot H_2O$, was prepared from uranyl acetate and freshly distilled acetylacetone, following the procedure of Belford *et al.* [16]. The synthesis and characterization of binuclear and trinuclear uranyl polyketonate complexes has been reported elsewhere [17]. All solvents used in this study were spectroscopic grade. The uranyl complexes were incorporated into the polymethylmethacrylate (PMM) film by dissolving methyl methacrylate and the uranyl complex in $CHCl_3$ ([methyl methacrylate]/[uranyl complex] ~ 10^3) and allowing the solution to dry in an aluminum foil dish in the dark. The structures and

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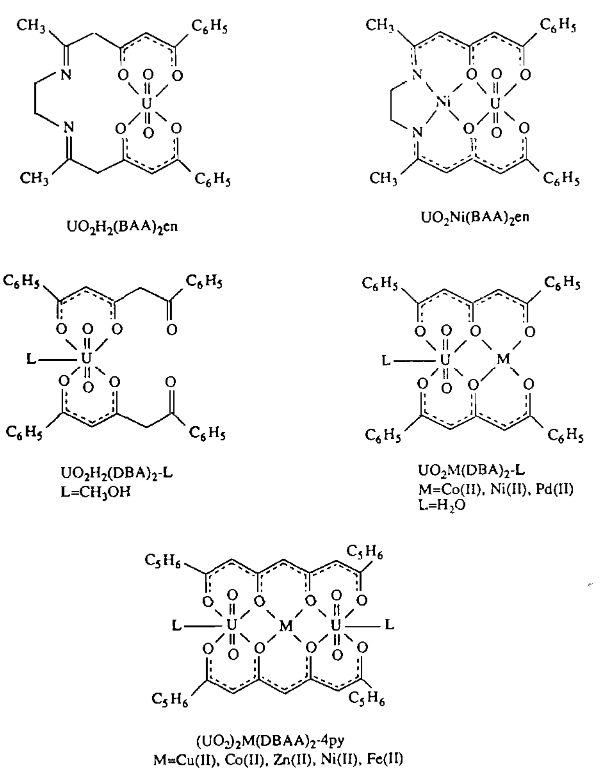
Structure of Uranyl Polyketonates



$UO_2H_2(BAA)_2en$

$UO_2Ni(BAA)_2en$

$UO_2H_2(DBA)_2$-L
L=CH_3OH

$UO_2M(DBA)_2$-L
M=Co(II), Ni(II), Pd(II)
L=H_2O

$(UO_2)_2M(DBAA)_2$-4py
M=Cu(II), Co(II), Zn(II), Ni(II), Fe(II)

Fig. 1. Structural formulas of polyketonate complexes. M = Co(II), Ni(II), or Pd(II) in $UO_2M(DBA)_2 \cdot H_2O$ and M = Cu(II), Co(II), Zn(II), Ni(II) or Fe(II) in $(UO_2)_2M(DBAA)_2 \cdot$ 4py. Abbreviations: acac, acetylacetone; H_2BAA, benzoylacetylacetone; H_2DBA, dibenzoylacetone; H_2DBAA, dibenzoylacetylacetone; en, ethylenediamine.

abbreviations for the polyketonate complexes are summarized in Fig. 1.

Methods

The luminescence spectra were determined using a Molectron UV-1000 nitrogen laser pumped DL-14 dye laser as the excitation source and a Princeton Applied Research OMA-1 with SIT vidicon as a detector. The UV-1000 was gated to fire at the beginning of the vidicon scan. Emission spectra were obtained in EPA (ether:isopentane:ethanol = 5:5:2 by volume), ethanol, methyltetrahydrofuran and in PMM film. Since the complexes had very limited solubilities, saturated solutions were usually employed. Deaeration was accomplished by five or six freeze–evacuate–thaw cycles.

The luminescence decay rate constants were based on a least-squares fit of the luminescence decay, stimulated by a single dye laser pulse and detected using an RCA 7102 photomultiplier coupled to a Nicolet Explorer III digital oscilloscope. The digital data were transmitted to a Data General Eclipse computer to obtain the rate parameters.

Luminescence lifetimes were determined for uranyl complexes incorporated into PMM films by mounting the films in a quartz cuvette at an angle of 45° to the excitation beam inside a thermostatted PRA cell housing. Temperatures were regulated in the range of –30 to –150 °C using a stream of cooled N_2; at high temperatures a circulating bath and a liquid coolant were used. Temperatures were determined using Omega digital thermometers and sensors mounted in the cell housing. The luminescence spectral and lifetime determinations at 77 K were made using a quartz sample tube and a Dewar flask with an optically transparent window.

Excitation spectra were obtained at 77 K using a Perkin-Elmer Model 44B spectrometer[§].

The relative emission quantum yields, ϕ_r', of uranylpolyketonates were measured at 77 K using diphenylanthracene as the standard reference (emission quantum yield of 1.00 for 386 nm excitation) [18]. The integrated emission intensity was determined for solutions with substrate absorbance adjusted to 0.500 and using 386 nm excitation.

Results

The uranyl excited state is readily quenched in fluid media and lifetimes are very dependent on the medium. However, in the absence of strongly complexing ligands, the characteristic, structured luminescence is not very sensitive to the medium; e.g., the vibronic bands are red shifted by 5 nm or less for $UO_2(NO_3)_2$ in a PMM film compared to acetonitrile solutions. In contrast, there is an appreciable red shift of the uranyl emission in the uranyl ketonate complexes (Fig. 2). Emission spectra of some of the samples were complicated by the appearance of vibronic components at about 520, 545, 570 and 600 nm, superimposed on the progressions typical of uranyl ketonate complexes. The appearance of these additional components seemed to depend on the pretreatment of the samples and can be readily attributed to a small amount (less than 10%) of dissociation of the UO_2^{2+}, Ni^{2+} complexes to produce some strongly emitting, uncomplexed UO_2^{2+}. The luminescence spectra of the ketonate complexes did not exhibit the resolvable fine structure of the vibronic components which are characteristic of $UO_2(NO_3)_2$ [5–14]. We were unable to detect luminescence from the uranyl ketonate complexes in fluid solutions. The energies of the vibronic band maxima were somewhat matrix-dependent (±3 nm)

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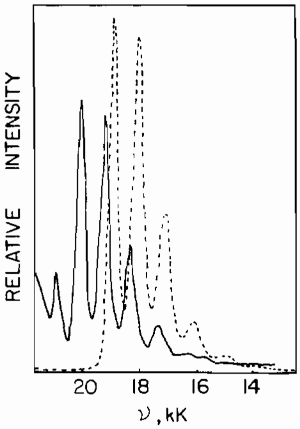

Fig. 2. Luminescence spectra of $UO_2(NO_3)_2{\cdot}6H_2O$ (solid line) and $UO_2(acac)_2{\cdot}H_2O$ (dashed line) in ethanol glass at 77 K. Intensities not corrected for detector distortion.

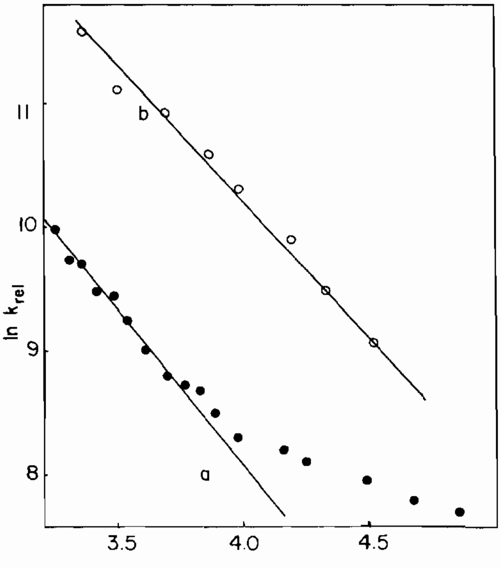

Fig. 3. Variations of the excited state relaxation rate constants with temperature for (a) $UO_2(NO_3)_2{\cdot}6H_2O$ and (b) $UO_2(acac)_2{\cdot}H_2O$ in PMM films.

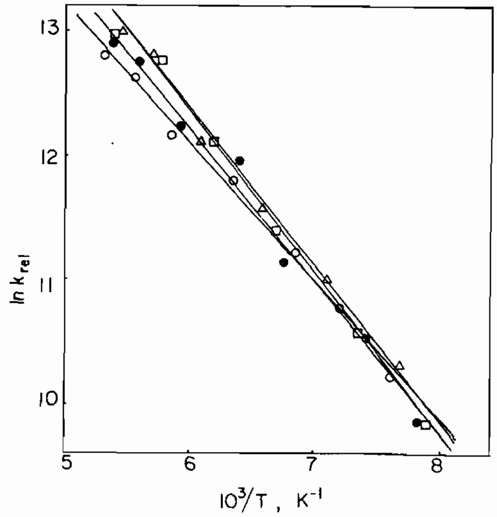

Fig. 4. Variations of the excited state relaxation rate constants with temperature (PMM films) for $(UO_2)_2Fe(DBAA)_2py_4$, □; $(UO_2)_2Co(DBAA)_2py_4$, ●; $(UO_2)_2Ni(DBAA)_2py_4$, △; $(UO_2)_2Cu(DBAA)_2py_4$, ○.

at 77 K, and somewhat excitation energy-dependent (±3 nm) (Table S-I, supplementary material). There were larger variations in the vibronic structure of the uranyl emission with changes in the adjacent metal and for the different polyketonate ligands.

The excited state lifetimes of the uranyl polyketonate complexes decreased abruptly near the temperature of the glass–fluid transition for low temperature glassy media, but a relatively shallow temperature dependence of the lifetimes was observed in PMM films (Figs. 3 and 4, and Table I).

While the emission quantum yields of the uranyl polyketonate complexes vary over a 300-fold range, the uranyl excited-state lifetimes vary over less than a 3-fold range at 77 K (Table II). The compounds with the smallest emission yields, the $(UO_2)_2M(DBAA)_2$ complexes, all have an intense, broad (full width, half height ~ 100 nm) absorption band with an absorption maximum at about 470–480 nm (Table II). This is most likely a tetraketonate → uranyl charge-transfer (CT) absorption and similar absorption features occur at 405–424 nm in the triketonates, and at 365 nm in $UO_2(acac)_2{\cdot}H_2O$. Irradiations in the low-energy CT-band of the tetraketonate complexes do not produce the characteristic uranyl emission (Figs. 5 and 6). While the excitation spectra of the tetraketonate complexes lack the resolvable fine structure that one finds for UO_2^{2+} in simple salts (Fig. 5), all the uranyl compounds have excitation spectra with two major bands, one at about 400 nm and the other at 320–340 nm.

Discussion

In fluid solutions the UO_2^{2+} excited state is collisionally quenched by most transition metals, including Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} [7, 9, 19]. When these same metals are bound into a polyketonate complex with the UO_2^{2+} moiety, they are ineffective quenchers, at least at low temperatures. The tetraketonates are the most interesting of the uranyl polyketonate complexes that we have examined, since these systems so dramatically illustrate the poor communication between the uranyl chromophore and other excited states in these molecules (see Fig. 7).

TABLE I. Kinetic Parameters for Uranyl Complexes in PMM Films and EPA Glasses

Complex	τ, μs [a] (77 K)	τ, μs [b] (−90 °C)	E_a [c] (kJ mol^{-1})	$A \times 10^{-8}$ [b] (s^{-1})
$UO_2(NO_3)_2 \cdot 6H_2O$	425		20[d]	
			(55)[e]	(1.9×10^5)[e]
$UO_2(acac)_2 \cdot H_2O$	310 (190)[f]	72	18[d]	26
$UO_2H_2(DBA)_2 \cdot CH_3OH$	133 (211)[f]	1.5	11	6.9
$UO_2Co(DBA)_2 \cdot 3H_2O$	126 (250)[f]	4.0	11	3.9
$UO_2Ni(DBA)_2 \cdot 3H_2O$	122 (80)[f]	1.8	8.7	1.7
$(UO_2)_2Fe(DBAA)_2py_4$	(125)[f]	2.3	12	15
$(UO_2)_2Co(DBAA)_2py_4$	200 (302)[f]	3.2	10	3
$(UO_2)_2Ni(DBAA)_2py_4$	(202)[g]	2.3	10.5	4.9
$(UO_2)_2Cu(DBAA)_2py_4$		2.7	9.0	1.1

[a] EPA glass. [b] PMM film. [c] Based on a +35° to −150 °C temperature range. [d] Based on a −80° to −150 °C temperature range. [e] Based on a +80° to +35 °C temperature range (ref. 8b). [f] Ethanol glass. [g] Methyl tetrahydrofuran glass.

TABLE II. Relative Emission Quantum Yields and Spectroscopic Parameters for Uranyl Polyketonates

Complex	ϕ_r [a]	η_{isc} [b]	$\epsilon \times 10^{-4}$ [c] (M^{-1} cm^{-1})	λ_{max}(CT)[d] (nm)
$UO_2(acac)_2 \cdot H_2O$	0.67	1.00	0.171	365
$UO_2H_2(DBA)_2 \cdot CH_3OH$	0.083	0.289	2.51	405
$UO_2Co(DBA)_2 \cdot 3H_2O$	0.023	0.084	3.74	410
$UO_2Ni(DBA)_2 \cdot 3H_2O$	0.072	0.273	1.89	405
$UO_2Pd(DBA)_2 \cdot H_2O$	0.041	0.102	2.91	424
$(UO_2)_2Co(DBAA)_2py_4$	0.003	0.007	3.76	480
$(UO_2)_2Ni(DBAA)_2py_4$	0.002		1.41	475
$(UO_2)_2Cu(DBAA)_2py_4$	0.006	(0.0134)[e]	1.72	480

[a] Yields for 386 excitations at 77 K relative to diphenylanthracene. Solutions of samples or the reference were adjusted so that the absorbance at 386 nm was 2.59. [b] Relative efficiencies from $\phi_r = \eta_{isc} k_r \tau$, assuming k_r to be a constant and setting $\eta_{isc} = 1$ for $UO_2(acac)_2 \cdot H_2O$. [c] Molar absorptivity at 386 nm. [d] Absorption maximum of the lowest energy CT transition. [e] Based on the lifetime measured in MeTHF.

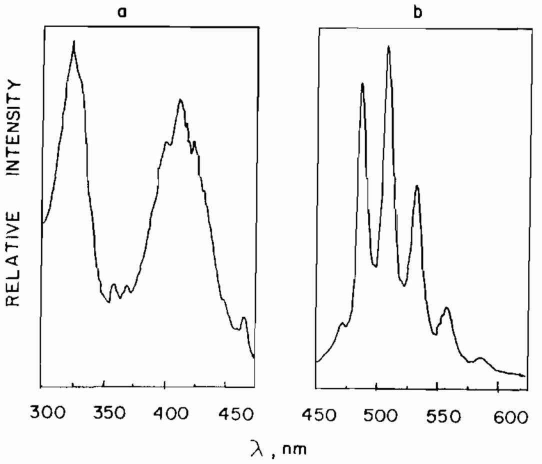

Fig. 5. Emission (a) and excitation (b) spectra of $UO_2(O_2CCH_3)_2 \cdot 6H_2O$ in 1 M HNO_3 (25 °C). Corrected for detector distortion.

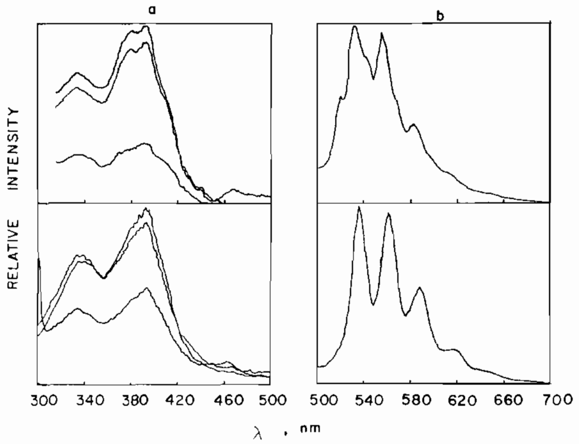

Fig. 6. Excitation (a) and emission (b) spectra of $(UO_2)_2Ni(DBAA)_2py_4$ (upper) and $(UO_2)_2Zn(DBAA)_2py_4$ (lower) in ethanol glasses at 77 K. Emission spectra for 400 nm excitations. Excitation spectra for observations of emission intensities at 535 nm (upper curve), 560 nm (middle curve) and 588 nm (lower curve). Spectra are corrected for detector distortion.

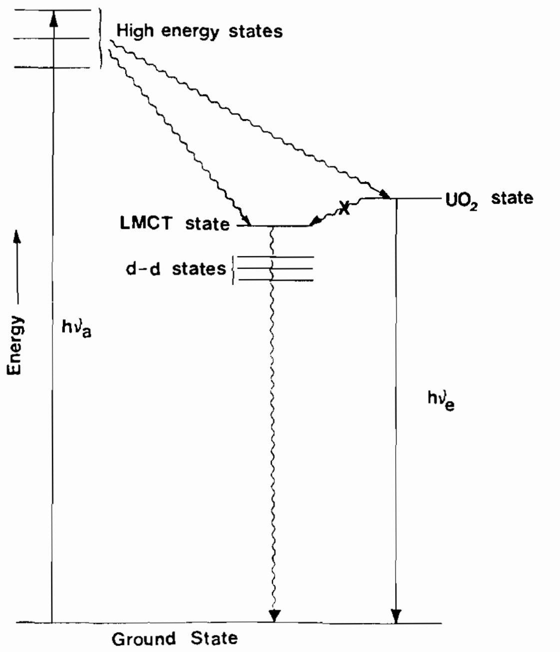

Fig. 7. Qualitative energy level diagram indicating the relative disposition of excited states in transition metal–bis-uranyl tetraketonate complexes. Light absorption, $h\nu_a$, and emission, $h\nu_e$, indicated by vertical lines; non-radiative processes indicated by wavy lines. The internal conversion from the uranyl excited state to the lower energy MLCT or metal-centered d–d excited states appears to be forbidden.

The lowest-energy electronic origin of the uranyl emission is probably about 19×10^3 cm^{-1} in the polyketonate complexes, compared to about 20.7×10^3 cm^{-1} for $UO_2(NO_3)_2$. The broad, low energy CT absorption bands in the polyketonates have their maxima in this energy region for the tetraketonate complexes, and the electronic origin of this CT absorption must be about 17×10^3 cm^{-1}. In most luminescent molecules one expects electronic excitation to be followed by a rapid cascade through the various excited state manifolds to populate the lowest-energy excited state. The dominant luminescence is nearly always from the lowest-energy molecular excited state. This is *not* the pattern found in the mixed metal–uranyl polyketonate complexes, in which transition metal d–d excited states are often lower in energy than the UO_2^{2+} excited state, and it is definitely not the behavior of the $(UO_2)_2M(DBAA)_2$ complexes in which there is a very prominent lower energy CT state. Rather, the only emission observed from any of these systems is that characteristic of the relatively high energy UO_2^{2+} chromophore as illustrated in Fig. 7.

The vibronic maxima of the UO_2^{2+} emissions do not vary a great deal from one polyketonate complex to another, but the details are usually sufficiently different that most of the complexes exhibit unique spectra (Fig. 2 and Table S-I).

The qualitative similarity of the excitation spectra (Figs. 5 and 6), which do not contain features corresponding to the low-energy ketonate → UO_2^{2+} absorption, together with the very small radiative quantum yield of most of the polyketonate complexes, suggests that the uranyl chromophores in these complexes are more efficiently excited by the direct absorption of radiation than by internal conversion or intersystem-crossing processes from the higher energy excited states (at 77 K). Apparently the uranyl chromophore is isolated from other molecular states of these molecules. This can be expressed more quantitatively in terms of the overall efficiency, η_u, of populating the uranyl chromophore. The radiative quantum yield is:

$$\phi_r = \eta_u k_r \tau$$

where the rate constant for radiative relaxation of $UO_2^{2+}(k_r)$ can be assumed to be approximately constant, and where τ is the lifetime of the uranyl excited state. Thus

$$\eta_u = \phi_r (k_r \tau)^{-1}$$

Relative efficiencies, compared to $UO_2(acac)_2$, for populating the uranyl excited state are compared in Table II. Since the uranyl excited-state lifetimes do not vary much, the very small values of ϕ_r found for several of the $(UO_2)_2M(DBAA)_2py_4$ complexes can be attributed to very inefficient population of the uranyl excited state from higher energy excited states in the molecule. While the effect on ϕ_r is not so dramatic, the uranyl chromophore is not efficiently populated even in the triketonate complexes.

The values found for ϕ_r are about 10 times larger in $UO_2(acac)_2$ than in the triketonate complexes, while the lifetime of the UO_2^{2+} emission is not much altered at 77 K. Since the changes in ϕ_r parallel the changes in absorptivity at the exciting wavelength, it appears that relaxation within the ketonate → UO_2^{2+} CT manifold is more efficient than crossing between the CT and UO_2^{2+} centered excited-state manifolds. The 77 K emission lifetimes are remarkably insensitive to variation of the metal in the mixed metal complexes. Thus the 200–300 μs lifetimes for $UO_2(acac)$, $(UO_2)_2Co(DBAA)_2py_4$ and $(UO_2)_2Cu(DBAA)_2py_4$ indicate that the adjacent transition metal centers do not quench the uranyl excited state by either electron or energy transfer in the tetraketonate complexes at 77 K.

Since the mean 77 K lifetimes of the triketonate complexes are comparable (182 ± 46 μs) with or without an adjacent transition metal, there can be little intramolecular quenching of the uranyl excited state in these molecules. The small variations in ϕ_r, and thus in η_u, for these complexes parallel the variations in absorptivity at the wavelength of excitation and can therefore be attributed to the fraction of light absorbed directly by the uranyl chromophore. Excitation spectra of the tetraketonates do not contain the low-energy CT absorption feature and lead to the same conclusion.

On balance, our observations indicate that the uranyl chromophore of the polyketonate complexes is effectively isolated within these molecules. It is not efficiently populated from higher energy, non-uranyl excited states, and the uranyl excited state is not effectively quenched by lower-energy charge-transfer or d–d excited states. This behavior of the transition metal–uranyl polyketonate complexes is in dramatic contrast to the very efficient electron-transfer quenching found, even at 77 K, for the $(bpy)_2Ru(CN)CNRu(NH_3)_5^{3+}$ binuclear complex [19]. It is pertinent that the collisional quenching of the UO_2^{2+} excited state by transition metals in fluid solution has been postulated to occur by means of a transition state in which the quencher is bound to a uranyl oxygen [9]. This pathway is not possible in the ketonate complexes. Consequently, the contrast in quenching efficiency between the cyano-bridged, bis-ruthenium complex [19] and the uranyl polyketonate complexes may be attributed to a combination of electronic and nuclear factors: (i) strong donor–acceptor electronic coupling (mediated by the π^*–CN^- orbitals) is expected in the bis-ruthenium complex, but excitation of UO_2^{2+} appears to be largely localized along the O–U–O axis; (ii) only small changes in nuclear coordinates are expected to accompany electron transfer in the bis-ruthenium complex, while there is an appreciable difference in the excited state and ground state U–O bond lengths [7–14]. These nuclear distortions will lead to appreciable reorganizational barriers for populating or quenching the uranyl excited state at 77 K. The implied barrier crossings should be thermally activated and the intramolecular quenching processes might be observed at higher temperatures. Our attempts to find such a process in solution were frustrated by the very efficient, transition metal-independent quenching which occurred when the medium became fluid. This behavior could be a consequence of partial dissociation of the complexes, bimolecular reactions, etc. Studies in PMM films were equally unsatisfactory, since the thermally activated quenching was nearly independent of the presence of transition metals and the nature of the polyketonate ligand. Since the polyketonates are much shorter lived than $UO_2(acac)_2$ in PMM matrices, it is likely that the thermally activated quenching does involve the polyketonate ligands, possibly through partial dissociation of the ligand, or through electron transfer from the ligand.

Vibronic trapping of valence-localized species will undoubtedly be a requirement for chemically useful, photoinduced charge separation in multinuclear complexes. However, the present study demonstrates that such a feature can interfere with the efficiency of the charge-separation process. A more inert chelating ligand system may overcome some of the problems by enabling studies to be performed over a wider temperature range.

Supplementary Material

Table of luminescence spectral data (5 pages) is available from the authors on request.

Acknowledgements

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References

1 J. Petersen, *Coord. Chem. Rev., 64,* 275 (1985).

2 J. I. Marshall, A. E. Stiegman and H. B. Gray, in A. P. B. Lever (ed.), 'Excited States and Reactive Intermediates', ACS Symposium Series, 307, American Chemical Society, Washington, D.C., 1986, p. 166.

3 (a) D. Earl Fenton, R. R. Schroeder and R. L. Lintvedt, *J. Am. Chem, Soc., 100,* 1931 (1978); (b) R. L. Lintvedt and L. S. Kramer, *Inorg. Chem., 22,* 796 (1983); R. L. Lintvedt, L. S. Kramer, G. Ranger, P. W. Corfield and M. D. Glick, *Inorg. Chem., 22,* 3580 (1983).

4 R. Sahai, D. A. Baucom and D. P. Rillema, *Inorg. Chem., 25,* 3843 (1986).

5 G. H. Dieke and H. B. F. Duncan, 'Spectroscopic Properties of Uranium Compounds', McGraw Hill, New York, 1949.

6 E. Rabinowich and R. L. Belford, 'Spectroscopy and Photochemistry of Uranyl Compounds', Pergamon, Oxford, 1964.

7 (a) H. D. Burrows and J. D. Pedrosa de Jesus, *J. Photochem., 5,* 265 (1976); (b) H. D. Burrows, S. J. Formosinho, M. D. G. Miguel and F. P. Coelho, *J. Chem. Soc., Faraday Trans. 1, 72,* 163 (1976); (c) H. D. Burrows, A. Cardosa and M. Da G. M. Miguel, *J. Chem. Soc., Faraday Trans. 1, 81,* 49 (1985).

8 (a) H. D. Burrows, T. J. Kemp, *Chem. Soc. Rev., 3,* 139 (1974); (b) S. R. Allsopp, A. Cox, T. J. Kemp, W. J. Reed, V. Carrassiti and O. Traverso, *J. Chem. Soc., Faraday Trans. 1, 75,* 342 (1979).

9 M. D. Marcantanatos, *J. Chem. Soc., Faraday Trans. 1, 75,* 2252 (1979).

10 D. P. Wong, A. Y. C. Wong and E. Y. Wong, *J. Chem. Phys., 56,* 2838 (1972).

11 (a) A. F. Leung and K. K. Tsang, *Can. J. Phys., 57,* 330 (1979); (b) A. F. Leung, *J. Phys. Chem. Solids, 43,* 467 (1982); (c) A. F. Leung and T. W. Lai, *J. Chem. Phys., 76,* 3913 (1982).

12 (a) C. D. Flint and P. A. Tanner, *J. Chem. Soc., Faraday Trans. 2, 74,* 7210 (1978); (b) *75,* 1168 (1979); (c) *78,* 839 (1982); (d) *Mol. Phys., 44,* 411 (1981); (d) *Inorg. Chem., 20,* 4405 (1981); (f) C. D. Flint, P. Sharma and P. A. Tanner, *Inorg. Chem., 86,* 1921 (1982).

13 R. G. Denning, D. N. P. Foster, T. R. Snellgrove and D. R. Woodwark, *Mol. Phys., 37,* 1089 (1979).

14 G. M. Kramer, M. B. Dines, A. Kaldor, R. Hall and D. McClure, *Inorg. Chem., 20,* 1421 (1981).

15 T. Rosenfeld-Grünwald and J. Rabani, *J. Phys. Chem., 84,* 2981 (1980).

16 R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. Nucl. Chem., 14,* 169 (1960).

17 (a) R. L. Lintvedt, M. J. Heeg, N. Ahmad and M. D. Glick, *Inorg. Chem., 21,* 2350 (1982); (b) R. L. Lintvedt and N. Ahmad, *Inorg. Chem., 21,* 2356 (1982); (c) R. L. Lintvedt, B. A. Schoenfelner, C. Ceccarelli and M. D. Glick, *Inorg. Chem., 21,* 2113 (1982); (d) *23,* (1984).

18 E. J. Bowen and J. Sahu, *J. Phys. Chem., 63,* 4 (1959).

19 C. A. Bignozzi, S. Roffia and F. Scandola, *J. Am. Chem. Soc., 107,* 1044 (1985).