assigned to the ^{3}LE transition, because the phosphorescence of salicylideneamine coordinating to the zinc(II) ion has the 0–0 band at 22 200 cm^{-1}.[30]

Registry No. $\mathrm{Cr(acac)_3}$, 21679-31-2; $\mathrm{[Cr(acac)_2(en)]^+}$, 59220-43-8; $\mathrm{[Cr(acac)(en)_2]^{2+}}$, 71723-96-1; $\mathrm{Cr(acacCl)_3}$, 13963-55-8; $\mathrm{[Cr(acacCl)_2(en)]^+}$, 104111-08-2; $\mathrm{[Cr(acacCl)(en)_2]^{2+}}$, 104111-09-3; $\mathrm{Cr(acacBr)_3}$, 15025-13-5; $\mathrm{[Cr(acacBr)_2(en)]^+}$, 104111-10-6; $\mathrm{[Cr(acacBr)(en)_2]^{2+}}$, 104111-11-7; $\mathrm{Cr(dbm)_3}$, 21679-35-6; $\mathrm{Be(dbm)_2}$, 19368-60-6; $\mathrm{[Cr(terpy)_2]^{3+}}$, 54984-99-5; $\mathrm{[Zn(terpy)]^{2+}}$, 104035-35-0; $\mathrm{Be(acac)_2}$, 10210-64-7; $\mathrm{[Cr(bpy)_3]^{3+}}$, 15276-15-0; $\mathrm{[Rh(bpy)_3]^{3+}}$, 47780-17-6; $\mathrm{[Rh(bpy)(mal)_2]^-}$, 104035-36-1; $\mathrm{[Cr(dp\text{-}phen)_3]^{3+}}$, 69178-81-0; $\mathrm{[Zn(dp\text{-}phen)]^{2+}}$, 16561-57-2; $\mathrm{[Cr(ox)(bpy)_2]^+}$, 32629-19-9; $\mathrm{[Cr(ox)_2(bpy)]^-}$, 21748-32-3; $\mathrm{[Cr(ox)_2(en)]^-}$, 46752-51-6; Cr(PC)(OH), 15053-50-6; Pb(PC), 15187-16-3.

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Phosphorescent 8-Quinolinol Metal Chelates. Excited-State Properties and Redox Behavior

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A number of metal complexes of 8-quinolinol (QOH) of general formula $\mathrm{M(QO)}_n$ (n = 3, M = Al(III), Bi(III), Rh(III), Ir(III); n = 2, M = Pt(II), Pb(II)) have been synthesized and characterized. The heavy-metal complexes (M = Pt(II), Pb(II), Bi(III), Ir(III)) exhibit long-lived ($\tau \simeq$ 2–4 μs) phosphorescence and excited-state absorption (ESA) in fluid solution. The photophysics of these complexes (emission spectra and lifetimes, ESA spectra and lifetimes, emission quantum yields, efficiencies of formation of the long-lived state) has been studied in some detail. The long-lived emitting state is assigned as a metal-perturbed triplet state of the 8-quinolinol ligand. On the basis of their ground-state redox potentials and on their excited-state properties, the heavy-metal 8-quinolinol complexes are predicted to behave as powerful excited-state reductants (potentials in the −0.8 to −1.3 V range vs. SCE). Quenching studies verify these expectations.

Introduction

The photophysics of metal chelates has been studied quite extensively in the last two decades, following the pioneering work of Crosby and his associates.[1,2] By far, the best studied class of metal chelates is that of transition-metal polypyridine complexes, for which a variety of long-lived, often emitting, lowest excited states have been observed.[3-13] Depending on the type of metal and of polypyridine ligand, metal-centered states (also indicated as MC or d–d), metal-to-ligand charge-transfer states (also indicated as MLCT or d–π^*), or ligand-centered states (also indicated as LC or π–π^*) can be the lowest spin-forbidden state in these systems. In particular cases, even very subtle changes in the periphery of the bipyridine ligand can be sufficient to bring about a change in the type of lowest excited state ("fine tuning").[1,2,10] Aside from these intrinsic points of interest, studies on metal polypyridine complexes have received additional momentum from the discovery that some of these compounds behave as effective photosensitizers for hydrogen or oxygen generation from water.[10,14-20] A remarkable amount of work has thus been devoted to the characterization of the excited-state redox properties and of the kinetics of excited-state electron-transfer reactions of these complexes.[21-23] In all these studies, phosphorescent emission in fluid solution has been the main handle for investigating the excited-state behavior of the complexes. In some instances, excited-state absorption (ESA) has also been used for this purpose.[24-26]

Looking for new classes of redox photosensitizers, we have undertaken an investigation of the photophysical and excited-state redox behavior of 8-quinolinol (QOH) metal chelates. Many chelates of this type, of general formula $\mathrm{M(QO)}_n$ (where n equals the oxidation state of the metal M) have been known for a long time in the analytical literature (under the name of metal oxinates).[27-30] Notably, a number of analytical methods for the determination of group III (13)[89] metals are based on the formation of such species.[31] On the other hand, little attention seems to have been devoted to the synthesis and characterization of specific metal chelates, in particular of the 8-quinolinol complexes of the heaviest non transition (6s, 6p) and transition (5d, 6d)

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Table I. Photophysical Properties of 8-Quinolinol and of Metal 8-Quinolinol Complexes

	298 K, DMF									77 K, EtOH			
	abs[a]	green emission			red emission			ESA		green emission		red emission	
	λ_{max}, nm	λ_{max}, nm	τ, ns	Φ	λ_{max}, nm	τ,[b] μs	Φ[b]	τ,[b] μs	η_{isc}	λ_{max}, nm	τ, ns	λ_{max}, nm	τ, μs
QOH	314	410	1.4	3×10^{-3}[c]	...	...	...	...	<0.02[c]	430[d]	<20	...	...
QO^-	400	550	11.1	1.00[e]	...	...	...	...		485[d]	<20	...	...
QOH_2^+	363	430	<1	$<1 \times 10^{-4}$	...	...	...	...		481[d]	<20	...	...
$Al(QO)_3$	388	540	9.9	0.116[e]	...	...	...	...		475	<20	...	...
$Rh(QO)_3$	425	...	...	...	...	...	...	...		...	...	622	220
$Ir(QO)_3$	448	...	...	...	660	2.5	8.6×10^{-3}	2.3	0.8	...	...	593	10
$Pt(QO)_2$	478	...	...	...	655	2.7	9.5×10^{-3}	2.5	0.9	...	...	623	14
$Pb(QO)_2$	397	550	0.4	$\sim 3 \times 10^{-3}$	~650[f]	~3	$<1 \times 10^{-4}$	4.0	0.1	510	<20	~610	180
$Bi(QO)_3$	387	540	<0.5	$\sim 6 \times 10^{-4}$	~650[f]	~2	$<1 \times 10^{-4}$	2.7		495	<20	625	80

[a] Low-energy band. [b] Deaerated solution. [c] Reference 52. [d] Reference 34. [e] Reference 36. [f] Hidden by the tail of the green emission; spectrum obtained in time-resolved experiments.

metals. For a number of reasons (see below), these complexes are more likely than the lighter metal ones to have long-lived excited states in fluid solution, which may be observable by either phosphorescent emission or ESA. Whereas fluorescence in 8-quinolinol chelates is quite commonplace and has been studied in a number of detailed specific investigations,[32-37] phosphorescence in fluid solution has been reported for the first time in a preliminary communication of some results of this work.[38] We report here the full results of our investigation, which, after a screening of the luminescent properties of a wide series of transition-metal and non-transition-metal 8-quinolinol complexes, has concentrated on the Al(III), Rh(III), Ir(III), Pt(II), Pb(II), and Bi(III) species. The results include the characterization of the photophysics and excited-state redox properties of these complexes.

Experimental Section

Materials. Rhodium(III) chloride hydrate (Fluka), ammonium hexachloroiridate(III) (Ventron), potassium tetrachloroplatinate(II) (Fluka), 8-quinolinol (Fluka), methylviologen (Ega Chemie), tetracyanoethylene (Fluka), quinones (Fluka), and nitroaromatics (Fluka) were commercial products of reagent grade. Spectrograde organic solvents (Merck Uvasol) were used.

Syntheses. The methods used in this work for preparing the metal 8-quinolinol complexes represent variations of general procedures developed in the past.[27-29,36,39]

The 8-quinolinol complex of Al(III) has been prepared by adding to a suspension of metal hydroxide in water a slight excess of ligand in ethanol. The suspension turned yellow and was stirred for 1 h at room temperature. The precipitate was filtered, washed with 1×10^{-3} M NaOH, water/ethanol, and ethanol, and dried under vacuum.

The 8-quinolinol complexes of Rh(III), Pb(II), and Bi(III) have been obtained by adding small amounts of dilute NaOH to a stirred solution of the metal salt and 8-quinolinol (50% excess over the stoichiometric amount) in glacial acetic acid until pH 5 was reached. The precipitate was washed with dilute acetic acid and ethanol and dried under vacuum. The complexes were purified by recrystallization from methanol until the emission spectra at 77 K did not undergo appreciable changes.

The Pt(II) complex was prepared by the following method, which was found to give better yields than that reported in a previous paper.[38] To a solution of K_2PtCl_4 and ligand in a 1:5 mole ratio in glacial acetic acid were added small amounts of dilute NaOH until pH 4 was reached. The mixture was stirred and heated at about 70 °C for 1 h. The brownish orange precipitate formed after cooling of the solution was filtered, washed with dilute acetic acid, ethanol, and CH_2Cl_2, and recrystallized from DMF to give a red crystalline compound. Anal. Calcd for $Pt(QO)_2$: C, 44.7; H, 2.50; N, 5.80; Pt, 40.39. Found: C, 43.07; H, 2.27; H, 5.76; Pt, 40.40.

The Ir(III) complex was prepared by the same method as used for the Pt(II) complex, starting from $(NH_4)_3[IrCl_6]$. The compound was purified from traces of charged species by column chromatography (neutral Al_2O_3 of activity 90 from Merck, 1:100, CH_2Cl_2–MeOH, first fraction collected). Anal. Calcd for $Ir(QO)_3$: C, 51.92; H, 2.90; N, 6.73. Found: C, 51.71; H, 2.53; N, 6.50.

Apparatus and Procedures. UV–vis spectra were recorded with a Varian Cary 219 spectrophotometer. The emission spectra were measured with a Hitachi-Perkin-Elmer MPF 44E spectrofluorimeter equipped with a R 928 Hamamatsu tube and with a DCSU-2 differential corrected spectra unit. The emission lifetimes were measured with a J & K System 2000 ruby laser (Q-switched, frequency doubled, pulse half-width 20 ns) in a single-shot mode, with oscillographic recording (Tektronix 7834 oscilloscope) or with a PRA (Photochemical Research Associates, London, Ontario, Canada) System 3000 nanosecond fluorescence spectrometer equipped with a 510B nanosecond pulsed lamp and a Model 1551 cooled photomultiplier (data collected on a Tracor Northern TN-1750 multichannel analyzer and processed on a Digital PDP 11/03 computer using original PRA software). The ESA spectra and ESA lifetimes were measured by using a laser flash photolysis apparatus (Applied Photophysics detection system coupled with a J & K System 2000 ruby laser source).

In electron-transfer quenching experiments, the quantum yields of formation of transient redox products and the rate constants of the back-electron-transfer reactions were measured by laser photolysis following the procedures described in a previous paper.[40]

Low-temperature emission spectra and lifetimes were measured in clear, glass-forming solvents (vide infra) by using Oxford Instruments liquid-nitrogen DN 704 cryostatic equipment with quartz windows and standard 1-cm spectrofluorimetric cuvettes equipped with an Oxford Instruments DTC 2 temperature controller and indicator.

The cyclic voltammetry experiments were performed with an Amel Electrochemolab multipurpose apparatus, with a saturated calomel electrode (SCE) as reference electrode and a hanging mercury drop electrode (HMDE) or a stationary platinum electrode (SPE) as working electrode.

All samples for lifetime determination in fluid solutions and for quenching experiments were freeze–pump–thaw degassed prior to the experiments (five cycles at 10^{-6} torr).

Results

General Properties. All the 8-quinolinol complexes studied are neutral and dissolve rather easily in most polar organic solvents. In solution, they appear to be stable both in the dark and under room light for long periods. The only exception to this general stability is represented by $Pt(QO)_2$, which is photochemically labile in the presence of oxygen (vide infra).

The absorption spectra of the complexes in DMF are shown in Figure 1. Characteristic of all these spectra is the presence of two high-intensity bands in the near-UV–vis region. The maxima of the low-energy bands are listed for all of the complexes studied in Table I. The absorption spectra and the band maxima

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Table II. Ground- and Excited-State Redox Potentials[a]

complex (S)	$E^{0-0}(S/S^*)$,[b] eV	$E_p(S^+/S)$,[c] V	$E_p(S/S^-)$,[d] V	$^*E(S^+/S^*)$, V	$^*E(S^*/S^-)$, V
$Ir(QO)_3$	2.02	0.98	−1.75	−1.04	0.27
$Pt(QO)_2$	2.01	1.08	−1.63	−0.93	0.38
$Pb(QO)_2$	~2.0	0.70	−1.50	~−1.3	~0.5
$Bi(QO)_3$	~1.9	1.13	−1.84	~−0.8	~0.1

[a] In DMF, vs. SCE, at 25 °C. [b] From 77 K emission spectra in 9:1 DMF–CH_2Cl_2 matrix. [c] Anodic peak potential. [d] Cathodic peak potential.

for free 8-quinolinol, QOH, and its deprotonated, QO^-, and fully protonated, QOH_2^+, forms are also reported in Figure 1 and in Table I. The spectra of the $M(QO)_n$ complexes are sensitive to the solvent polarity. For example, in ethanol, a general blue shift was observed with respect to DMF (about 0.08 μm^{-1} for the low-energy bands of all the complexes).

Photophysical Behavior. The emission spectra of the Al(III), Rh(III), Ir(III), Pt(II), Pb(II), and Bi(III) complexes in absolute ethanol at 77 K are shown in Figure 2. While the emission intensities varied considerably among these complexes, the emission maxima span two distinct but rather narrow spectral ranges, i.e., 470–510 nm ("green emission") and 590–630 nm ("red emission"). In particular, the Al(III) complex only gives the green emission, the Rh(III), Ir(III), and Pt(II) complexes only give the red one, and the Pb(II) and Bi(III) complexes give both.

That the green and the red emissions actually represent two distinct types of luminescence was shown by lifetime measurements (Table I). While the green emission was invariably faster than the time resolution of the laser apparatus (<20 ns), the red luminescence was long-lived, with lifetimes in the 10^{-5}–10^{-4}-s range, typical of a phosphorescent emission.[41]

When the samples were heated to room temperature, the emission spectra remained substantially similar to the low-temperature spectra, except for a general red shift and for a more or less pronounced decrease in intensity. At room temperature negligible solvent shifts were observed in the emission spectra of all the complexes. Room-temperature data for deaerated DMF solutions are reported in Table I. The lifetimes of the green emission remained in the nanosecond range, while those of the red phosphorescence decreased, converging to values of a few microseconds (Table I). In aerated solutions, the red phosphorescence intensities and lifetimes were quenched by a factor of ca. 10 with respect to deaerated conditions.

Quantum yield values are reported in Table I for the room-temperature emissions. The values for the $Ir(QO)_3$ and $Pt(QO)_2$ phosphorescence were obtained with use of corrected emission spectra and $Ru(bpy)_3^{2+}$ ($\Phi = 0.042$)[6] as a reference emitter. For the other complexes, the values represent order-of-magnitude estimates.

Transient excited-state absorptions (ESA) were looked for in room-temperature laser flash photolysis experiments. No ESA signals were obtained with the Al(III) and Rh(III) complexes. In contrast, more or less intense ESA signals were observed for the Pb(II), Bi(III), Pt(II), and Ir(III) complexes. The experimental ESA spectra (put on an apparent[42] molar absorptivity scale by using a relative actinometric method based on the benzophenone triplet ESA[40]) are reported in Figure 3. The excited-state lifetimes measured by monitoring the decay of the ESA signals are also reported in Table I. They agree satisfactorily with the lifetimes of the red phosphorescence, indicating that the same excited state is responsible for both the phosphorescence and the ESA signal. The oxygen effect on ESA lifetimes was the same as observed for the phosphorescence lifetimes and intensities.

A number of sensitization experiments were performed in order to determine the efficiency of formation of the phosphorescent state (i.e. the intersystem crossing efficiency). The method makes use of the following energy-transfer processes involving hexacyanochromate(III) as the acceptor (eq 1). As first described

$$^*M(QO)_n + Cr(CN)_6^{3-} \rightarrow M(QO)_n + {}^*Cr(CN)_6^{3-} \quad (1)$$

by Bolletta et al.,[43] the method is based on the measurement of the dependence of the intensity of the sensitized emission of the acceptor on the donor and acceptor concentrations. The $Cr(CN)_6^{3-}$ ion was chosen as acceptor because of the following useful features: (i) its lowest excited state (^2E_g, 1.24 μm^{-1}) can be conveniently monitored in DMF solution through its sharp emission (λ_{max} 805 nm); (ii) the complex is quite resistant to reduction ($E° = -1.28$ V), and this minimizes the possibility of electron-transfer quenching (vide infra) paralleling the postulated energy-transfer quenching. In the course of these experiments, the following values for the rate constants of reaction 1 were also obtained: 9.2×10^7, 5.5×10^7, and 3.7×10^8 M^{-1} s^{-1} for $M(QO)_n$ = $Pt(QO)_2$, $Ir(QO)_3$, and $Pb(QO)_2$, respectively. The efficiencies of population of the phosphorescent state, η_{isc}, obtained in these experiments are reported in Table I.

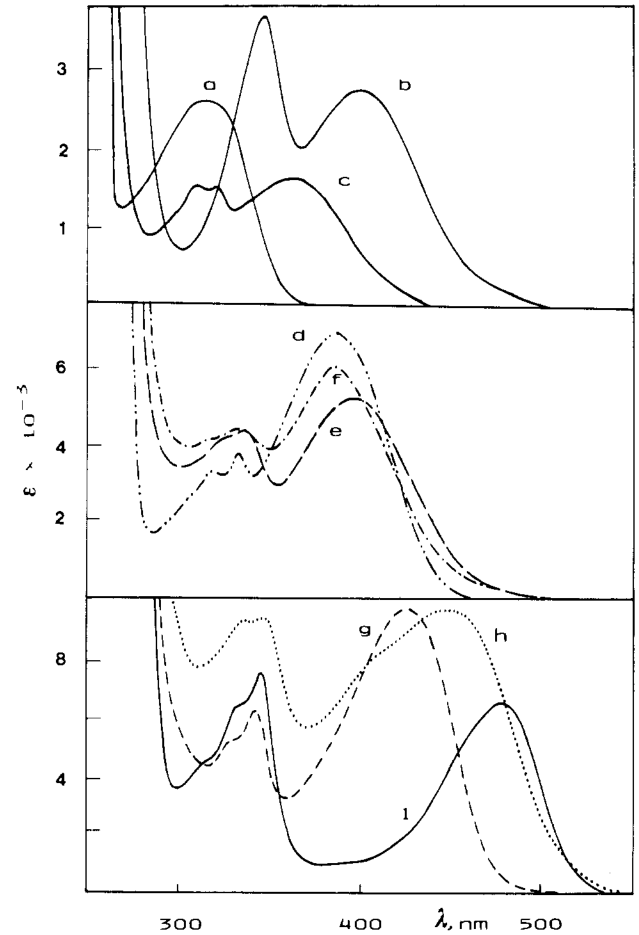

Figure 1. Absorption spectra in DMF solution at room temperature: (a) QOH; (b) QO^-; (c) QOH_2^+; (d) $Al(QO)_3$; (e) $Pb(QO)_2$; (f) $Bi(QO)_3$; (g) $Rh(QO)_3$; (h) $Ir(QO)_3$; (i) $Pt(QO)_2$.

Redox Behavior. Cyclic voltammetry of several $M(QO)_n$ complexes was performed in DMF. The 0.0 to +1.4 V potential range (vs. SCE) was investigated with use of an SPE working

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[41] Phosphorecence at 77 K for $Pb(QO)_2$ and $Bi(4\text{-}Me\text{-}QO)_3$ was observed many years ago by Bhatnagar et al.[34]

[42] The apparent molar absorptivity differences shown in Figure 3 are based on the number of laser photons absorbed and should be corrected for the efficiency of the intersystem-crossing step (values for $Ir(QO)_3$, $Pt(QO)_2$, and $Pb(QO)_2$ reported in Table I) in order to arrive at true $\Delta\epsilon$ values.

[43] Bolletta, F.; Maestri, M.; Balzani, V. *J. Phys. Chem.* **1976**, *80*, 2499.

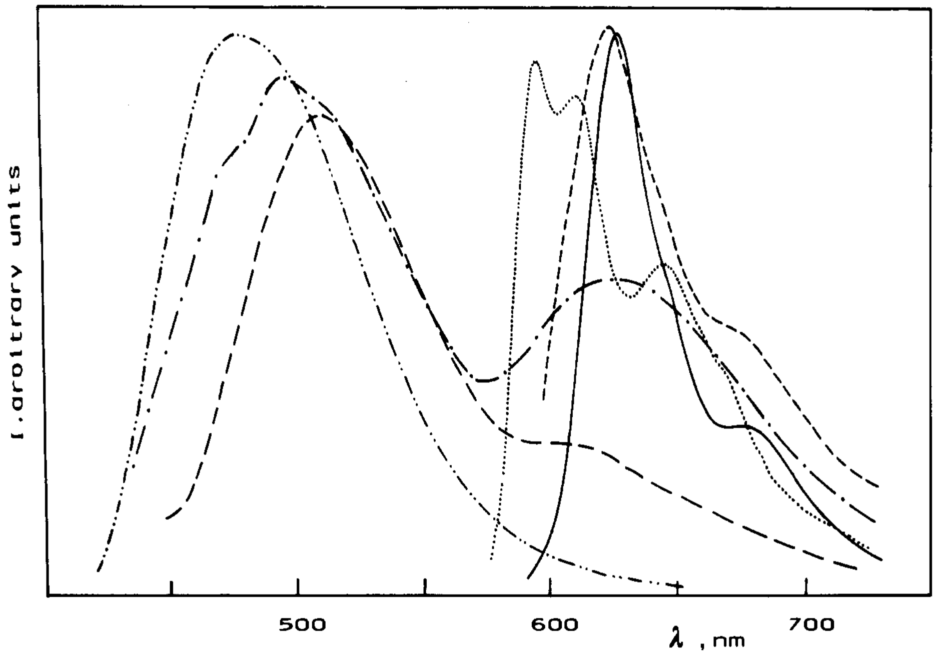

Figure 2. Emission spectra of the M(QO)$_n$ complexes at 77 K in absolute EtOH: (-‥-) Al(QO)$_3$; (--) Pb(QO)$_2$; (-·-) Bi(QO)$_3$; (---) Rh(QO)$_3$; (···) Ir(QO)$_3$; (—) Pt(QO)$_2$. The spectra, which span a wide intensity range (Al(III) > Pt(II) ≃ Ir(III) > Pb(II) ≃ Bi(III) >> Rh(III)), have been normalized for graphical purposes.

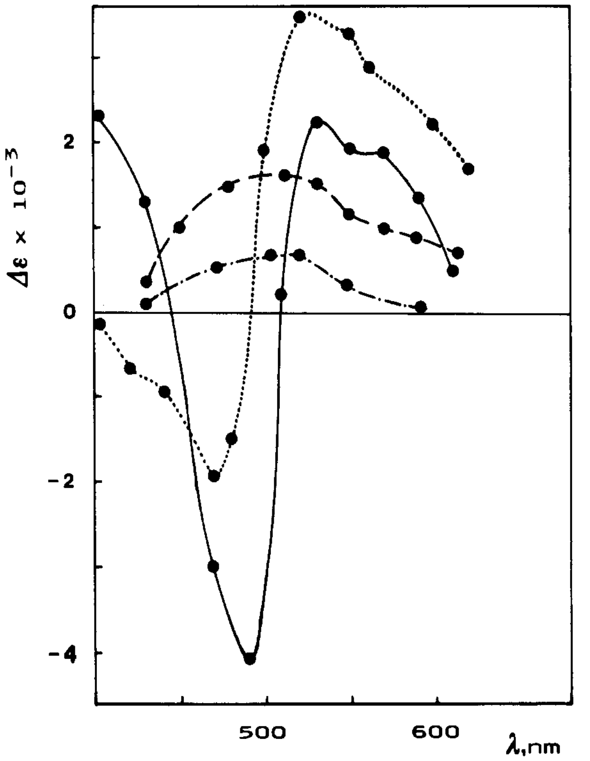

Figure 3. Excited-state absorption (ESA) spectra in DMF solution at room temperature: (---) Pb(QO)$_2$; (-·-) Bi(QO)$_3$; (···) Ir(QO)$_3$; (—) Pt(QO)$_2$. The apparent molar absorptivity difference scale (Δε) is based on the total number of laser photons absorbed.[41]

microelectrode and sweep rates in the 0.4–1.0 V s^{-1} range. All the complexes investigated exhibited several poorly reversible anodic peaks. The potential of the first anodic peak is given for each complex in Table II. The 0.0 to −2.6 V potential range (vs. SCE) was investigated with use of a HMDE working electrode and a sweep rate of 1.0 V s^{-1}. All the complexes exhibited several poorly reversible cathodic peaks. The potential of the first cathodic peak is given for each complex in Table II. A complete account of the voltammetric behavior of Ir(QO)$_3$ has been reported by Roffia et al.[44]

Electron-Transfer Quenching. The excited states of Pt(QO)$_2$ and Ir(QO)$_3$ were efficiently quenched by the methylviologen dication (MV^{2+}) in CH$_3$CN solutions (0.01 M TEAP). The quenching constant values are 1.1×10^{10} and 1.6×10^{10} M^{-1} s^{-1} for Pt(QO)$_2$ and Ir(QO)$_3$, respectively. Laser flash photolysis showed that the quenching was accompanied by transient formation of the characteristic absorption of reduced methylviologen (λ_{max} = 605 nm, ϵ_{max} = 1.0×10^4 M^{-1} cm^{-1}).[45] The quantum yields for the formation of the redox products are 0.35 for Pt(QO)$_2$ and 0.24 for Ir(QO)$_3$. After the laser flash, the MV$^+$ transient absorption disappeared by clean second-order kinetics with rate constant values of 4×10^9 M^{-1} s^{-1} for the Pt(II) complex and 7×10^9 M^{-1} s^{-1} for the Ir(III) complex.

In order to estimate the effective reducing power of the excited states of Pb(QO)$_2$, Pt(QO)$_2$, and Ir(QO)$_3$, quenching experiments were performed in CH$_3$CN solutions using quinones and nitroaromatics of different reduction potentials[46] as quenchers. The bimolecular quenching constant values, k_q, are reported in Table III.

Discussion

Chelate Structures. The M(QO)$_n$ complexes considered in this work span a number of different coordination geometries.

As far as the M(QO)$_3$ complexes are concerned (M = Al(III), Bi(II), Rh(III), Ir(III)), there is little doubt that the basic coordination geometry is pseudooctahedral. Of the two possible geometric isomers, the trans (*mer*) one should be favored due to the steric asymmetry of the ligand. For the Al(III) and Rh(III) complexes, evidence for the trans (*mer*) structure has been obtained from NMR spectra.[47] The absorption (Figure 1) and low-temperature emission (Figure 2) spectra of Ir(QO)$_3$ exhibit shoulders or band splittings which strongly suggest that the material isolated[48] and studied is actually a mixture of the two geometric isomers.

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Table III. Rate Constants for Quenching of $*M(QO)_n$ Complexes in CH_3CN Solution at 25 °C

quencher (A)	$E_{1/2}(A/A^-)$,[a] V	k_q, $M^{-1}\ s^{-1}$ Pb(QO)$_2$	Pt(QO)$_2$	Ir(QO)$_3$
tetracyanoethylene	+0.24		2.4×10^{10}	
1,4-benzoquinone	−0.51		2.1×10^{10}	
9,10-phenanthraquinone	−0.66		1.7×10^{10}	
1,2-dinitrobenzene	−0.81		1.1×10^{10}	
4-nitrobenzaldehyde	−0.86		1.2×10^{10}	
4-nitrobenzonitrile	−0.87		1.0×10^{10}	
1,3-dinitrobenzene	−0.90		7.4×10^{9}	
3-nitrobenzonitrile	−0.94		4.8×10^{9}	
3-nitrobenzaldehyde	−1.02		1.1×10^{9}	
4-bromo-1-nitrobenzene	−1.05		3.2×10^{8}	
4-chloro-1-nitrobenzene	−1.06	1.2×10^{9}	1.8×10^{8}	1.7×10^{9}
4-fluoro-1-nitrobenzene	−1.13		2.8×10^{7}	
nitrobenzene	−1.15	1.5×10^{9}	5.5×10^{6}	1.7×10^{8}
4-methyl-1-nitrobenzene	−1.20		1.9×10^{6}	

[a] From ref 46.

In the $M(QO)_2$ complexes, differences are expected between the closed-shell Pb(II) and the open-shell Pt(II) complexes. For the Pb(II) complex a pseudotetrahedral geometry is likely to be preferred, at least in solution, and NMR spectra[47] point indeed toward this conclusion. On the other hand, there is little doubt that the d^8 $Pt(QO)_2$ complex is planar. The geometry is most probably trans, since crystal structures indicate a trans arrangement for the analogous Pd(II) complex.[49]

Absorption Spectra. The spectrum of the free ligand is known to be highly dependent on pH, due to protolytic equilibria between the neutral species QOH and the cationic QOH_2^+ and anionic QO^- forms.[50,51] For both the QOH_2^+ and QO^- forms, the lowest energy absorption band is strongly red shifted with respect to the QOH species (see Figure 1 and Table I). This is consistent with previous proposals that the lowest energy band of the free ligand is associated with a π–π^* transition,[52] in which a substantial charge density is transferred from oxygen to nitrogen.[50] It should be noticed that the intensity of the band is a bit small for a pure π–π^* transition. This fact, together with the substantial intramolecular charge-transfer character of the transition, suggests that an appropriate description of the lowest absorption band of the free ligand could be made in terms of an l–π^* transition as defined by Kasha and Rawls.[53]

The spectra of all the $M(QO)_n$ complexes studied in this work are qualitatively similar to that of the free ligand (Figure 1 and Table I). They consist of two prominent bands, which are red shifted to a different extent (very little for the high-energy band but substantially for the low-energy band) with respect to those of the QO^- ligand. The shift is roughly constant for the closed-shell metal ions, whereas it is much larger and sensitive to the metal for the open-shell transition-metal ions. The similarity of all the spectra suggests that the absorption bands correspond in all cases to l–π^* ligand-centered transitions perturbed to a different extent by coordination to the metal. On the basis of the partial O → N charge-transfer character of the ligand transition, the increasing red shift observed by increasing the covalent character of the metal–ligand bonding seems to indicate that the predominant covalent interaction in these complexes occurs at the nitrogen donor atom. Actually, model zwitterions such as 1-methyl-8-oxyquinolinium exhibit the lowest absorption band at about the same energy as that observed in $Pt(QO)_2$.[52] Independent NMR evidence also points toward a covalent character of the metal–nitrogen bond vs. a relatively ionic character of the metal–oxygen bond in these complexes.[47]

The blue shift observed by increasing the solvent polarity is also consistent with the polar character of the ligand-centered transition.

In a study of some photophysical aspects of $Pt(QO)_2$, Bartocci et al.[54] attributed the lowest absorption band of this complex to a d–π^*, metal-to-ligand charge-transfer transition. As the spectrum is similar to that of the other complexes, we favor a ligand-centered assignment also for the Pt(II) complex.

Emission. The complexes studied exhibit two distinct types of emission.

The green emissions shown by the Al(III), Pb(II), and Bi(III) complexes have lifetimes in the nanosecond range at room temperature, which are not substantially increased by freezing at 77 K (Table I). As proposed many years ago by several authors,[34,36] this emission can be assigned as a ligand-localized fluorescence. The Stokes shift with respect to the lowest energy absorption band is essentially constant among the various complexes (ca. 0.65 μm^{-1} at room temperature). This remarkable shift is comparable to that observed for the free ligand,[52] either in the QO^- form or in the QOH_2^+ form. In spite of their common origin, the fluorescent emissions exhibited by the various complexes differ by orders of magnitude in intensity (Table I). This implies that substantial changes in the efficiency of the nonradiative decay of the ligand singlet excited state are brought about by changes in the metal ion. This point will be discussed in some detail later on.

The red emission is shown very clearly under all experimental conditions by the Pt(II) and Ir(III) complexes. For the Pb(II) and Bi(III) complexes, this emission is more clearly seen in 77 K glasses, but it is still detectable at room temperature in time-resolved experiments, where it can be separated from the tail of the fluorescent band. For the Rh(III) complex, this emission can only be seen at low temperature. In spite of these differences, all these emissions span a very narrow energy range (640–655 nm at room temperature and 590–625 nm at 77 K). The lifetimes of these emissions at low temprature are in the 10^{-5}–10^{-4} s range whereas, at room temperature, they become typically a few microseconds (presumably much less than this for the Rh(III) complex). These figures clearly indicate that the red emission is in all cases phosphorescence.

As far as the orbital origin of this emission is concerned, there seems to be little doubt that for the non-transition-metal complexes (Pb(II), Bi(III)) the assignment is that of a ligand-centered phosphorescence.[55] For the transition-metal complexes (Rh(III), Ir(III), Pt(II)) two additional assignments could in principle be considered, namely d–π^* metal-to-ligand charge transfer and d–d metal-centered transitions.

Regarding the d–d hypothesis, the following points play against such a type of assignment: (i) d–d emissions are known to be

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(55) Most frequently, ligand-centered phosphorescent emission in complexes containing heteroaromatic ligands appears at low temperature as a highly structured band.[2] Although there can be no doubt about the ligand-centered assignment for these non-transition-metal complexes, the emissions here appear as structureless bands. As discussed below, it is not possible to check the phosphorescence band shape of free 8-quinolinol in any of its forms, QO^-, QOH, or QOH_2^+.

Gaussian shaped, braod (typical half-widths in the 0.2–0.3-μm^{-1} range),[1,2,56,57] and structureless, whereas the phosphorescence of the Rh(III), Ir(III), and Pt(II) complexes is asymmetric, sharp (half-width lower than 0.15 μm^{-1}), and structured; (ii) the low-temperature lifetimes of bona fide d–d phosphorescent emissions of Rh(III)[56-59] and Ir(III)[56,59] complexes are at least 1 order of magnitude lower than those observed here. In a previous study, Bartocci et al.[54] assigned the emission of $Pt(QO)_2$ as a metal-centered d–d phosphorescence. For the above reasons, we regard this assignment as incorrect.

As regards the d–π^* hypothesis, this assignment can be easily discarded for the Rh(III) complex as oxidation of Rh(III) to Rh(IV) would certainly require very high energies. In fact, no example of such behavior for Rh(III) complexes has ever been reported. For the Ir(III) and Pt(II) complexes, the situation is less clear. With a favorable donor atom set, d–π^* transitions could lie at relatively low energies with such metals. In fact, d–π^* emission has been reported or suggested for a number of Ir(III)[60,61] and Pt(II)[62,63] complexes. However, the $Ir(QO)_3$ and $Pt(QO)_2$ emissions (Figure 2) are very similar to that of $Rh(QO)_3$ in both energy and band shape[64] and thus are likely to have the same orbital origin.

In conclusion, although a metal-to-ligand d–π^* assignment cannot be definitely ruled out for $Pt(QO)_2$ and $Ir(QO)_3$, we favor the assignment of the long-lived emission of all the complexes examined as a ligand-centered phosphorescence.

One point that could be raised concerning this assignment is that the energy of the ligand-centered phosphorescence seems to be less sensitive to changes in the metal (Table I) and in the solvent polarity than that of the lowest energy absorption band (which was assigned as a metal-perturbed ligand-centered transition). This could suggest that different types of transitions are responsible for the two processes. In this regard, it may be noticed that the second absorption band of the complexes at about 340 nm (Figure 1) is relatively insensitive to the above-mentioned changes. Correlating the phosphorescence with this band, however, would require some rather exceptional values for the singlet–triplet splitting and/or the Stokes shift in these systems. If, on the other hand, it is assumed that the phosphorescence and the lowest absorption band originate from the same transition, some kind of compensation either in the singlet–triplet splitting or in the Stokes shift should be invoked to make the phosphorescence energy virtually metal and solvent independent.

Finally, it should be mentioned that the electrochemical data on the $M(QO)_n$ complexes are also consistent with the view that the lowest excited states of these complexes are ligand-localized. In fact, the oxidation and reduction potentials of different complexes (Table II) fall within relatively narrow ranges (±0.2 V) in spite of the large differences expected in the redox properties of different metals. This is consistent with the redox orbitals[65] (which are conceptually related to HOMOs and LUMOs)[66] being substantially localized on the ligands.

Role of the Metal in the Photophysics of $M(QO)_n$ Complexes. The previous discussion has shown that ligand-centered phosphorescence is exhibited by several $M(QO)_n$ complexes either at room temperature or at low temperature. The intensity of this emission, however, is seen to depend dramatically on the nature of the metal ion.

In order to discuss the role of the metal in the photophysical behavior of these complexes, it is practical to use a perturbational approach similar to that usually adopted for other metal chelates (e.g. the metal porphyrins).[67,68] In principle, the metal may affect the quantum yield of ligand emission by changing the rate of any of the following photophysical processes of the ligand: $S_1 \rightarrow T_1$ intersystem crossing, $T_1 \rightarrow S_0$ phoshporescent emission, $T_1 \rightarrow S_0$ intersystem crossing.

As far as the behavior of the free ligand is concerned, it has been known for a long time that 8-quinolinol does not phosphoresce either at room temperature or at low temperature in rigid media under any conditions.[52,69] The reason for this result is to be found in a very inefficient $S_1 \rightarrow T_1$ intersystem-crossing process. Goldman and Wehry,[52] on the basis of negative results for sensitization of olefin isomerization, estimated that the intersystem crossing efficiency (η_{isc}) in QOH must be lower than 0.02. While the reasons for this exceptionally low intersystem-crossing efficiency of the free ligand are not obvious, it seems quite reasonable to ascribe the appearance of ligand-centered phosphorescence in the $M(QO)_n$ complexes to enhanced η_{isc} due to perturbation by the metal. Since the metal ions involved in this work are all diamagnetic, the perturbing effect of the metal is likely to consist in heavy-atom-induced spin–orbit coupling. Heavy-atom effects have been invoked several years ago by Lytle et al.[36] to explain variations in the fluorescence parameters (lifetimes or quantum yields) for a series of $M(QO)_n$ complexes and by Crosby[69] to interpret the 77 K phosphorescent behavior of rare-earth chelates. Some comments on the details of the photophysical behavior of the single complexes are given in the following paragraphs.

The Al(III) complex can be taken as a reference system resembling in behavior free hydroxyquinoline[34] and most non-transition-metal oxyquinoline complexes.[32-34,36] It gives rise to a very intense fluorescent emission (Table I) in both fluid solution at room temperature and rigid glasses at 77 K. No phosphorescent emission can be detected even at low temperature, indicating that the intersystem-crossing efficiency, η_{isc}, is negligible as in the free ligand. As a matter of fact, no appreciable heavy-atom effect is expected for a light metal such as aluminum.[70]

The Rh(III) complex behaves quite differently from the Al(III) complex in that it does not exhibit fluorescence under any experimental conditions. Moreover, phosphorescence is observed at low temperature. This shows that intersystem crossing is appreciably efficient, indicating that a substantial heavy-atom perturbation of the ligand states takes place in this complex. This is consistent with both the relatively high atomic number of rhodium *and* the covalent character of the metal–ligand bond. Contrary to what happens for the other phosphorescent complexes (vide infra), the emission completely disappears in going to room temperature. This could be associated with the presence of metal-centered d–d states in the same energy range as the ligand-centered triplet, which may provide an efficient thermally activated deactivation path for the emitting state. This situation is reminiscent of that found for Rh(III) polypyridine complexes.[71-73] The presence of low-lying d–d states is no doubt the reason

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(70) It can be pointed out that, according to preliminary results, a Zn(II) 8-quinolinol complex (undefined stoichiometry) shows a definite, though very weak, phosphorescent emission at low temperature. This indicates that the increase in the atomic number of the metal from Al to Zn is already sufficient to bring about a very small, but sizable, η_{isc} value. The very long lifetime of the triplet state (3.5 ms) indicates that the heavy-atom effect on the $T_1 \rightarrow S_0$ processes is still relatively poor.

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for the nonluminescent behavior of $3d^n$ ($1 \leq n \leq 9$) transition-metal 8-quinolinol complexes.[34,74]

The Pt(II) and Ir(III) complexes are remarkable in exhibiting strong phosphorescent emission at *both* room temperature and low temperature. Fluorescence is completely absent in these complexes, in agreement with the plausible hypothesis of unitary η_{isc}. For these complexes, this hypothesis has been experimentally confirmed (Table I). The high phosphorescence yield and the relatively short triplet lifetime (Table I) indicate a substantial heavy-atom-induced enhancement of both radiative and nonradiative deactivations of the "triplet" state.[75-77] This is quite plausible in view of the high atomic number of the metals and the highly covalent character of the metal–ligand bond. The lack of large temperature effects on the triplet lifetime is consistent with the notion that in these complexes the metal-centered states should lie too high in energy to be thermally accessible from the emitting state.

The Pb(II) and Bi(III) complexes behave in some respects as an intermediate case between the phosphorescing (e.g. Pt(II)) and the fluorescing (e.g. Al(III)) complexes. In fact they emit both fluorescence and phosphorescence at room temperature as well as at 77 K. Thus, in spite of the high atomic number of the metals, intersystem crossing is not totally efficient for these complexes, as verified experimentally in the Pb(II) case (Table I). This can be traced back to the relatively ionic character of the metal–ligand bond in these complexes. The intermediate degree of heavy-atom perturbation in these complexes is also pointed out by the relatively long low-temperature triplet lifetimes (Table I), reflecting relatively slow $T_1 \rightarrow S_0$ processes. These values are comparable to that obtained for the Rh(III) complex, in which, possibly, a more covalent interaction compensates for the lower atomic number of the metal.

Excited-State Redox Properties. The $Pt(QO)_2$, $Ir(QO)_3$, $Pb(QO)_2$, and $Bi(QO)_3$ complexes have a number of properties (high yields of formation of the phosphorescent state, microsecond lifetimes in fluid solution) that make them attractive as bimolecular excited-state reactants or photosensitizers.[17,78,79]

The ground-state redox potentials and the excited-state energies allow the calculation, according to standard procedures,[22] of the excited-state redox potentials shown in Table II. These values clearly show that all these complexes are expected to be very good excited-state reductants and very poor excited-state oxidants.

That the complexes actually behave as excited-state reductants is demonstrated by the quenching of excited $Pt(QO)_2$ and $Ir(QO)_3$ by the standard acceptor methylviologen. In both cases, high yields of redox products (eq 2) are formed. The products recombine

$$^{*}M(QO)_n + MV^{2+} \rightarrow M(QO)_n^{+} + MV^{+} \qquad (2)$$

with diffusion-controlled kinetics without any appreciable loss in the initial complex concentration. Thus, the poor reversibility observed in the voltammetric oxidation does not show up in the faster time scale of the reversible electron-transfer quenching.

Since irreversible ground-state potentials were used in the calculation of the excited-state potentials of Table II, some caution should be used in taking these figures as a measure of the effective reducing power of the excited states. This point can be checked by using the experimental kinetic data in Table III. It has been shown by several authors[22,80,81] that homogeneous series of electron-transfer reactions obey specific free energy relationships and that fitting of experimental data according to these relationships may yield reliable estimates of unknown kinetic or thermodynamic parameters. Figure 4 shows a plot of the rate constants for the quenching of excited $Pt(QO)_2$ by a variety of organic one-electron acceptors as a function of the reduction potential of the quencher, $E_{1/2}(A/A^-)$ (data from Table III). The continuous line is a nonlinear least-squares fit obtained by using standard equations[82] and reasonable kinetic parameters[83] and treating the excited-state potential (eq 3) as a floating parameter. The best fitting value

$$\Delta G = E_{1/2}(Pt(QO)_2^{+}/{}^{*}Pt(QO)_2) - E_{1/2}(A/A^-) \qquad (3)$$

for the excited-state potential is −0.90 ± 0.05 V,[84] a value that is in good agreement with the calculated one (Table II). This shows that for $Pt(QO)_2$ the calculated excited-state potential is very nearly the effective one. The data available on the other complexes (Table III), though much more limited in number, tend to confirm this conclusion.

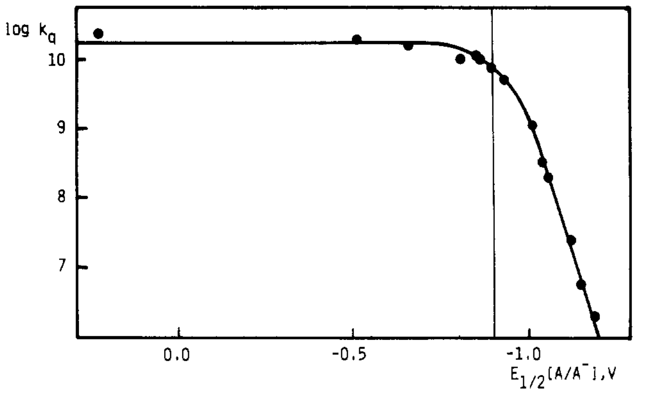

Figure 4. Free-energy correlation of rate constants for the quenching of $^{*}Pt(QO)_2$ by organic electron acceptors (see text). The vertical line corresponds to the best fitting value for the excited-state potential.

The excited states of all the phosphorescent complexes of this series are quenched by oxygen at almost diffusion-controlled rates. The behavior of $Pt(QO)_2$ is exceptional with respect to that of the other complexes in that the oxygen quenching is accompanied by an irreversible reaction of the complex. This suggests that quenching occurs by an electron-transfer mechanism. The peculiarity of the Pt(II) complex may lie in the possibility for the one-electron-oxidized product, $Pt(QO)_2^{+}$, to be further oxidized by O_2^- to Pt(IV) species.

The phosphorescent complexes of 8-quinolinol studied in this work have comparable excited-state reducing powers and longer lifetimes than the popular $Ru(bpy)_3^{2+}$ photosensitizer.[6] Unlike $Ru(bpy)_3^{2+}$, however, these new photosensitizers are insoluble in water. This might be a drawback for using these complexes in homogeneous water-splitting photochemical cycles,[14-20] although appropriate functionalization of the quinolinol ligand may be used to avoid this limitation.[85-87] On the other hand, the hydrophobic character of the 8-quinolinol complexes becomes a useful feature when these molecules are used for spectral sensitization of sem-

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(82) An equation relating k_q to $E_{1/2}(A/A^-)$ can be obtained from eq 28 and 74 of ref 22 and eq 3 of this paper.

(83) The following values have been used in the calculations: $\kappa = 1$, $\nu_N = 6.2 \times 10^{12}$, $k_d = 1.8 \times 10^{10}\ M^{-1}\ s^{-1}$, $k_{-d} = 1.7 \times 10^{10}\ s^{-1}$, $k_x = 2.0 \times 10^{11}\ s^{-1}$, $\Delta G^{*}(0) = 4.7$ kcal/mol. The symbols are defined as in ref 22.

(84) The error limits given on $E_{1/2}(Pt(QO)_2^{+}/{}^{*}Pt(QO)_2)$ are based on a series of two-parameter fits ($\Delta G^{*}(0)$ also floating) in which the maximum reasonable variation in the input value for k_x (6.2×10^{12}–$5 \times 10^{10}\ s^{-1}$) was allowed for.

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(86) For example, Pt(II) and Ir(III) complexes of 5-sulfonato-8-quinolinol are water-soluble and maintain excited-state properties very similar to those of the parent complexes.[85,87]

(87) Ballardini, R., unpublished results.

iconductor particles in aqueous solution.[88] Finally, it should be pointed out that the poor reversibility observed upon electrochemical oxidation may be a major practical limitation, unless appropriate fast oxidation relay species are coupled with these sensitizers.

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Registry No. Al(QO)$_3$, 2085-33-8; Rh(QO)$_3$, 21689-22-5; Ir(QO)$_3$, 15671-12-2; Pt(QO)$_2$, 21710-20-3; Pb(QO)$_2$, 14976-96-6; Bi(QO)$_3$, 16029-28-0; tetracyanoethylene, 670-54-2; 1,4-benzoquinone, 106-51-4; 9,10-phenanthraquinone, 84-11-7; 1,2-dinitrobenzene, 528-29-0; 4-nitrobenzaldehyde, 555-16-8; 4-nitrobenzonitrile, 619-72-7; 1,3-dinitrobenzene, 99-65-0; 3-nitrobenzonitrile, 619-24-9; 3-nitrobenzaldehyde, 99-61-6; 4-bromo-1-nitrobenzene, 586-78-7; 4-chloro-1-nitrobenzene, 100-00-5; 4-fluoro-1-nitrobenzene, 350-46-9; nitrobenzene, 98-95-3; 4-methyl-1-nitrobenzene, 99-99-0; methylviologen dication, 4685-14-7.

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(89) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Metal–Nitroxyl Interactions. 48. EPR Spectra of Spin-Labeled Pyridines Coordinated to Chromium(III) Tetraphenylporphyrin Chloride ($S = {}^{3}/_{2}$) and Comparison of the Electron–Electron Exchange Interaction with Analogous Complexes with Metal $S = {}^{1}/_{2}$

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EPR spectra were obtained for 13 spin-labeled pyridines coordinated to chromium(III) tetraphenylporphyrin chloride. In fluid solution weak electron–electron exchange interaction caused broadening of the nitroxyl signal and stronger interaction caused resolved splitting. Resolved spin–spin splitting was observed in frozen solution. Values of the exchange coupling constant, J, between ±0.005 and ±0.27 cm^{-1} were obtained by computer simulation of the frozen-solution spectra. The stronger exchange interaction for 4-substituted pyridines than for analogous 3-substituted pyridines is consistent with π delocalization of the unpaired spin density from the metal into the pyridine ring. π delocalization was also dominant in the vanadyl trifluoroacetylacetonate complexes of these spin-labeled pyridines. The values of J for the Cr(III) ($S = {}^{3}/_{2}$) complexes were ${}^{1}/_{2}$ to ${}^{2}/_{3}$ of the values observed for the vanadyl ($S = {}^{1}/_{2}$) complexes of the same spin-labeled pyridines.

Introduction

Recent studies of homonuclear and heteronuclear metal–metal dimers have shown that the electron–electron exchange interaction decreased as the number of unpaired electrons on the metal increased.[1-5] If the geometry of a metal–nitroxyl complex is held constant and the electron–electron spin–spin interaction involves a single half-filled orbital on the metal, the value of the exchange coupling constant, J, is expected to be proportional to $1/n$ where n is the number of unpaired electrons on the metal.[6] The value of n cannot be varied experimentally without altering other properties of the metal that may also contribute to changes in the value of J. When spin-labeled pyridines were coordinated to Mn(II), the value of J was ${}^{1}/_{4}$ to $<{}^{1}/_{50}$ of that observed for analogous complexes of Cu(II) and ${}^{1}/_{8}$ to $<{}^{1}/_{40}$ of that observed for vanadyl.[7] Mn(II) has half-filled d orbitals with both σ (d_{z^2}) and π (d_{xz}, d_{yz}) symmetry relative to the pyridine orbitals of the spin-labeled ligand. The metal–nitroxyl interaction probably has significant contributions from orbitals of both symmetries. If the resultant contributions to J were of similar magnitude and of opposite sign, this could cause the value of J for $S = {}^{5}/_{2}$ Mn(II) to be less than ${}^{1}/_{5}$ of the values observed for $S = {}^{1}/_{2}$ Cu(II) or vanadyl. In this context it was of interest to determine how much change in J would be observed as a function of n for metal–radical interactions in which the spin–spin interaction was through a single half-filled orbital.

The equilibrium constant for coordination of pyridine to chromium tetraphenylporphyrin chloride (Cr(TPP)Cl) in toluene solution at room temperature is 2×10^5.[8,9] This equilibrium is sufficiently favorable to permit EPR studies of spin-labeled pyridines bound to Cr(TPP)Cl without interference from large amounts of dissociated nitroxyl or metalloporphyrin. We have therefore examined the EPR spectra of spin-labeled pyridines I–XIII coordinated to Cr(TPP)Cl. We have previously reported the EPR spectra of I–XII bound to copper(II) and vanadyl β-diketonates.[10-14]

Experimental Section

Physical Measurements. EPR spectra were obtained on a Varian E9 interfaced to an IBM CS9000[15] or on an IBM ER200 interfaced to an IBM CS9000. Spectra were obtained with 100-kHz modulation at modulation amplitudes that did not distort the line shapes and microwave

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