assures electron density overlap. Further theoretical interpretation and clarification of the role of counterions in the rearrangement of **1a** and related systems[19] are needed.

Acknowledgment. We thank Dr. Paul Schleyer for helpful comments.

References and Notes

(1) For a full account see R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970; *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(2) (a) N. D. Epiotis, *Angew. Chem., Int. Ed. Engl.*, **13**, 751 (1974), especially ref 2–9; (b) D. M. Silver, *J. Am. Chem. Soc.*, **96**, 5959 (1974).

(3) J. A. Berson and L. Salem, *J. Am. Chem. Soc.*, **96**, 9107 (1972).

(4) M. S. Dewar and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, 1939 (1974).

(5) Similar but less dramatic facilitation of sigmatropic rearrangement by amine substituents has been reported: (a) R. Scheidt and W. Kirmse, *J. Chem. Soc., Chem. Commun.*, 716 (1972); (b) J. Brown and M. M. Ogilvy, *J. Am. Chem. Soc.*, **96**, 292 (1974); (c) A. P. TerBorg, E. Razenberg, and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **84**, 1230 (1965).

(6) For an excellent bibliography of 1,3-sigmatropic shifts, see R. K. Lustgarten and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **96**, 6393 (1974), especially ref 54–56, 80–84.

(7) G. Krow and J. Reilly, *J. Org. Chem.*, **40**, 136 (1975).

(8) Amines **1a**[9] or **2a** and ethyl chloroformate afforded urethanes **1d** and **2d**.

(9) L. A. Paquette, J. Malpass, G. Krow, and T. Barton, *J. Am. Chem. Soc.*, **91**, 5296 (1969).

(10) Various XF-1150 and SF-96 on Chrom G columns were used with complete rearrangement irrespective of column. Some catalysis occurs during GLPC, since when **1a** was passed through an acid-washed glass-bead-filled quartz tube at 420° (0.25 mm) only 20% rearrangement of **1a** to **2a** resulted. Above 500° the amines decomposed. Unsuccessful thermal rearrangement of *N*-benzylamine **1b** by GLPC at increasing temperatures ultimately resulted only in decomposition.

(11) The structure of amine **2a** was confirmed by lithium aluminum hydride reduction of its benzoylamide **2e** to *N*-benzylamine **2b**.[7]

(12) Attempts to measure the rate of rearrangement by ^{1}H NMR were unsuccessful. When an NMR tube containing **1a** and methyllithium in ether was brought from −76° to 20° the spectrum remained unchanged. Above 30° the sample exploded.

(13) Deuterated *N*-benzylamine **1b** was synthesized as previously,[7] but substituting sodium borodeuteride for sodium borohydride. The benzyl group was cleaved[14] from **1b** using phenyl chloroformate (12 hr, $CHCl_3$, 80% yield) to afford **1c**. The carbamate was cleaved with excess methyllithium (8 hr, 4°, 20%) to give amine **1a**. Despite the rapidity of the room temperature reaction of **1a** with methyllithium no rearrangement to **2a** occurred under the cleavage conditions.

(14) J. D. Hobson and J. G. McCluskey, *J. Chem. Soc. C*, 2015 (1967).

(15) (a) A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Lett.*, 233 (1964); (b) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969); (c) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(16) Reversible allylic Grignard addition to ketones is known.[17] We observed no trapping by methyl- or phenyllithium (35°) of the imine formally formed by ring opening of **1a** anion. After 4 hr polymerization occurred by some pathway.

(17) R. A. Benkeser and W. E. Broxterman, *J. Am. Chem. Soc.*, **91**, 5162 (1969).

(18) For the importance of overlap of the nonbonding electrons on nitrogen during a solvolysis, see P. G. Gassman, R. L. Cryberg, and K. Shudo, *J. Amer. Chem. Soc.*, **94**, 7600 (1972).

(19) (a) Acid catalyzed facilitation of a 1,3-shift has been reported without stereochemical details: B. Miller, *J. Am. Chem. Soc.*, **96**, 7155 (1974); (b) G. A. Russell and K. Schmitt, *ibid.*, **94**, 8918 (1972), report a facile 1,3-shift in a semidione.

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Luminescent Osmium(II) and Iridium(III) Complexes as Photosensitizers

Sir:

The luminescent transition metal complexes $Ru(bipy)_3{}^{2+}$, $Ru(bipy)_2(CN)_2$, $Ru(phen)_3{}^{2+}$, and $Ru(phen)_2(CN)_2$ (bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline) have been widely used as a versatile new class of photosensitizers.[1-12] Although possessing nearly ideal sensitizer properties, including intense fluid solution emissions, applications have been seriously restricted by their narrow range of donor energies (~18–19 kK) and excited-state reduction potentials. We report here the first successful use of highly luminescent Ir(III) and Os(II) complexes as photosensitizers. These complexes enormously increase the range of donor energies available (~15–23 kK) and roughly double the available number of luminescent transition-metal complex photosensitizers. A correspondingly wide range in the reducing power of the excited states is also expected.

Table I. Optical Properties of Os(II) and Ir(III) Photosensitizers in Methanol at ~21°

Complex[a]	E_0, kK	τ_0, μsec[b]
$Os(bipy)_3{}^{2+}$	14.9	0.049
$Os(phen)_3{}^{2+}$	15.3	0.183
$Os(phen)_2(Ph_2phen)^{2+}$	15.0	0.212
$Os(phen)_2[(SO_3Ph)_2phen]$	14.8	0.093
$Ir(bipy)_3{}^{3+}$	22.7	2.4
$Ir(phen)_3{}^{3+}$	22.5	2.9

[a] bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline; Ph_2phen = 4,7-diphenyl-1,10-phenanthroline; $(SO_3Ph)_2phen^{2-}$ = disulfonated 4,7-diphenyl-1,10-phenanthroline. [b] Estimated accuracy ±5%. Precision ±1%.

Table I lists two iridium and four osmium complexes which sensitize photooxygenations of organic singlet-oxygen scavengers. Also listed are the zero-point donor energies, E_0's, and the mean lifetimes in deoxygenated methanol, τ_0's, at ~21°. Using either lasers or water-filtered tungsten lamp radiation, all complexes in O_2-saturated methanol yield rapid photooxidation of tetramethylethylene and trimethylethylene. The Os(II) complexes sensitize oxidation of thiourea, but the Ir(III) complexes are strongly quenched by thiourea and yield negligible O_2 uptakes. All successful photooxidations were catalytic in complex (10–100 mol of O_2 consumed/mol of sensitizer).

With the osmium complexes, $^1O_2$ was confirmed as the reactive species by comparing the mole ratio of the two hydroperoxides formed with that obtained using $^1O_2$ (obtained by Rose Bengal sensitized photooxidation). Within experimental error (~10%), the mole ratios of the products were the same. Similar experiments with $Ir(bipy)_3{}^{3+}$ (351, 356 nm) were hampered by the photosensitivity of the complex and apparent interference of the decomposition products with our analytical procedure.[13] By analogy with the Os(II) and Ru(II) complexes, we infer, however, that energy rather than electron transfer was the dominant quenching mode in all cases.

Energy-transfer efficiencies to O_2 are high (>0.5). For example, the Os(II) complexes are more efficient $^1O_2$ generators than Methylene Blue, absorb strongly across the entire visible and near uv, and are being studied for use in chemical actinometers for high power Kr, Ar, and He-Ne lasers. There does, however, appear to be a small component of nonenergy transfer quenching by O_2 with all complexes, except perhaps the iridium ones.[13]

Unlike the Os(II) complexes which exhibit no noticeable degradation under our experimental conditions, the iridium(III) complexes are somewhat photosensitive in methanol, which somewhat restricts their usage, although in other solvents such as dimethylformamide the sensitivity may be much less.[14,15] The photosensitivity is not a serious problem, however, for many mechanistic studies where only small conversions of acceptor are needed or where quenching of the luminescence only is required to establish the presence of electron transfer or a low lying quencher state and to measure rate constants. For example, see ref 3, 4, and 10 where good data were obtained even when the donor disappeared with yields >0.1–0.5.

$Os(bipy)_3{}^{2+}$, at least in methanol, has a very short lifetime and an E_0 near that of the other Os(II) complexes. Consequently, the other Os(II) complexes are to be preferred for exploratory studies.

The Ir(phen)$_3^{3+}$ absorption and blue-green emission are similar to that of Ir(bipy)$_3^{3+}$. Both complexes can be readily pumped at higher concentrations (10^{-3} to 10^{-4} M) in the 350-360 nm region; however, pumping the much more intense $\pi \rightarrow \pi^*$ absorptions at shorter wavelength would minimize transmission corrections. The Os(II) complexes absorb intensely (ϵ >2000) across the entire visible and are readily pumped in this region as well as the uv. Their emissions are ~700 nm in fluid solutions which makes them difficult to measure on spectrofluorimeters without extended red response photomultipliers. In all cases, the E_0's are not very sensitive to changes in solvent. A 0.1-0.2 kK shift, which is within our experimental error, sometimes occurs on changing from 4:1 (v/v) ethanol-methanol glass to 4:1 (v/v) methanol-water glass.

As is characteristic of charged complexes of this type, the solubility, but not the emission properties, is affected by the counterion. The nitrate salts of the Ir(III) complexes and the chloride salts of the cationic Os(II) complexes used here are soluble in a wide variety of polar organics and water, and we recommend these as the form of choice for most solvents. The perchlorates are all of limited solubilities which would make them more difficult to use as sensitizers.

Especially noteworthy with transition-metal sensitizers is the ability to vary the donor charge and to fine tune E_0 by ligand modifications. The charge factors are especially important with ionic quenchers.

Energies of the thermally equilibrated emitting state, E_0's, were estimated from 77 K emission spectra in ethanol-methanol 4:1 (v/v) glasses using the Fleischauer criterion.[16] τ_0's were estimated using a N_2 laser system which is described elsewhere;[17] semilogarithmic plots were linear over at least 3 half-lives. Photolysis studies used Ar (488 nm at 0.1-1.5 W) and Kr (351, 356 nm at 0.1 W) lasers and water-filtered 500-W tungsten lamps. Ir(bipy)$_3^{3+}$ was synthesized as recently described,[18] and Ir(phen)$_3^{2+}$ can be prepared and purified by an analogous procedure.[15] Os(bipy)$_3^{2+}$ and Os(phen)$_3^{2+}$ can be prepared by literature methods.[19] The other two Os(II) complexes were prepared by reaction of aqueous Os(phen)$_2$Cl$_2$ with the appropriate ligand. All osmium complexes were purified by column chromatography with Sephadex LH-20 (methanol) and/or Cellex P (aqueous 0.1 F HCl).[20]

Current work is devoted to obtaining other metal complexes with a wider range of E_0's, ionic charges, and longer τ_0's. Attempts to stabilize the Ir(III) complexes by using different solvents or different ligand combinations are underway.[15]

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References and Notes

(1) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **93**, 1800 (1971).
(2) P. Natarajan and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 3635 (1972).
(3) H. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, **94**, 8238 (1972).
(4) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **95**, 5159 (1973).
(5) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974).
(6) F. Bolleta, M. Maestri, L. Moggi, and V. Balzani, *J. Am. Chem. Soc.*, **95**, 7866 (1973).
(7) J. N. Demas, D. Diemente, and E. W. Harris, *J. Am. Chem. Soc.*, **95**, 6864 (1973).
(8) J. N. Demas and J. W. Addington, *J. Am. Chem. Soc.*, **96**, 3663 (1974).
(9) J. N. Demas and J. W. Addington, submitted.
(10) G. Navon and N. Sutin, *Inorg. Chem.*, **13**, 2159 (1974).
(11) M. Wrighton and J. Markham, *J. Phys. Chem.*, **77**, 3042 (1973).
(12) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Lawrence, *Coord. Chem. Rev.*, in press.
(13) J. N. Demas, R. P. McBride, and E. W. Harris, work in progress.
(14) V. Ballardini et. al., *J. Am. Chem. Soc.*, **97**, 728 (1975).
(15) C. M. Flynn, Jr., and J. N. Demas, work in progress.
(16) P. D. Fleischauer, A. W. Adamson, and G. Sartori, *Inorg. React. Mech., Part 2*, 1 (1972).
(17) J. N. Demas and C. M. Flynn, Jr., submitted.
(18) C. M. Flynn, Jr., and J. N. Demas, *J. Am. Chem. Soc.*, **96**, 1959 (1974).
(19) (a) F. H. Burstall, F. P. Dwyer, and E. C. Gyarfas, *J. Chem. Soc.*, 953 (1950); (b) F. P. Dwyer, N. A. Gibson, and E. C. Gyarfas, *J. Proc. R. Soc. N.S.W.*, **84**, 68 (1950).
(20) J. N. Demas, M. Weiss, and D. Diemente, work in progress.

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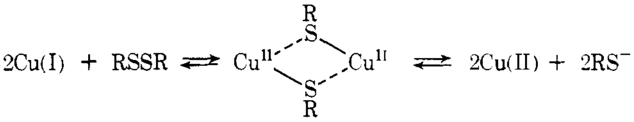
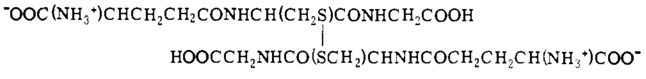
Models for the Electron Paramagnetic Resonance Nondetectable Copper in "Blue Oxidases".[1] A Binuclear Copper(II) Complex with Oxidized Glutathione

Sir:

In recent years we have studied the properties of binuclear cupric mercaptides,[2] which are formed both from Cu(II) and chelating thiols RSH (R = -CH$_2$CH$_2$NH$_2$, -C(CH$_3$)$_2$CH(COO$^-$)NH$_2$, or -CH$_2$CH(CONH$_2$)NH$_2$) or Cu(I) and the corresponding disulfides.



Generally clusters of this type can be regarded as models for the two-electron-accepting EPR-nondetectable copper pair in "Blue Oxidases",[1] which is diamagnetic in the oxidized and the reduced state. From recent results by Byers et al.[3] and Driving and Deinum,[4] it seems now quite clear that cyste(i)ne sulfur does not participate in electron transfer during the catalytic cycle but that there might be antiferromagnetic coupling between the two Cu nuclei via a coordinated but redox inactive disulfide bridge similar to the cupric mercaptide cluster mentioned above, which prompted us to reinvestigate the complexation of Cu(II) by oxidized glutathione (I, GSSG) and related compounds. According to the polarographic measurements of Li et al.,[5] GSSG only forms a 1:1 species with the metal, although theoretically it could bind two copper ions per molecule. In addition to the



$$\begin{array}{l} {}^{-}\mathrm{OOC(NH_3^{+})CHCH_2CH_2CONHCH(CH_2S)CONHCH_2COOH} \\ \qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad \mathrm{HOOCCH_2NHCO(SCH_2)CHNHCOCH_2CH_2CH(NH_3^{+})COO^{-}} \end{array}$$

I

carboxy protons of glycine, GSSG has six potentially titratable protons, four on peptide and two on amino nitrogen atoms, i.e., LH$_8$.[6] Upon pH titration of a 2:1 mixture of Cu(II) and the disulfide, precipitation of a pale blue solid occurs around pH 6, which is dissolved at pH greater than 9.5 yielding a clear violet solution with a single absorption maximum at 590 nm (ϵ 90 M^{-1} cm^{-1}). The entire process is accompanied by the liberation of four proton equivalents per Cu present. Furthermore maximum formation of the species absorbing at 590 nm is obtained at a metal:ligand