Charge Distribution in Schiff-base Biquinone Complexes. Electrochemical, Spectroelectrochemical and Electron Spin Resonance Studies of Complexes of Co^{III}, Ni^{II}, Zn^{II}, Cu^{II}, and Cd^{II} with the *N*-(2′-Hydroxy-3′,5′-di-t-butylphenyl)-4,6-di-t-butyl-*o*-benzoquinone Imine Ligand System in CH_2Cl_2†

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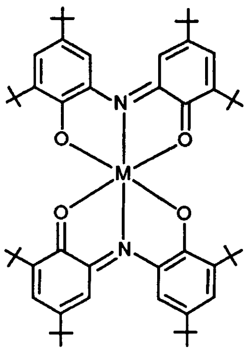
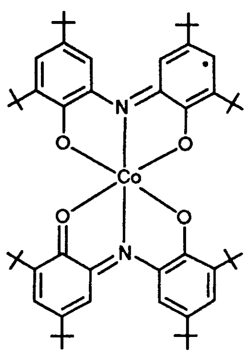
Five different Schiff-base biquinone complexes were examined by electrochemical, spectroelectrochemical, and e.s.r. methods: $[M^{II}(hbqi)_2]$ and $[Co^{III}(hbqi)(hbsqi)]$ [M = Ni, Zn, Cu, or Cd; hbqi is the anion of *N*-(2′-hydroxy-3′,5′-t-di-butylphenyl)-4,6-di-t-butyl-*o*-benzoquinone imine and hbsqi is singly reduced hbqi, *N*-(2′-hydroxy-3′,5′-di-t-butylphenyl)-4,6-di-t-butyl-*o*-benzosemiquinone iminate(2−)]. Each compound was characterized by e.s.r. and u.v.–visible spectroscopy as well as by electrochemistry and spectroelectrochemistry in CH_2Cl_2 containing 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$. The first one-electron oxidation and the first one-electron reduction of the complexes both occur at ligand-based orbitals. The voltammetric and e.s.r. data are self consistent and indicate that an oxidized hbqi ligand dissociates from $[M^{II}(hbqi)_2]$ after a one-electron abstraction. Singly oxidized $[Co^{III}(hbqi)(hbsqi)]$ does not undergo a loss of ligand and $[Co^{III}(obsq)(hbsqi)]^+$ is electrogenerated where obsq is singly oxidized hbqi. This complex does not exhibit coupling between the two unpaired electrons. The one-electron reduction of $[M^{II}(hbqi)_2]$ (M = Ni, Zn or Cd) produces a stable $[M^{II}(hbqi)(hbsqi)]^-$ species in which the unpaired electron resides on the hbsqi ligand. The stable reduction product of $[Co^{III}(hbqi)(hbsqi)]$ is identified as $[Co^{III}(hbsqi)_2]^-$, a species in which the two unpaired electrons independently interact with the cobalt nucleus and two hydrogens. Finally, e.s.r. spectra suggest that a structural change in $[Cu^{II}(hbqi)_2]$ occurs upon going from the solid state to methylene chloride solutions at low temperature.

Numerous metal–*o*-quinone complexes have been studied as to their spectroscopic, magnetic, and electrochemical properties.[1–15] Redox potentials for transition-metal *o*-quinone complexes,[3–6,8–13] including those of hbqi the anion of *N*-(2′-hydroxy-3′,5′-di-t-butylphenyl)-4,6-di-t-butyl-*o*-benzoquinone imine,[2] have been published but the products generated in the one-electron oxidation or reduction of these latter derivatives have never been reported. This is done in the present study which presents electrochemical and spectroscopic data for five transition-metal complexes which contain either hbqi or hbsqi ligands where hbsqi is singly reduced hbqi, i.e. *N*-(2′-hydroxy-3′,5′-di-t-butylphenyl)-4,6-di-t-butyl-*o*-benzosemiquinone iminate(2−).

The investigated compounds are represented as $[Co^{III}(hbqi)(hbsqi)]$ and $[M^{II}(hbqi)_2]$ where M = Ni, Zn, Cu, or Cd. U.v.–visible and e.s.r. techniques were used to characterize the neutral complexes as well as the products of each one-electron oxidation or reduction in methylene chloride containing 0.1 mol dm^{-3} tetra-n-butylammonium perchlorate. In addition, e.s.r. results are presented which describe the change in electronic structure of $[Cu^{II}(hbqi)_2]$ upon going from the solid state to CH_2Cl_2 solutions at 298 and 128 K. As will be shown in this paper, the charge distribution in each electro-oxidized or electroreduced biquinone complex will depend upon the structure of the co-ordinated ligand, the net charge on the complex, and the type of co-ordinated metal ion.



$[M^{II}(hbqi)_2]$



$[Co^{III}(hbqi)(hbsqi)]$

Experimental

Instrumentation and Methods.—U.v.–visible spectra were recorded with an IBM 9430 spectrophotometer, a Perkin-Elmer 330 spectrophotometer or a Tracor Northern 1710 holographic optical spectrometer/multichannel analyzer. Electroreduction or electro-oxidation of each complex was carried out under an inert atmosphere using Schlenk techniques, after which the compounds were transferred to an e.s.r cell which had been modified for use on a Schlenk line. E.s.r. spectra were recorded on an IBM model ER-100D system. Quantitative e.s.r. measurements were performed with a Bruker ESP-300 e.s.r. spectrometer. Spin intensities were compared before and after exhaustive electrolysis. Diphenylpicrylhydrazyl (dpph) was used as the *g* marker ($g = 2.0036 \pm 0.0002$).

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† *Non-S.I. unit employed:* G = 10^{-4} T.

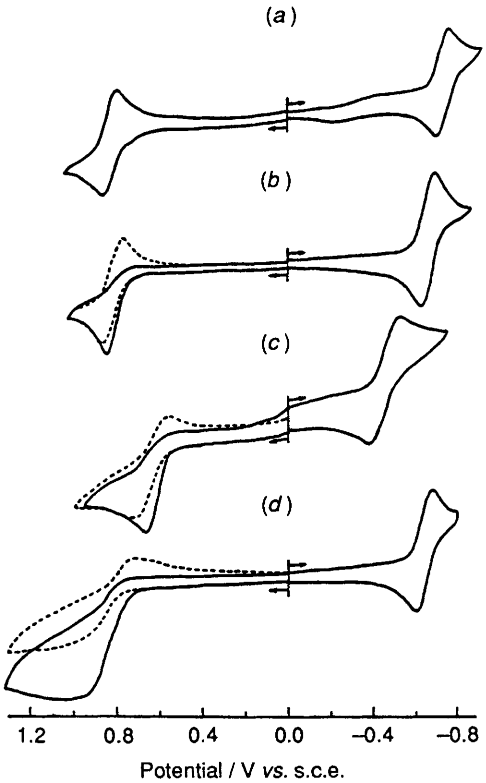

Figure 1. Cyclic voltammograms of [M^{II}(hbqi)$_2$] [M = Ni^{II} (*a*), Zn^{II} (*b*), Cu^{II} (*c*), or Cd^{II} (*d*)] in CH_2Cl_2, 0.1 mol dm^{-3} NBu$^n{}_4$ClO$_4$ at 298 K (solid line) and 196 K (broken line)

The e.s.r. spectra of several complexes were also obtained after *in-situ* electrolysis using a modified e.s.r./electrochemical cell.[16] The spectra of the final products were obtained after 1—3 min electrolysis and were identical to those obtained after bulk controlled-potential electrolysis where complete radical generation required 15—20 min. In both cases, an oxidation of the singly reduced species regenerated the original complex in high yield (90—95%), as determined by u.v.-visible spectra.

Cyclic voltammetry and bulk controlled-potential coulometry were carried out with an IBM 225 voltammetric analyzer or a PAR model 174A/175 polarographic analyzer/potentiostat which was coupled with a PAR model RE 0074 X-Y recorder.

Both the working and counter electrodes were platinum. A platinum minigrid electrode was used for the thin-layer spectroelectrochemical cell. Details of the construction of this cell have been reported.[17] Potentials were measured *versus* a saturated calomel electrode (s.c.e) which was separated from the bulk solution by means of a fritted-glass-disk junction. Potentials for thin-layer spectroelectrochemical measurements were applied with a PAR model 175 potentiostat and spectra were obtained with a Tracor Northern 1710 spectrometer multichannel analyzer which had an operating wavelength region of 300—930 nm. All experiments were carried out at 298 ± 2 K, unless otherwise specified.

Materials—The complexes [M^{II}(hbqi)$_2$] where M = Ni, Zn, Cu, or Cd were synthesized according to published procedures;[1] [Co^{III}(hbqi)(hbsqi)] was prepared using a method reported by Larsen and Pierpont.[2] The final products were recrystallized from a CH_2Cl_2–CH_3OH mixture and their purity confirmed by comparison with u.v.-visible, ^{1}H n.m.r., or e.s.r. spectra reported in the literature.[1,2] The supporting electrolyte was 0.1 mol dm^{-3} tetra-n-butylammonium perchlorate for both electrochemical and spectroelectrochemical experiments. This salt was purchased from Fluka Chemical Co., twice recrystallized from ethyl alcohol, and stored in a vacuum oven at 313 K. Methylene chloride was distilled over calcium hydride prior to use.

Results

Electrode Reactions of [M^{II}(hbqi)$_2$] *and* [Co^{III}(hbqi)(hbsqi)].—Each [M^{II}(hbqi)$_2$] complex undergoes two or three reductions and two oxidations in CH_2Cl_2, 0.1 mol dm^{-3} NBu$^n{}_4$ClO$_4$. Only the first oxidation and the first reduction were examined as to their reaction products in this study and gave cyclic voltammograms of the type shown in Figure 1. The measured peak and half-wave potentials for the illustrated reactions and those at more positive or more negative potentials are summarized in Table 1.

The complexes of Ni^{II}, Zn^{II}, and Cd^{II} all undergo a reversible one-electron diffusion-controlled reduction at room temperature. These reactions occur at $E_{\frac{1}{2}} = -0.64$ to -0.72 V and are characterized by a constant $i_p/v^{\frac{1}{2}}$ and an $|E_{p_a} - E_{p_c}| = 65 \pm 5$ mV. The complex [Cu^{II}(hbqi)$_2$] differs from the other three derivatives in that it undergoes a quasi-reversible reduction located at $E_{\frac{1}{2}} = -0.46$ V (scan rate = 0.1 V s^{-1}). However, $i_p/v^{\frac{1}{2}}$ remains constant over the scan rate range of 0.05—0.5 V s^{-1}.

The complex [Ni^{II}(hbqi)$_2$] undergoes a reversible room temperature oxidation at $E_{\frac{1}{2}} = +0.83$ V; [Zn^{II}(hbqi)$_2$] undergoes an irreversible room-temperature oxidation at $E_p = +0.85$ V for a potential scan rate of 0.1 V s^{-1} (solid line, Figure 1), but this oxidation becomes reversible when the scan rate is increased to values larger than 0.5 V s^{-1} or when the solution temperature is lowered to 196 K. A voltammogram under this latter condition is shown in Figure 1.

The complexes [Cd^{II}(hbqi)$_2$] and [Cu^{II}(hbqi)$_2$] both undergo irreversible oxidations at room temperature. The oxidation of [Cd^{II}(hbqi)$_2$] occurs at $E_p \approx +1.04$ V for a scan rate of 0.1 V s^{-1} and the shape of the oxidation peak is given by $|E_p - E_{p/2}| = 210$ mV. This process becomes quasi-reversible at 196 K (see broken line in Figure 1) and the overall data suggest the occurrence of a chemical reaction following an electron-transfer step (*i.e.* an e.c. type mechanism).[18] The oxidation of [Cu^{II}(hbqi)$_2$] also becomes quasi-reversible at 196 K (broken line, Figure 1) and the peak-to-peak separation is 150 mV for a scan rate of 0.1 V s^{-1}.

The complex [Co^{III}(hbqi)(hbsqi)] undergoes a reversible one-electron room-temperature oxidation at $E_{\frac{1}{2}} = +0.15$ V and a reversible one-electron room-temperature reduction at $E_{\frac{1}{2}} = -0.42$ V. These values are both comparable to $E_{\frac{1}{2}}$ values given in the literature.[2] A second irreversible reduction is located at $E_{p_c} = -1.27$ V for a scan rate of 0.1 V s^{-1}. This reaction remains irreversible at all temperatures down to 196 K, and contrasts with data in the literature where the second reduction process is reported to be quasi-reversible at room temperature.[2a]

U.V.–Visible Spectra of Neutral, Oxidized, and Reduced Complexes.—The [M^{II}(hbqi)$_2$] complexes all have strong absorption bands centred at 700—900 and 340—450 nm. The measured wavelength maxima and molar absorptivities in CH_2Cl_2, 0.1 mol dm^{-3} NBu$^n{}_4$ClO$_4$ are listed in Table 2 and are similar to values in the literature for the same complexes in either neat CH_2Cl_2 or neat toluene.[1,2] The [M^{II}(hbqi)$_2$] derivatives all have similar u.v.–visible spectra and because of this it has been suggested that the absorptions are due to ligand-based transitions.[1]

Figure 2 shows time-resolved u.v.–visible spectra obtained during the first one-electron oxidation of [Ni^{II}(hbqi)$_2$] and the spectral data before and after electro-oxidation of each [M^{II}(hbqi)$_2$] species are summarized in Table 2. The oxidations are all irreversible on the thin-layer spectroelectrochemical timescale (≈2 min) and the resulting spectra are therefore due to a product of the chemical reaction following electron abstraction.

The reduction of [Ni^{II}(hbqi)$_2$] is electrochemically and

Table 1. Peak and half-wave potentials (V *versus* s.c.e.) for the room-temperature oxidation or reduction of hbqi and hbsqi complexes in CH_2Cl_2, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$ (n.r. = no reaction).

	Oxidation		Reduction		
Compound	First ($E_{\frac{1}{2}}$)	Second ($E_p{}^a$)	First ($E_{\frac{1}{2}}$)	Second ($E_p{}^a$)	Third ($E_p{}^a$)
$[Ni^{II}(hbqi)_2]$	0.83	1.21	−0.72	−1.07	−1.70
$[Zn^{II}(hbqi)_2]$	0.81[b]	1.17	−0.66	−1.02	−.167
$[Cu^{II}(hbqi)_2]$	0.67 ($E_p{}^a$)	1.33[c]	−0.46	−0.88[d]	n.r.
$[Cd^{II}(hbqi)_2]$	~1.04 ($E_p{}^a$)	n.r.	−0.64	−0.88 ($E_{\frac{1}{2}}$)	−1.65
$[Co^{III}(hbqi)(hbsqi)]$	0.15	n.r.	−0.42	−1.27	n.r.

[a] Peak potential at 0.1 V s^{-1}. [b] $E_{\frac{1}{2}}$ at scan rate $\geqslant$0.5 V s^{-1}. [c] E_p at 0.4 V s^{-1}. [d] Quasi-reversible reaction, $|E_{p_c} - E_{p_a}| = 0.16$ V at 0.02 V s^{-1}.

Table 2. Maximum absorbance wavelengths (λ_{max}) and corresponding molar absorptivities (ε/dm^3 mol^{-1} cm^{-1}) of neutral, reduced and oxidized hbqi and hbsqi complexes in CH_2Cl_2, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$.

Compound	Neutral	Reduced	Oxidized
$[Ni^{II}(hbqi)_2]$	431 (18.1), 769 (29.9), 844 (27.9)	413 (21.6), 836 (18.7)	417 (16.3), 697 (19.7), 773 (16.3), 854 (15.9)
$[Zn^{II}(hbqi)_2]$	368 (7.8), 430 (9.8), 527 (3.8), 735 (40.1), 796 (34.9)	410 (13.9), 783 (15.6)	374 (14.6), 745 (16.7)
$[Cu^{II}(hbqi)_2]$	326 (8.0), 438 (11.4), 766 (30.3), 824 (sh), (25.0)	402 (22.4), 807 (15.0)	462 (12.9), 766 (14.6), 896 (12.4)
$[Cd^{II}(hbqi)_2]$	430 (6.3), 532 (2.2), 742 (35.2), 797 (sh) (30.6)	399 (16.1), 796 (21.5)	378 (19.5)
$[Co^{III}(hbqi)(hbsqi)]$	388 (18.9), 436 (12.1), 519 (9.2), 891 (10.1)	404 (25.4), 556 (6.1)	458 (29.1), 464 (sh) (28.8), 930 (13.7)

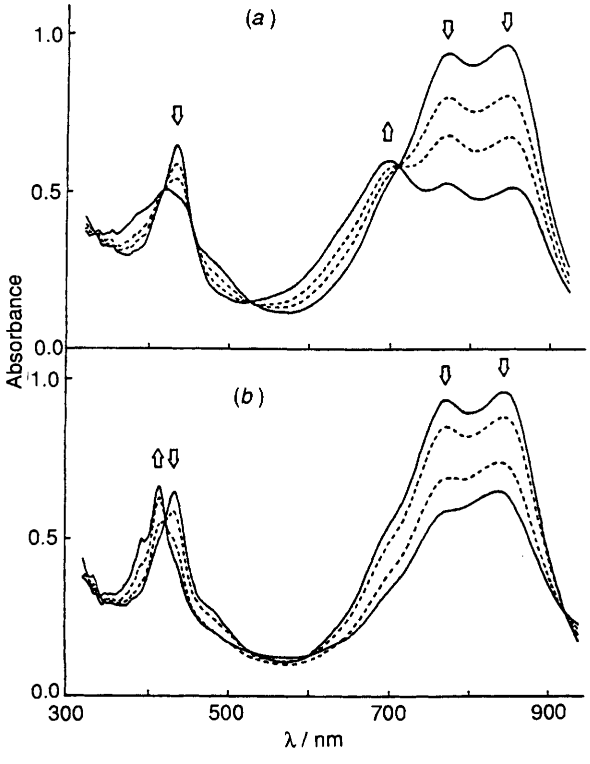

Figure 2. U.v.–visible spectral changes obtained for $[Ni^{II}(hbqi)_2]$ in CH_2Cl_2, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$ during the first one-electron (*a*) controlled-potential oxidation at +1.00 V and (*b*) controlled-potential reduction at −0.86 V. The initial and final spectra are given by solid lines and the intermediate spectra by broken lines

spectrally reversible and the electrogenerated product has peaks at 393 and 413 nm [see Figure 2(*b*)]. Similar reversible spectral changes occur during reduction of $[Zn^{II}(hbqi)_2]$, $[Cu^{II}(hbqi)_2]$ or $[Cd^{II}(hbqi)_2]$ and the spectral data for the neutral and singly reduced complexes are summarized in Table 2.

Table 2 also summarizes the spectra changes obtained after one-electron electro-oxidation or electroreduction of $[Co^{III}(hbqi)(hbsqi)]$. Singly oxidized $[Co^{III}(hbqi)(hbsqi)]$ has peaks at 458, 464, and 930 nm while the singly reduced product of the original complex has peaks at 404 and 556 nm (see Figure 3). The neutral cobalt(III) complex has a band at 1 030 nm which remains after bulk electrolysis at −0.70 V.

E.S.R. Spectroscopy—E.s.r. data for the neutral complexes of Cu^{II} and Co^{III} as well the singly oxidized or singly reduced hbqi derivatives are summarized in Table 3. The reductions are reversible on both the thin-layer and bulk controlled-potential time-scales. In contrast the oxidations are irreversible and none of the initial species, except for $[Co^{III}(hbqi)(hbsqi)]$, could be regenerated after reduction of the singly oxidized complex.

The e.s.r. behaviour of the investigated complexes varied as a function of the metal ion and the results are represented in three groups for the purpose of discussion. These are $[M^{II}(hbqi)_2]$ (M = Zn, Cd, or Ni), $[Cu^{II}(hbqi)_2]$, and $[Co^{III}(hbqi)(hbsqi)]$.

$[Zn^{II}(hbqi)_2]$, $[Cd^{II}(hbqi)_2]$ *and* $[Ni^{II}(hbqi)_2]$. The room-temperature e.s.r. spectrum of singly reduced $[Zn^{II}(hbqi)_2]$ in CH_2Cl_2 is shown in Figure 4(*a*) and is similar to the spectrum for singly reduced $[Cd^{II}(hbqi)_2]$ under the same solution conditions. Both complexes show a hyperfine splitting pattern consistent with a coupling of the unpaired electron to one nitrogen ($I = 1$) and four hydrogens ($I = \frac{1}{2}$) (see Table 3). This pattern is invariant with changes in complex concentration over a range of 10^{-4}—10^{-3} mol dm^{-3} as well as with changes in the modulation amplitude from 0.2 to 2.0 G. The spectrum of singly reduced $[Ni^{II}(hbqi)_2]$ has a broad signal centred at $g = 2.018$ and a peak-to-peak separation, ΔH_{pp}, of 27 G [see Figure (4*b*)]. This spectrum is also invariant with changes in complex concentration or modulation amplitude.

The chemical oxidation of hbqi in benzene results in an e.s.r. spectrum which consists of 29 lines with $A^N = 10.0$ G, $A^H = 2.5$ G (2 H), and $A^H = 1.2$ G (2 H).[19] This spectrum can be compared to a theoretical spectrum of singly oxidized hbqi [*i.e.* (6′-oxo-3′,5′-di-t-butylcyclohexa-2′,4′-dien-1-ylidene-

Table 3. Room-temperature e.s.r. parameters of hbqi and hbsqi complexes in CH_2Cl_2, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$.[a]

	Neutral				Reduced				Oxidized			
Compound	g	A^M	A^N	A^H	g	A^M	A^N	A^H	g	A^M	A^N	A^H
$[Ni^{II}(hbqi)_2]$					2.018				2.019			
$[Zn^{II}(hbqi)_2]$					2.003		7.0	1.9	2.006			
$[Cu^{II}(hbqi)_2]$	2.198[b], 2.095[d]	[c]122[c]			2.003				2.006			
$[Cd^{II}(hbqi)_2]$					2.003		6.5	2.1	2.007			
$[Co^{III}(hbqi)(hbsqi)]$	2.005	9.2		3.4	2.003	14.6		14.6	2.005[e]	15.9	7.6	4.1 (2 H), 2.6 (2 H)

[a] All coupling constants are reported in Gauss. [b] $g_{\parallel}$ at 128 K. [c] $A_{\parallel}{}^{Cu}$. [d] $g_{\perp}$ at 128 K. [e] Value for the central multiplet shown in Figure 7(*b*).

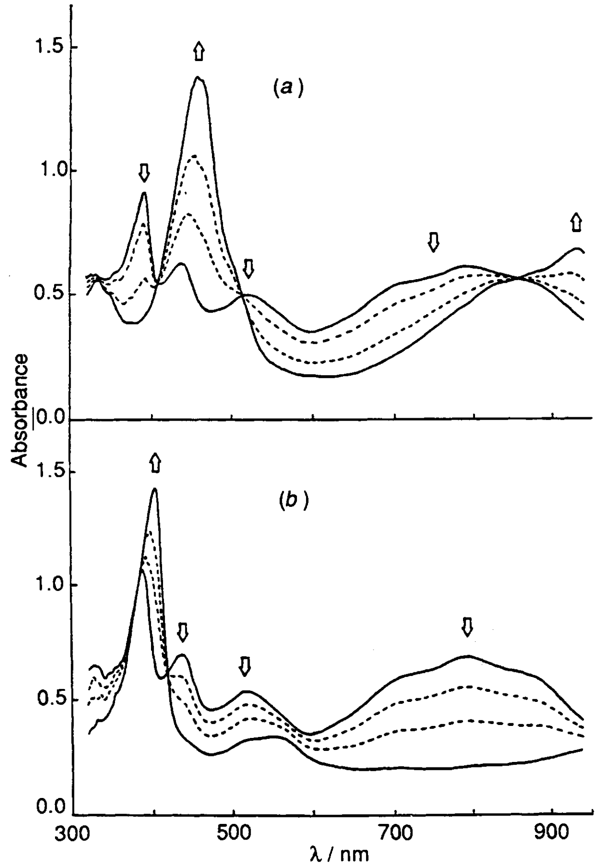

Figure 3. U.v.–visible spectral changes observed for $[Co^{III}(hbqi)(hbsqi)]$ in CH_2Cl_2, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$ during (*a*) one-electron controlled-potential oxidation at +0.40 V and (*b*) one-electron controlled-potential reduction at −0.70 V. The initial and final spectra are given by solid lines and the intermediate spectra by broken lines

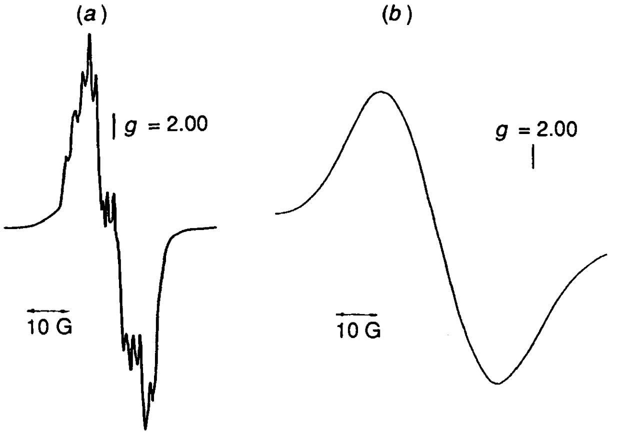

Figure 4. Room-temperature e.s.r. spectra obtained after controlled-potential reduction of (*a*) $[Zn^{II}(hbqi)_2]$ at −0.82 V and (*b*) $[Ni^{II}(hbqi)_2]$ at −0.84 V in CH_2Cl_2, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$

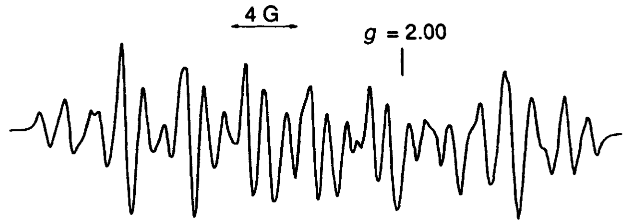

Figure 5. Room-temperature e.s.r. spectrum obtained after controlled-potential oxidation of $[Cd^{II}(hbqi)_2]$ at 1.20 V in CH_2Cl_2, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$

amino)-4,6-di-t-butyl-*o*-benzosemiquininone, obsq] which would have 27 lines if the unpaired electron interacted with one nitrogen and two sets of two equivalent hydrogens. The spectrum obtained after bulk electro-oxidation of $[Cd^{II}(hbqi)_2]$ in CH_2Cl_2, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$ is shown in Figure 5 and has twenty-six resolved lines, several of which show additional unresolved splittings. Similar spectra are obtained for each oxidized $[M^{II}(hbqi)_2]$ complex. The spectrum of oxidized $[M^{II}(hbqi)_2]$ differs from both the theoretical and experimentally observed spectrum of oxidized hbqi and was analyzed in terms of an interaction of the unpaired electron with one nitrogen ($A^N \approx 11.8$ G) and two sets of two hydrogens [A^H = 3.5 (2 H) and 1.5 G (2 H)].

$[Cu^{II}(hbqi)_2]$. The e.s.r. spectrum of magnetically diluted $[Cu^{II}(hbqi)_2]$ (5% w/w in 3,5-di-t-butylcatechol) at 298 K is shown in Figure 6(*a*). The value of $g_{\parallel}$ (2.032) is less than $g_{\perp}$ (2.182) and $A_{\parallel}{}^{Cu}$ = 105 G and these results agree with values of 2.028 ($g_{\parallel}$), 2.226 ($g_{\perp}$), and 105 G ($A_{\parallel}{}^{Cu}$) given in the literature for the same compound under similar experimental conditions.[1] Solid samples of $[Cu^{II}(hbqi)_2]$ doped in either 3,5-di-t-butylcatechol or $[Zn^{II}(hbqi)_2]$ also have the same spectral patterns between 298 and 128 K.

Millimolar solutions of $[Cu^{II}(hbqi)_2]$ in CH_2Cl_2 at 298 K show a broad e.s.r. signal centred at g = 2.140 which is similar to a room-temperature spectrum reported in the literature.[1] The low-temperature spectrum of $[Cu^{II}(hbqi)_2]$ in CH_2Cl_2 is shown in Figure 6(*b*) and has never been reported. Surprisingly, the value of $g_{\parallel}$ (2.198) is greater than $g_{\perp}$ (2.095), which contrasts with the order of g values observed for the same species in the solid state.

The e.s.r. spectrum of singly reduced $[Cu^{II}(hbqi)_2]$ has

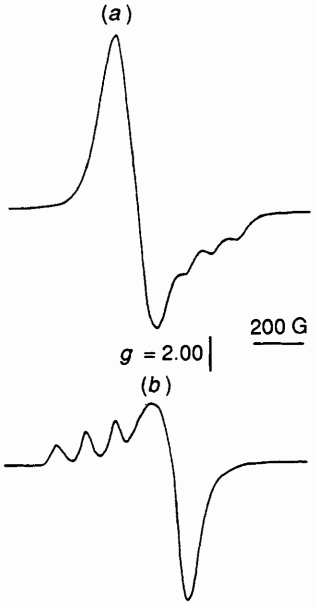

Figure 6. E.s.r. spectra of [$Cu^{II}(hbqi)_2$] (*a*) in 3,5-di-t-butylcatechol ($\approx 5\%$ w/w copper complex) at 298 K and (*b*) in CH_2Cl_2 (≈ 1 mmol dm^{-3}) at 128 K

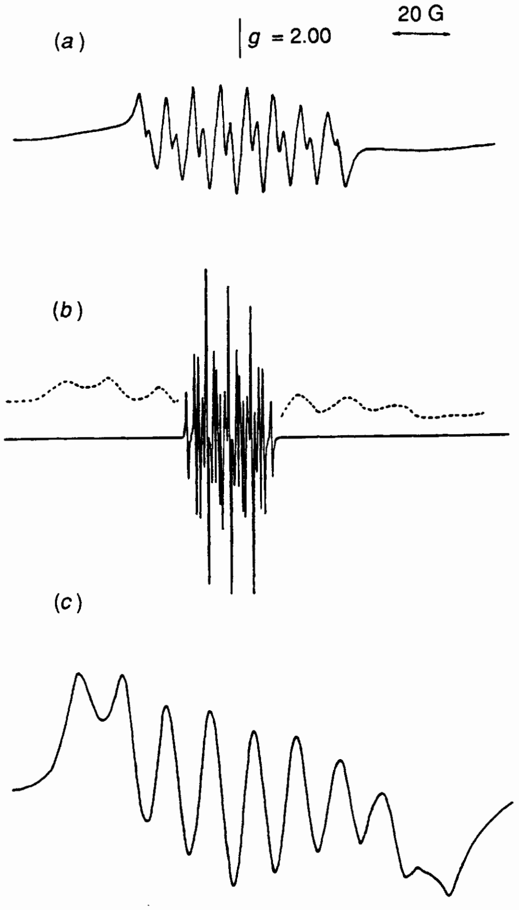

Figure 7. Room-temperature e.s.r. spectra of [Co^{III}(hbqi)(hbsqi)] in CH_2Cl_2, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$ (*a*) before controlled-potential oxidation or reduction, (*b*) after controlled-potential oxidation at +0.40 V, and (*c*) after controlled-potential reduction at −0.70 V. The central multiplet and the broad signals at its wings in (*b*) are obtained at modulation amplitudes of 0.2 (——) and 4.0 G (– – – –), respectively

complex multiplets with an intensity ratio that could not be analyzed in terms of any conceivable model of hyperfine coupling. For this reason the spectrum was not analyzed with respect to a possible structure.

[Co^{III}(hbqi)(hbsqi)]. The neutral, singly oxidized, and singly reduced [Co^{III}(hbqi)(hbsqi)] complexes all show room-temperature e.s.r. spectra in CH_2Cl_2, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$. These spectra are illustrated in Figure 7 and the spectral data are summarized in Table 3. The measured spin intensity almost doubles after either reduction or oxidation of the complex and this is consistent with the electro-oxidized or electroreduced product containing two unpaired electrons. An analysis of the spectra for these electrogenerated derivatives also suggests that there are two unpaired electrons in the singly oxidized and singly reduced products.

The initial [Co^{III}(hbqi)(hbsqi)] complex has a signal centred at $g = 2.005$ [Figure 7(*a*)] and can be analyzed in terms of one unpaired electron interacting with the cobalt nucleus ($I = \frac{7}{2}$) and a hydrogen. The hyperfine coupling values for these ineteractions are $A^{Co} = 9.2$ G and $A^{H} = 3.4$ G, both of which are similar to values reported for the compound in toluene.[2]

The spectrum of singly oxidized [Co^{III}(hbqi)(hbsqi)] [Figure 7(*b*)] exhibits a central complex multiplet pattern for a modulation amplitude of 0.2 G. This results from an interaction of the unpaired electron with one nitrogen and two sets of two equivalent hydrogens. Additional broad signals are also observed at both ends of this spectrum when the modulation amplitude is set to 4.0 G [see broken line in Figure 7(*b*)]. These signals are equally spaced and number eight, including two 'hidden' lines inside the main intense multiplet. No additional splittings are observed for the eight broad lines, even at modulation amplitudes as low as 0.5 G.

The e.s.r. spectrum of singly reduced [Co^{III}(hbqi)(hbsqi)] [Figure 7(*c*)] is centred at $g = 2.003$ and has peaks which are separated by 14.6 G. Additional lines are not observed when the modulation amplitude is varied over a range of 1.0—5.0 G. Thus, the observed nine-line spectrum might suggest that there is an interaction of the unpaired electrons with the cobalt nucleus and a proton, as is the case for the neutral complex.

Discussion

It has been suggested that the oxidation of hbqi will result in a ligand having a 'benzoquinone-like' structure with double carbon–oxygen and carbon-nitrogen bonds.[2b] This would lead to a lowering of the complexing ability of the oxidized ligand (*i.e.* obsq) (compared to that of hbqi) and dissociation from the metal after electro-oxidation of [$M^{II}(hbqi)_2$]. The first oxidation of each [$M^{II}(hbqi)_2$] complex is irreversible on the bulk electrolysis time-scale and the voltammetric data are consistent with the generation of a radical obsq ligand[2c] which then dissociates. The rate of this ligand dissociation is fast and, according to the scan-rate and temperature-dependence data from the cyclic voltammograms in Figure 1, follows the order: Cd > Cu > Zn > Ni. E.s.r. data for the oxidation product (Figure 5) suggest that the dissociated ligand is similar to, but not identical with obsq.

It was not possible to isolate any of the singly oxidized complexes on the spectroelectrochemical time-scale other than the one generated from [Co^{III}(hbqi)(hbsqi)]. A disproportionation reaction has been reported to occur after electro-oxidation of iron,[9] vanadium,[20] nickel,[21] and zinc[22] catecholate or semiquinonate complexes in aprotic media but a similar reaction does not appear to occur for electro-oxidized [$M^{II}(hbqi)_2$] in CH_2Cl_2, 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$.

Spectroelectrochemical data provide no information with respect to the metal–ligand bonding properties in [$M^{II}(hbqi)_2$] and this is not surprising since the spectral bands between 350 and 900 nm are due to ligand-based transitions.[1] Nevertheless, the decreased band intensity after electro-oxidation or electroreduction is consistent with both electron transfers involving ligand-based orbitals.

The e.s.r. data for singly reduced [Zn^{II}(hbqi)$_2$] and [Cd^{II}(hbqi)$_2$] suggest that the unpaired electron is localized on only one of the two ligands in electrogenerated [M^{II}(hbqi)(hbsqi)]$^-$ [2c] (where M = Zn or Cd) and further suggests that this electron interacts with one nitrogen and four hydrogens of the hbsqi radical.[19] This is similar to the case of SnPh$_2$(hbsqi),[23a] where the unpaired electron interacts with the nitrogen and two sets of equivalent hydrogens. Singly reduced [Ni^{II}(hbqi)$_2$] has a broad e.s.r. signal which may indicate the formation of a nickel(II)-stabilized ligand radical species, as is the case for singly reduced [Ni(cbqo)$_2$] (cbqo = 4-chloro-1,2-benzoquinone 2-oximate).[23]

E.s.r. data for [Cu^{II}(hbqi)$_2$] in the solid state indicate that the unpaired electron occupies the d_{z^2} orbital of the Cu^{II} and that the complex has an axially compressed tetragonal distortion.[1,24,25] On the other hand, it should be noted that the majority of other tetragonally distorted, six-co-ordinate copper complexes have $g_{\parallel} > g_{\perp}$ which is consistent with an elongation or a weaker field along the tetragonal axis.[26] The spectrum of [Cu^{II}(hbqi)$_2$] in Figure 6(*b*) exhibits features similar to the above copper(II) complexes and is consistent with a tetragonally distorted ligand geometry and axial elongation. The fact that $g_{\parallel}$ is greater than $g_{\perp}$ suggests that the unpaired electron is situated in the $d_{x^2-y^2}$ orbital.[26]

Temperature-dependent structural changes have been reported for several copper(II) complexes containing *o*-quinone type ligands. For example, [Cu^{II}(dbsq)$_2$] (dbsq = 3,5-di-t-butyl-*o*-benzosemiquinone) and [Cu^{II}(bipy)(dbcat)][13] (bipy = 2,2′-bipyridine and dbcat = 3,5-di-t-butylcatecholate) both undergo a dimer–monomer equilibrium upon going from the solid state to frozen liquid solutions.[27] A change in structure of the monomeric copper(II) complex has not been reported nor is there a cross-over of the $g_{\parallel}$ and $g_{\perp}$ values for metal–quinone complexes. Thus, the observed cross-over upon going from the solid state to CH$_2$Cl$_2$ solutions of [Cu^{II}(hbqi)$_2$] is novel in that it provides the first example in metal-quinone chemistry.

The addition of one electron to [Co^{III}(hbqi)(hbsqi)] may occur at the metal or at the hbqi ligand.[2c] The observed nine-line splitting pattern in Figure 7(*c*) and the small coupling constant of 14.6 G both seem to suggest a ligand-based reduction to generate [Co^{III}(hbsqi)$_2$]$^-$. The two hbsqi radicals in the reduced complex do not interact with each other but rather appear to interact independently with the cobalt nucleus and one hydrogen.

The first one-electron oxidation of [Co^{III}(hbqi)(hbsqi)] has been postulated to produce [Co^{III}(hbqi)$_2$]$^+$ [2c] which would be e.s.r. silent. However, as seen in Figure 7(*b*), the oxidized cobalt complex does have an e.s.r. spectrum and this spectrum seems to result from a sum of signals due to two species. The central part of the spectrum shows coupling of an unpaired spin to one nitrogen and to two sets of two hydrogens while the other unpaired electron shows only a cobalt hyperfine structure with a coupling constant of 15.9 G. One possible explanation for these features is that a disproportionation occurs after oxidation of [Co^{III}(hbqi)(hbsqi)] to give [Co^{III}(obsq)(hbqi)]$^{2+}$ and [Co^{III}(hbsqi)$_2$]$^-$ in solution. [Co^{III}(hbsqi)$_2$]$^-$ should exhibit e.s.r spectral features similar to those shown in Figure 7(*c*) and is different from what is actually obtained for singly oxidized [Co^{III}(hbqi)(hbsqi)] [Figure 7(*b*)]. Furthermore, a bulk electrolysis of the neutral complex at +0.40 V gives only 1.0 ± 0.1 electrons transferred. There is a fairly well defined current–time curve during reduction which indicates the absence of coupled chemical reactions. Thus, both e.s.r. and voltammetric data suggest that a disproportionation of the oxidized cobalt complex does not occur.

All of the data are self consistent in indicating that the one-electron oxidation of [Co^{III}(hbqi)(hbsqi)] generates [Co^{III}(obsq)(hbsqi)]$^+$. The unpaired electron on the obsq ligand in this oxidized complex interacts with one nitrogen and two sets of two hydrogens. The unpaired electron on the hbsqi ligand which was originally coupled with the cobalt nucleus and one proton then becomes localized close to the cobalt atom in [Co^{III}(obsq)(hbsqi)]$^+$ after electro-oxidation. This results in an increase in the coupling constant, A^{Co}, from 9.2 G in the initial complex to 15.9 G in the oxidized species. There is an apparent lack of interaction between the two unpaired spins and this may indicate the presence of mutually orthogonal spin orbitals in the singly oxidized cobalt complex.[28] As discussed earlier, this is also true for the singly reduced cobalt complex.

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