Table III. Interatomic Distances (Å) and Bond Angles (deg) for Non-Hydrogen Atoms in $Cu(C_{18}N_3H_{12})Cl$[a]

Interatomic Distances			
Cu-Cl	2.235 (7)	Cu-N2	1.935 (2)
Cu-N1	1.982 (2)	Cu-N3	1.985 (2)
N1-C1	1.325 (3)	N3-C18	1.332 (3)
N1-C5	1.365 (3)	N3-C15	1.366 (3)
N2-C9	1.373 (3)	N2-C10	1.381 (3)
C1-C2	1.387 (4)	C18-C17	1.387 (4)
C2-C3	1.348 (4)	C17-C16	1.353 (5)
C3-C4	1.404 (4)	C16-C14	1.403 (4)
C4-C5	1.411 (3)	C14-C15	1.414 (3)
C4-C6	1.418 (4)	C14-C13	1.407 (4)
C6-C7	1.355 (4)	C13-C12	1.355 (5)
C7-C8	1.402 (4)	C12-C11	1.405 (4)
C8-C9	1.387 (4)	C11-C10	1.373 (4)
C5-C9	1.435 (3)	C15-C10	1.436 (3)
Bond Angles			
Cl-Cu-N1	96.4 (1)	Cl-Cu-N3	98.0 (1)
N1-Cu-N2	82.6 (1)	N3-Cu-N2	82.9 (1)
Cl-Cu-N2	175.4 (1)	N1-Cu-N3	165.2 (1)
Cu-N1-C1	128.6 (2)	Cu-N3-C18	129.0 (2)
Cu-N1-C5	112.0 (1)	Cu-N3-C15	112.1 (1)
C1-N1-C5	119.3 (2)	C18-N3-C15	118.9 (2)
Cu-N2-C9	115.4 (1)	Cu-N2-C10	114.9 (1)
C9-N2-C10	128.6 (2)		
N1-C1-C2	122.4 (2)	N3-C18-C17	122.3 (3)
C1-C2-C3	119.4 (3)	C18-C17-C16	119.7 (3)
C2-C3-C4	120.5 (2)	C17-C16-C14	120.4 (3)
C3-C4-C5	117.3 (2)	C16-C14-C15	117.2 (2)
C3-C4-C6	124.2 (2)	C16-C14-C13	124.2 (3)
C5-C4-C6	118.4 (2)	C15-C14-C13	118.6 (2)
N1-C5-C4	121.0 (2)	N3-C15-C14	121.5 (2)
N1-C5-C9	116.7 (2)	N3-C15-C10	116.6 (2)
C9-C5-C4	122.3 (2)	C10-C15-C14	121.9 (2)
C4-C6-C7	119.0 (2)	C14-C13-C12	119.3 (3)
C6-C7-C8	122.8 (3)	C13-C12-C11	122.2 (3)
C7-C8-C9	121.1 (2)	C12-C11-C10	121.6 (3)
C8-C9-C5	116.2 (2)	C11-C10-C15	116.4 (2)
C8-C9-N2	130.9 (2)	C11-C10-N2	130.3 (2)
C5-C9-N2	113.0 (2)	C15-C10-N2	113.3 (2)

[a] The esd's given in parentheses for the interatomic separations and bond angles were calculated from the standard errors in the fractional coordinates of the corresponding atomic positions.

in the opposite direction by 0.074 Å.

The Cu-ionized amine bond (Cu-N2) distance (1.935 (2) Å) is 0.05 Å shorter than the Cu-quinoline N bond distances. Since the Cu-pyridine N bond distance[9] in (2,6-diacetylpyridine dioxime)copper(II) chloride (1.932 (3) Å) is similar to that of $Cu-N_2$ in $[Cu(H_{-1}DQA)Cl]$, doubt is cast on whether the short bond distance is due to the increased basicity of an ionized amine group. Both ligands, $H_{-1}DQA$ and $DAPDH_2$, are prevented on the basis of steric requirements from bonding to Cu(II) with ideal N-Cu-N bond angles of 90°. In order to position the terminal N donors for optimal bonding, the copper ion is drawn more closely to the central N donor than in the absence of these steric constraints. As a result in $Cu(H_{-1}DQA)Cl$, the C9-N2-C10 bond angle of the tridentate ligand is significantly greater than 120° and is accompanied by internal N-Cu-N bond angles (N1-Cu-N2, 82.6 (1)°; N2-Cu-N3, 82.9 (1)°) that are substantially less than 90°.

Kinetic Implications. The Cu-Cl bond length in $[Cu(H_{-1}DQA)Cl]$ is typical of those found in a wide variety of Cu(II) complexes. Since there is no lengthening of the Cu-Cl bond trans to an ionized amine group it appears that any increase of lability of the chloride ion should not reside in a ground state effect. Since Sargeson's experiment[6] clearly showed that there is no π-stabilization of the transition state and/or intermediate and these data indicate no Cu-Cl bond lengthening, it appears that the high basicity of the ionized amine group would apparently be involved in stabilizing the transition state and/or intermediate of reduced coordination number (eq 4), a necessary feature of the S_N1CB mechanism.

The ability of strong σ-donors to induce stereochemical changes in metal chelates is well documented. Upon ionization of peptide or amide protons in Ni(II) complexes containing polypeptide or polyamide ligands, Ni(II) undergoes a change from an octahedral to a square-planar geometry.[11,12] Similarly, Zn(II) has been proposed to undergo an octahedral to tetrahedral stereochemical change upon amide proton ionization in a Zn(II) chelate.[13] Furthermore, weak σ-donors usually yield octahedral O_h Zn(II) complexes in aqueous solution (H_2O, Cl^-) while strong σ-donors often yield tetrahedral Zn(II) complexes (CN^-).[14] In the latter case, since ligand field effects can be ruled out in a d^{10} system, the increased acidity of a tetrahedral site compared to that of an octahedral one is apparently the driving force for the stereochemical change.[13] Therefore, our current models for substrate release at metalloenzymes centers continue to be in agreement with the features generally attributed to an S_N1CB mechanism.

Acknowledgment. Computer time for the structural refinement and analysis of the X-ray diffraction data was provided by the West Virginia Network for Educational Telecomputing.

Registry No. DQA, 88783-63-5; $[Cu(H_{-1}DQA)Cl]$, 104035-43-0; 8-aminoquinoline, 578-66-5; 8-hydroxyquinoline, 148-24-3.

Supplementary Material Available: Tables of refined thermal parameters, hydrogen bond distances and angles, and pertinent least-squares planes (3 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Physical and Chemical Quenching of Excited Uranyl Ion by Dialkyl Sulfides

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A recent paper[1] has dealt with the photochemical reduction of uranyl ion by several dialkyl sulfides. The results described therein intrigued us because (i) we had been working on a closely similar study, which formed the basis of our contribution to a recent Faraday Discussion,[2] (ii) there is a major disagreement concerning the magnitudes of the quantum yields for U(IV) production for the group of compounds in general and for di-*n*-butyl sulfide in particular (see Table I), and (iii) we have ESR evidence for the intermediacy of semioxidized substrate with a sulfur-centered singly occupied molecular orbital in several but not all cases,[2-4] which conflicts with the oxygen atom transfer mechanism proposed in ref 1. Concentrating on point ii, we note there is a possibly significant difference in methodology between the actinometric techniques of Sandhu et al.[5] and ourselves in that whereas the former group use a very broad band of irradiation wavelengths, i.e. the output of a 125-W medium-pressure Hg lamp filtered through Pyrex (the reaction vessel), which is both polychromatic and more intense, we use the output of a current-stabilized 200-W medium-pressure Xe/Hg lamp filtered through a Balzer metal interference filter ($\lambda_{transmitted} = 401 \pm 20$ nm). Both groups use

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Table I. Quantum Yields for U(IV) Formation in the Photooxidation of Dialkyl Sulfides (R_2S):[a] Comparison of Data from Ref 1 and 2

R_2S	[R_2S], M	irrad wavelength, nm	ϕ[U(IV)]	ref
$(C_2H_5)_2S$	0.0100	>300	0.20	1
$(n\text{-}C_3H_7)_2S$	0.0100	>300	0.49	1
$(n\text{-}C_4H_9)_2S$	0.0100	>300	0.69	1
$(n\text{-}C_4H_9)_2S$	0.200	401 ± 20	0.023	2
1,3-dithiane	0.100	401 ± 20	0.011	2
$(CH_2)_5S$	0.200	401 ± 20	0.067	2
$(CH_2)_4S$	0.200	401 ± 20	0.037	2

[a] Conditions: ref 1, [U(VI)] (as acetate) = 0.005 M, [H_3O^+] = 0.10 M, T = 30 °C ([U(VI)] = 0.0075 M for Et_2S experiment); ref 2, [U(VI)] (as nitrate) = 0.08 M, [$HClO_4$] = 0.30 M, T = 21 °C (nominal).

Table II. Quantum Yields for U(IV) Formation in the Photooxidation of Dialkyl Sulfides (R_2S): Effect of Irradiation Wavelength and Bandwidth

R	[R_2S], M	irrad wavelength, nm	ϕ[U(IV)]
	(a) Uranyl Acetate as Oxidant[a,b]		
C_2H_5	0.01	401 ± 20	0.039[b,c]
		>300	0.033[b,c]
$n\text{-}C_4H_9$	0.01	401 ± 20	0.046[b,c]
		>300	0.036[b,c]
	(b) Uranyl Nitrate as Oxidant		
$n\text{-}C_4H_9$	0.01	401 ± 20	0.051[b,d]
	0.01	>300	0.043[b,d]
	0.01	401 ± 20	0.019[c,e]
$n\text{-}C_3H_7$	0.01	401 ± 20	0.0215[c,e]
C_2H_5	0.01	401 ± 20	0.0240[c,e]

[a] Under the greater light intensity, the reaction mixture *without* R_2S gave small yields of U(IV), but not with simple zero-order kinetics. We associate this with the photooxidation of the acetate ligands. [b] [U(VI)] = 0.05 M, medium 3:4 v/v aqueous H_2SO_4 (0.1 M)-acetone, T = 25 °C. [c] Actinometry with ferrioxalate. [d] Actinometry by comparison with development of U(IV) in a uranyl sulfate (0.05 M)-ethanol (1.5 M) mixture in aqueous H_2SO_4 (3.00 M) with an independently determined quantum yield for U(IV) of 0.655. [e] [U(VI)] = 0.08 M, medium 75%:25% $MeCN\text{-}H_2O$ (v/v), [$HClO_4$] = 0.1 M, T = 20 °C.

ferrioxalate actinometry. In order to ascertain whether the origin of the discrepancy lies in the conditions of irradiation, we photoirradiated R_2S (R = Et, n-Bu) under two very different radiation bandwidths with results summarized in Table II. From this it appears that the difference does *not* lie in questions of intensity, position, or bandwidth of absorbed radiation nor in the choice of uranium (VI) salt or solvent, but rather there is simply a large discrepancy between our results and those of ref 1.

To test the question further, we have made a comparison of our quantum yields for production of U(IV) from the disulfides with those obtained during photoreduction of ethanol, for which there is a generally agreed figure of ca. 0.6 (Bell and Billings give 0.603 ± 0.037 at 25 °C for 476.5-nm argon ion laser irradiation,[6] Kireeva et al. give ca. 0.6 at 20 °C (extrapolated figure) for 410-nm radiation but ~0.3 for polychromatic light,[7] Zheng et al. give 0.69 ± 0.03 for 441.6-nm radiation (Cd/He laser)[8]). Our own figure is 0.65_5 for 401-nm irradiation, with [EtOH] = 1.5 M, [UO_2^{2+}] = 0.0648 M, and [H_2SO_4] = 3.0 M. As can be seen from Figure 1, the ratio of *relative* yields of U(IV) production, under identical actinometric conditions with λ_{irr} = 401 ± 20 nm, for di-n-butyl sulfide and ethanol is 0.077:1, which implies a quantum yield for U(IV) in the case of di-n-butyl sulfide of 0.051, in good agreement with our figure of 0.046 given in Table II, obtained by using ferrioxalate actinometry. The analogous relative yields using Pyrex-filtered light (Figure 2) yield ϕ[U(IV)] = 0.043. The use of ferrioxalate actinometry for "white light" irradiation is doubtful as the action spectra of the actinometer and the uranyl solutions need to match exactly. However, an approximate figure can be arrived at, which in our case was 0.036 for di-n-butyl sulfide. From the general consistency of our results, using different bandwidths, U(VI) salts, and actinometric procedures, we conclude that, for di-n-butyl sulfide at least, the quantum yield reported by Sandhu, Kohli, and Brar[1] is erroneously high.

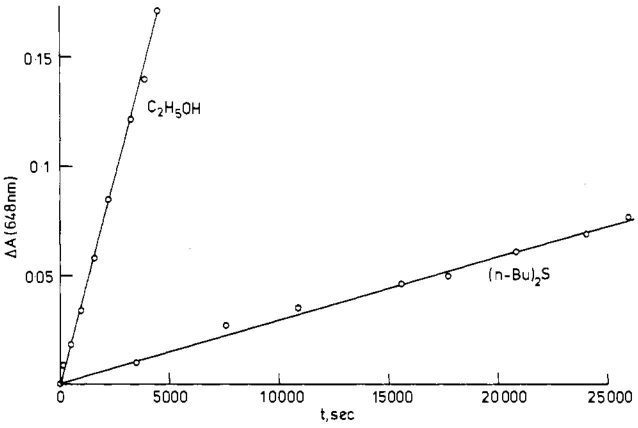

Figure 1. Development of absorbance of U(IV) at 648 nm during monochromatic (401 ± 20 nm) photolysis of N_2-flushed acidic U(VI) solutions (0.05 M) containing ethanol (1.5 M) and di-n-butyl sulfide (0.01 M). Media: ethanol experiment, aqueous H_2SO_4 (3 M) containing uranyl sulfate; di-n-butyl sulfide experiment, 3:4 v/v aqueous H_2SO_4 (0.1 M)-acetone containing uranyl acetate. Cells: 5 cm path length.

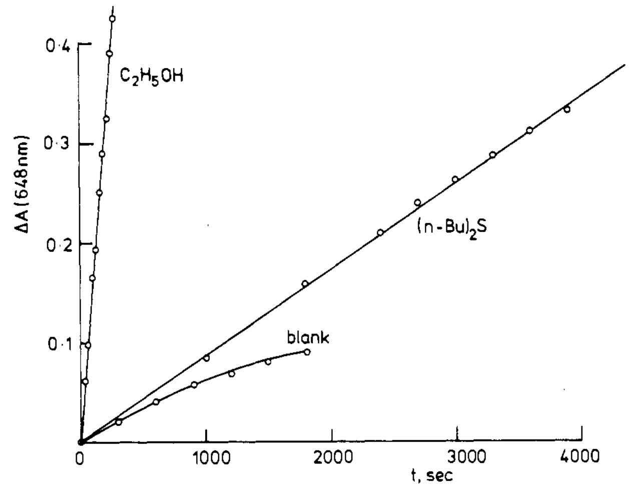

Figure 2. Development of absorbance of U(IV) at 648 nm during broad-band (λ > 300 nm) photolysis of N_2-flushed acidic U(VI) solutions (0.05 M) containing ethanol (1.5 M) and di-n-butyl sulfide (0.01 M). Media and cells are as for Figure 1.

Table III. Quantum Yields for U(IV) Formation in the Photooxidation of Di-n-butyl Sulfide: Effect of Substrate Concentration[a]

[$n\text{-}Bu_2S$], M	ϕ[U(IV)]	[$n\text{-}Bu_2S$], M	ϕ[U(IV)]
0.0050	0.0182	0.0133	0.0210
0.0075	0.0187	0.0150	0.0215
0.0100	0.0192	0.0175	0.0237
0.0125	0.0194	0.0190	0.0250

[a] [$UO_2(NO_3)_2$] = 0.08 M, [$HClO_4$] = 0.1 M, solvent 75%:25% $MeCN\text{-}H_2O$ (v/v), λ = 401 ± 20 nm, T = 20 °C.

We measured ϕ[U(IV)] for the other dialkyl sulfides investigated in ref 1, and the results are summarized in Table II. Our values of ϕ[U(IV)] for R = Et and n-Pr are similar to that for R = n-Bu, i.e. much lower than those reported in ref 1 of up to 0.23 and 0.58 for R = Et and n-Pr, respectively.

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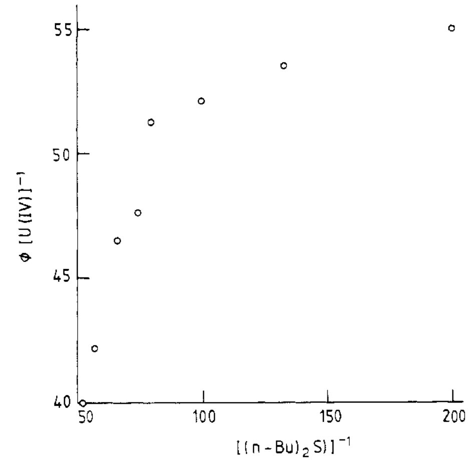

Figure 3. Double-reciprocal plot for the dependence of the quantum yield of U(IV) production upon the concentration of di-*n*-butyl sulfide (cf. eq 8). Data were taken from Table III.

We also measured $\phi[\mathrm{U(IV)}]$ for di-*n*-butyl sulfide over a wide concentration range of sulfide (Table III). While $\phi[\mathrm{U(IV)}]$ increases with $[n\text{-}\mathrm{Bu_2S}]$ (Table III), the double reciprocal plot (Figure 3) is nonlinear. This contrasts with the plots given in ref 1 and is unusual for U(VI) photosystems where such linearity is common.[9] We conclude that the simple kinetic schemes, eq 1–7,

$$[\mathrm{UO_2}^{2+}] \xrightarrow{h\nu} [\mathrm{UO_2}^{2+}]^* \quad (1)$$

$$[\mathrm{UO_2}^{2+}]^* \xrightarrow{k_2} [\mathrm{UO_2}^{2+}] + h\nu \quad (2)$$

$$[\mathrm{UO_2}^{2+}]^* \xrightarrow{k_3} [\mathrm{UO_2}^{2+}] \quad (3)$$

$$[\mathrm{UO_2}^{2+}]^* + \mathrm{R_2S} \xrightleftharpoons[k_{-4}]{k_4} [\mathrm{UO_2}^{2+}\cdot\mathrm{R_2S}]^* \quad (4)$$

$$[\mathrm{UO_2}^{2+}\cdot\mathrm{R_2S}]^* \xrightarrow{k_5} \mathrm{UO_2}^{2+} + \mathrm{R_2S} \quad (5)$$

$$[\mathrm{UO_2}^{2+}\cdot\mathrm{R_2S}]^* \xrightleftharpoons[k_{-6}]{k_6} \mathrm{UO_2}^{+} + \mathrm{R_2S}^{\cdot+} \quad (6)$$

$$2\mathrm{UO_2}^{+} \xrightarrow{k_7} \mathrm{UO_2}^{2+} + \mathrm{U(IV)} \quad (7)$$

normally operating in these systems do not hold for $\mathrm{R_2S}$; in particular, the normal practice of regarding step k_{-4} as negligible is probably incorrect in this case. The steady-state approximation leads to

$$\frac{1}{\phi[\mathrm{U(IV)}]} = \left(2 + 2\frac{k_5}{k_6}\right)\{1 + (k_{-4}[\mathrm{R_2S}] + k_2 + k_3)/(k_4[\mathrm{R_2S}])\} \quad (8)$$

and only if k_{-4} is set to zero does the plot of $\phi[\mathrm{U(IV)}]^{-1}$ vs. $[\mathrm{R_2S}]^{-1}$ become linear.

Another point refers to the "second-order rate constants" detailed in ref 1 (Tables II and III). These are not, we believe, true rate constants but appear to be derived from dividing pseudo-first-order rate constants for appearance of U(IV) by the disulfide concentration. The Stern–Volmer constant for quenching of $[\mathrm{U(VI)}]^*$ as the acetate salt by di-*n*-propyl sulfide is given in ref 1 as 780 $\mathrm{M^{-1}}$, which, taking $\tau[\mathrm{U(VI)}]^*$ under exactly these conditions as 3.46 μs,[4] yields k_2 for the second-order rate constant as 0.225×10^9 $\mathrm{M^{-1}\ s^{-1}}$, which accords roughly (bearing in mind the different U(VI) salts employed) with the figure of $(1.41 \pm 0.06) \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$ obtained directly from laser flash-photolysis measurements for di-*n*-butyl sulfide made by using the nitrate salt (see below).[2] It has no relation to the figure of 1.240 $\mathrm{M^{-1}\ min^{-1}}$ given for di-*n*-propyl sulfide in Table III of ref 1.

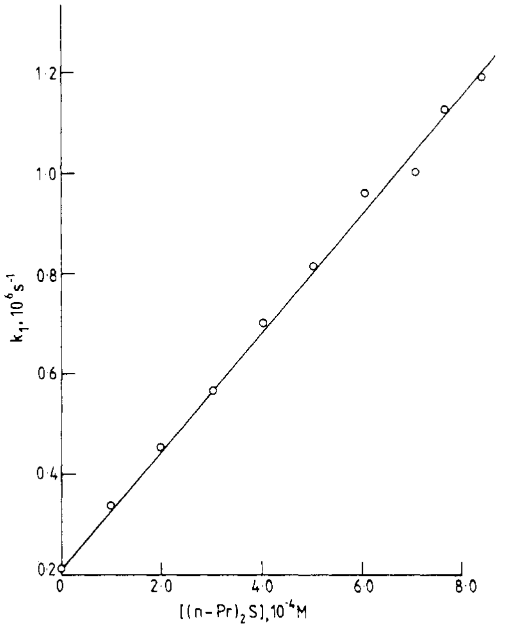

Figure 4. Dependence of reciprocal luminescence lifetime ($k_1 = 1/\tau_1$) of uranyl ion upon the concentration of di-*n*-propyl sulfide: $[\mathrm{UO_2(NO_3)_2}] = 0.1$ M, $[\mathrm{HClO_4}] = 0.1$ M, solvent 75%:25% $\mathrm{MeCN{-}H_2O}$.

Table IV. Absolute Second-Order Rate Constants for the Quenching of Uranyl Luminescence by Dialkyl Sulfides ($\mathrm{R_2S}$) by Laser Flash Photolysis[a]

R	$10^{-9}k_2$, $\mathrm{M^{-1}\ s^{-1}}$	R	$10^{-9}k_2$, $\mathrm{M^{-1}\ s^{-1}}$
Me	4.11 ± 0.11	*n*-Pr	1.16 ± 0.03[b]
Et	1.68 ± 0.09	*n*-Bu	0.956 ± 0.054

[a] $[\mathrm{UO_2(NO_3)_2}] = 0.1$ M, $[\mathrm{HClO_4}] = 0.1$ M, solvent 75%:25% $\mathrm{MeCN{-}H_2O}$. [b] Reference 2 gives $(1.41 \pm 0.06) \times 10^9$ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ in acetone–water medium.

Table V. Stern–Volmer Constants for the Quenching of Uranyl Luminescence by Dialkyl Sulfides ($\mathrm{R_2S}$) Obtained by Using Fluorometry[a]

R	K^{SV}, $\mathrm{M^{-1}}$	$10^{-9}k_2$,[b] $\mathrm{M^{-1}\ s^{-1}}$
Me	$(3.72 \pm 0.13) \times 10^4$	8.65
Et	$(3.24 \pm 0.07) \times 10^4$[c]	7.53
n-Pr	$(1.105 \pm 0.11) \times 10^4$[d]	2.57
n-Bu	$(6.74 \pm 0.09) \times 10^3$	1.57

[a] $[\mathrm{UO_2(NO_3)_2}] = 0.1$ M, $[\mathrm{HClO_4}] = 0.1$ M, solvent 75%:25% $\mathrm{MeCN{-}H_2O}$ $\lambda_{\mathrm{exc}} = 410 \pm 10$ nm, $\lambda_{\mathrm{em}} = 510 \pm 10$ nm. [b] Taking $\tau_0 = 4.30$ μs. [c] Reference 1 gives 1.367×10^3 $\mathrm{M^{-1}}$ in acetone–water, which, taking $\tau_0 = 3.46$ μs, yields $k_2 = 0.395 \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$. [d] Reference 1 gives 7.80×10^2 $\mathrm{M^{-1}}$ in acetone–water, which, taking $\tau_0 = 3.46$ μs, yields $k_2 = 0.225 \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$.

We have measured absolute quenching rate constants of excited U(VI) nitrate by $\mathrm{R_2S}$ (R = Me, Et, *n*-Pr, *n*-Bu) using 353-nm laser flash photolysis ($\mathrm{Xe/F_2}$ excimer laser, 15-ns pulse), employing what we believe to be the most photoinert medium capable of dissolving $\mathrm{R_2S}$, namely 75%:25% $\mathrm{MeCN{-}H_2O}$ (v/v). A typical plot is shown in Figure 4 and the results are summarized in Table IV. We also measured the Stern–Volmer constants for $\mathrm{R_2S}$ in the same medium, and these are summarized in Table V, while a typical plot is given in Figure 5. The Stern–Volmer constants K^{SV} are equal to $k_q\tau_0$ (k_q is the quenching rate constant and τ_0 is the lifetime of $[\mathrm{UO_2}^{2+}]^*$ under the conditions of the experiment). For the solvent system $\mathrm{MeCN{-}H_2O}$, τ_0 was determined at 4.30 μs, and the resulting values of k_q are given in Table V. These uniformly exceed those measured directly by laser photolysis, indicating some contribution from static quenching.

The considerably lower values of K^{SV} given in ref 1 originate from two possible causes, i.e. shorter lifetimes τ_0 and lower kinetic quenching constants, k_2. We determined the value of τ_0 for U(VI)

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[9] Burrows, H. D.; Kemp, T. J. *Chem. Soc. Rev.* **1974**, *3*, 139.

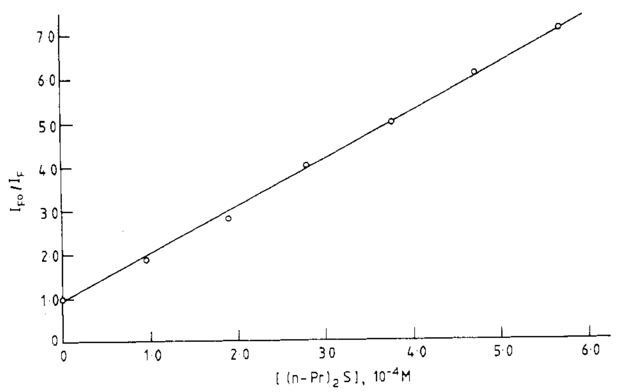

Figure 5. Stern–Volmer plot for the quenching of the luminescence intensity of uranyl ion by di-*n*-propyl sulfide: $[UO_2(NO_3)_2]$ = 0.05 M, $[HClO_4]$ = 0.1 M, λ_{exc} = 410 ± 10 nm, λ_{em} = 510 ± 10 nm, solvent 75%:25% MeCN–H_2O.

acetate in 0.1 M sulfuric acid as 3.46 μs, which implies a second-order quenching rate constant of 0.225×10^9 M^{-1} s^{-1}, i.e. rather lower than our values given in Table V. Accordingly we have measured K^{SV} for the quenching of excited [U(VI)] acetate (0.02 M) in dilute H_2SO_4 (0.1 M) in a water–acetone medium (3:4 v/v) by di-*n*-butyl sulfide as 1402 ± 20 M^{-1}, in fair agreement with the figures for other R_2S compounds given in ref 1; i.e., the use of acetate salt gives a ca. factor of 5 reduction in K^{SV} compared with the value for the nitrate salt. Finally we determined the absolute second-order quenching rate constant for quenching of $[U(VI)]^*$ in this same system as $(3.10 \pm 0.53) \times 10^8$ M^{-1} s^{-1}; i.e., the excited U(VI) acetate is only one-third as reactive as the excited nitrate salt (cf. Table IV).

Clearly there are some unusual features associated with the quenching by R_2S of $[UO_2^{2+}]^*$; thus a large kinetic quenching rate constant, nearing the diffusion-control limit of ca 1.8×10^{10} dm^3 mol^{-1} s^{-1} is *not* matched by a large photoredox quantum yield, implying that the vast majority of exciplexes $[R_2S{\cdot}UO_2^{2+}]^*$ decay by nonchemical pathways, particularly those described by k_5 and k_{-4} in the reaction scheme.

In summary, we support the values given in ref 1 for K^{SV}, we note a marked difference in kinetic reactivity toward R_2S between excited uranium(VI) nitrate and acetate, and we believe the quantum yields for U(IV) production in ref 1 are erroneously high.

Registry No. $(n\text{-}C_4H_9)_2S$, 544-40-1; $(n\text{-}C_3H_7)_2S$, 111-47-7; $(CH_3)_2S$, 75-18-3; $(C_2H_5)_2S$, 352-93-2; uranyl acetate, 541-09-3; uranyl nitrate, 10102-06-4.

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Strongly Luminescing Ruthenium(II)/Ruthenium(II) and Ruthenium(II)/Platinum(II) Binuclear Complexes

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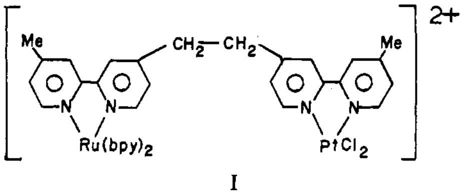
One goal in our laboratories is to prepare and characterize binuclear and oligonuclear multielectron-transfer agents designed for both light sensitivity and catalytic activity. The importance of multielectron-transfer agents can be illustrated by considering the photochemical "splitting" of water. Both $Ru(bpy)_3^{2+}$,[1-3] where bpy is 2,2′-bipyridine, and metalloporphyrins[4-6] have been suggested or used as photocatalysts for this process. Unfortunately, these compounds transfer only one electron from the excited-state upon visible-light absorpton, which causes problems mechanistically in their use for the reduction or oxidation of substrates. As a step toward overcoming this dilemma, two strongly luminescing complexes have been prepared and characterized. The one is a ruthenium(II)/ruthenium(II) homobinuclear complex; the other is a ruthenium(II)/platinum(II) heterobinuclear complex. The heterobinuclear complex is shown in I for illustrative purposes.



I

The important structural feature of the complex is the novel 4,4′-dimethyl-2,2′-bipyridine dimer, Mebpy–Mebpy,[7] which provides two bidentate sites for coordination. The mononuclear ruthenium(II), the binuclear ruthenium(II)/ruthenium(II), and heterobinuclear ruthenium(II)/platinum(II) complexes were isolated as described below. The yellow mononuclear dichloroplatinum(II) and binuclear bis(dichlorplatinum(II)) analogues were also prepared but were too insoluble for characterization studies.

The ligand, Mebpy–Mebpy, was prepared by an adaptation of the procedure of Elliott and co-workers.[7] Purification of the crude product was achieved through several recrystallizations from toluene, which resulted in a final yield of ~60%. The purity of the product was checked by melting point (186–188 °C), mass spectrometry, and NMR spectroscopy.

The preparative procedure for $[Ru(bpy)_2(Mebpy\text{–}Mebpy)](CF_3SO_3)_2$[8] involved substitution of acetone for chloride ion in the coordination sphere of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (0.2 mmol) by reaction with $Ag(CF_3SO_3)$ (0.40 mmol) in 80 mL of acetone.[9] The AgCl that formed was removed by filtration, and the brownish red filtrate was added drop by drop (1 drop/10 s) to a refluxing solution of 0.80 g (2.2 mmol) of Mebpy–Mebpy dissolved in 1500 mL of acetone contained in a 3-L round-bottom flask. The resulting bright orange solution, which luminesced very strongly under UV light, was allowed to reflux for 30 min after the last addition (total addition time was about 8 h). The crude product was isolated by reducing the solvent volume to ~20 mL with a rotary evaporator and precipitating the product by the addition of the concentrated solution to ether. The complex was purified by column chromatography (neutral alumina developed with acetone). The middle fraction was precipitated in 60% yield, filtered out under nitrogen in Schlenkware, and dried under vacuum.

$[(bpy)_2Ru(Mebpy\text{–}Mebpy)Ru(bpy)_2](CF_3SO_3)_4$[8] was prepared by the same procedure as the mononuclear species except the reactants were mixed in stoichiometric amounts and the reaction was allowed to reflux for 5 days. The pure binuclear complex was obtained in 81% yield.

The preparation of $[(bpy)_2Ru(Mebpy\text{–}Mebpy)PtCl_2](PF_6)_2{\cdot}2H_2O$[8] was effected in the dark. A 0.065-g (0.15-mmol) sample of *cis*-$[Pt(Me_2SO)_2Cl_2]$[10] was suspended in 75 mL of methanol

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(8) Anal. Calcd for $[Ru(bpy)_2(Mebpy\text{–}Mebpy)](CF_3SO_3)_2$: C, 51.25; H, 3.55; N, 10.39. Found: C, 51.17; H, 3.73; N, 10.33. Calcd for $[(bpy)_2Ru(Mebpy\text{–}Mebpy)Ru(bpy)_2](CF_3SO_3)_4$: C, 45.64; H, 3.04; N, 9.39. Found: C, 45.50; H, 3.27; N, 9.34. Calcd for $[Ru(bpy)_2(Mebpy\text{–}Mebpy)PtCl_2](PF_6)_2{\cdot}2H_2O$: C, 38.52; H, 3.09; N, 8.17; Cl, 5.17. Found: C, 38.58; H, 3.06; N, 8.18; Cl, 5.23.

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