Complexing and Protonation of Free-radical Imidazolin-1-oxyl and Imidazolin-1-oxyl 3-Oxide Ligands: a Magnetic-resonance Investigation

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Free-radical ligands consisting of 4,4,5,5-tetramethyl-Δ^2-imidazolin-1-oxyl 3-oxide, (II), or 4,4,5,5-tetramethyl-Δ^2-imidazolin-1-oxyl, (I), fragments with diamagnetic 2-substituents R [R = 2-pyridyl(py), 6-bromo-2-pyridyl (6-Brpy), 3-bromophenyl (3-BrPh), and Ph] are described and their interactions with closed-shell ions of non-zero nuclear spins (H^+, Li^+, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) are discussed. Unpaired spin density on the ligands is distributed over both imidazoline nitrogen atoms, and metal or proton hyperfine (h.f.) splittings appear in the e.s.r. spectra on interactions, so that electronic effects can be monitored. Protonations are fast on the e.s.r. time scale (τ *ca.* 3×10^{-8}), while complex lifetimes are long ($\tau \gg 10^{-7}$). Interaction with Li^+ does occur, but is too transient to be observable by e.s.r. spectroscopy. The derivatives (II) can be protonated but do not complex, while (I) both protonate and complex at the N(3) atom. For a given ligand e.s.r. spectrum, changes in ^{14}N h.f. splittings on complexing are closely correlated with determined complex-formation constants, K_f. For (I; R = py), unpaired electron delocalization increases by as much as 0·5 Å on co-ordination, and increases proportionately with K_f, as shown by matrix ENDOR. The diamagnetic 2-substituent R has a pronounced effect on the protonation and complexing interactions. Pseudo-first-order rate constants for protonation at N(3) in (I) increase from 3×10^6 to 1×10^9 l mol^{-1} s^{-1} on going from R = py to Ph, while complex K_f values decrease by one or two orders of magnitude. Electronic requirements on the imidazoline ring in chelated complexes of (I; R = py) are much smaller than in those of the unidentate ligands where R = 6-Brpy, 3-BrPh, and Ph, as shown by h.f. splittings of the e.s.r. spectra.

Electron spin resonance (e.s.r.) is perhaps the most revealing physical technique employed in the study of paramagnetic metal complexes. Such studies have traditionally focused on the hyperfine interaction of the unpaired electron on the metal with the magnetic nuclei of diamagnetic ligands. The converse approach, in which the unpaired electron residing on the ligand is perturbed by the bonding interaction with the metal, has obvious advantages but has until recently been hampered by a paucity of suitable paramagnetic ligands of sufficient stability and chemical interest.

Eaton has identified complexes of the *o*-semiquinone radical with bivalent Mg, Ca, Zn, and Cd from changes in proton hyperfine (h.f.) coupling constants in metal-ion solutions,[1] and several workers have investigated complexes of aliphatic nitroxides,[2] of α-di-imine radical anions,[3] and nitroxides in which the radical site does not participate in co-ordination.[4] In this work we examine the e.s.r. spectra of several aromatic chelating or unidentate imidazolin-1-oxyl radical ligands in the presence of d^{10} metal nitrates with non-zero nuclear spins to determine the chemical and physical parameters of the co-ordination interaction. These *N*-oxide ligands are well suited for e.s.r. complexation studies because they exhibit resolved h.f. lines for both nitrogen atoms on the imidazoline ring, with unpaired spin density residing partially on the ligand co-ordination site. E.s.r. spectra of organic imidazolin-1-oxyl compounds have been discussed by Ullman *et al.*, but interactions with metals were not reported.[5] A preliminary account of this study has appeared elsewhere.[6]

E.s.r. studies on stable free-radical ligand interactions with metal ions and acids may provide several of the following parameters: extent of complexation or solution equilibria, lifetimes of the interactions, base strengths, solvation effects, electron-density and electron-

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spin delocalization within the ligand and onto the metal ion, and molecular dynamics of the resulting complex. N.m.r. and double-resonance techniques (both ENDOR [7] and DNP [8]) further supplement this information.

Metal complexes of the biochemically important [9] imidazoline derivatives should be of general interest because of their applicability to metal–ligand bonding studies, and because they open the possibility for spin labelling of metal sites in enzyme systems. Specific chemical interactions with metal ions, and the effect of solvent, co-ligand, and anion co-ordination on the e.s.r. spectra of imidazolin-1-oxyl complexes are still under investigation.[10]

THEORY

The interaction of an unpaired electron spin with an atomic nucleus of spin I splits the e.s.r. line into $(2I + 1)$ components. The magnitude of the hyperfine splitting, a_Y, depends on the amount of unpaired spin density in a π-orbital of atom Y and on the amount of spin polarization of Y due to the presence of unpaired spin on the neighbouring atom X.[11] The magnitude of a_Y can be related to the π-spin density ρ^π on atoms Y and X by the Karplus–Fraenkel relation (1).[12] It has been shown that for a

$$a_Y = Q_Y{}^Y\rho_Y{}^\pi + Q_{XY}{}^Y\rho_X{}^\pi \qquad (1)$$

nitroxide spin site, $Q_N{}^N$ and $Q_{ON}{}^N$ are $23{\cdot}4 \pm 1{\cdot}5$ and $4{\cdot}2 \pm 0{\cdot}8$ G, respectively.[13] For an imine spin site the second part of equation (1) has been shown to be negligible,[11] so that for the present series of ligands the imine nitrogen h.f. splitting can be described adequately by the approximate relation (2). As Q values are known for several types of

$$a_N = Q_N{}^N\rho_N{}^\pi \qquad (2)$$

nitrogen radicals, the unpaired π-spin density on N can be calculated from the observed a_N.[14] For the protonation interaction at a nitrogen spin site, a_H is given by the second part of equation (1), so that we obtain (3).

$$a_H = Q_{NH}{}^H\rho_N{}^\pi \qquad (3)$$

For complexation interactions of a free-radical imine, ligand hyperfine coupling due to the nuclear spin on the metal M is given by equation (4). In contrast to the

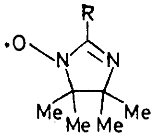
$$a_M = Q_M{}^M\rho_M{}^\pi + Q_{NM}{}^M\rho_N{}^\pi \qquad (4)$$

previous cases, both terms in equation (4) may contribute equally to a_M, and the two Q values may moreover have indeterminate sign. Only a_M is measured directly in solution, but $\rho_N{}^\pi$ can be obtained from a_N. Equation (4) can still not be evaluated as the relative magnitudes of Q are still not known. However, it can be assumed that Q values for a series of closely related ligands will not change significantly, so that changes in $\rho_M{}^\pi$ can be estimated from a series of a_M and a_N values. For simple nitroxide adducts, Cohen and Hoffman were able to obtain $\rho_M{}^\pi$ values from e.s.r. parameters of frozen-solution powder patterns.[2a]

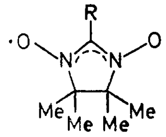
The spatial extent of unpaired electron delocalization can be measured by matrix ENDOR. Electron nuclear double resonance is the technique in which n.m.r. signals of nuclear spins coupled to an electron spin are saturated and resulting changes in the e.s.r. signal amplitude are measured.[15] ENDOR of disordered solids (frozen radical solutions) always lead to the detection of a broad line centred at the free nuclear-precession frequency. This line has been termed the matrix ENDOR line; [16] it arises from the electron nuclear interaction of the unpaired radical electron with coupled solvent nuclei of non-zero nuclear spins. It has been shown both theoretically and experimentally [17,18] that increasing delocalization of an unpaired radical electron leads to narrower matrix ENDOR lines. The average delocalization radius, $\bar{a}$, is defined as the distance from the paramagnetic centre to the particular matrix protons of the solvent at which the electron nuclear Fermi-contact coupling has become negligible. $\bar{a}$ Values are obtained by matching experimental and simulated line-widths (full width at half height) using the $\alpha = 80$ KHz standard calibration curve.[17] Different values of α slightly change the absolute magnitudes of calculated $\bar{a}$ values, but do not affect the changes in $\bar{a}$ within a series of similar compounds.

RESULTS

The ligands used in this work consist of paramagnetic imidazolin-1-oxyl 3-oxide, (II),[19] or imidazolin-1-oxyl, (I), fragments, with diamagnetic phenyl or pyridyl substituents. Although the nitroxide group in dialkyl and cyclic nitroxides has been found to co-ordinate to some metal ions,[2] e.s.r. spectra of the oxyl nitroxides showed no evidence of interaction with metal ions such as Li$^+$, Hg^{2+}, or Pt^{2+}. Because of the presence of the electron-withdrawing 1-oxyl substituent, imidazolin-1-oxyl radicals by themselves do not co-ordinate as strongly as analogous diamagnetic imidazoline ligands,[20] yet they do form weak to strong complexes with metal ions in solution depending on the extent of participation in bonding by the diamagnetic



(I) R = Ph, 3-BrPh, 2-py, and 6-Brpy



(II) R = Ph, 3-BrPh, 2-py, and 6-Brpy

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substituents R. Figure 1 illustrates the changes that occur in the nitrogen h.f. structure of (I; R = 2-py) e.s.r. spectra in the presence of bivalent Hg, Cd, and Zn nitrate salts in aqueous solution. The presence of unpaired spin on the imine nitrogen as well as on the 1-oxyl group allows facile detection of the actual co-ordination site. Metal h.f. structure was also observed for the Ag, Cd, Hg, and Pb isotopes of nuclear spin ½. The low natural abundance of ^{67}Zn precluded the detection of Zn h.f. structure. The intensities of observed metal h.f. lines are consistent with the relative natural abundances of the non-zero spin isotopes; ^{111}Cd and ^{113}Cd have nearly the same nuclear moments and act equivalent. Solution e.s.r. spectra did not reveal any interaction between (I; R = 2-py) and alkali metals or alkaline earths. This result is in contrast to the behaviour of α-di-imine radical ions.[3]

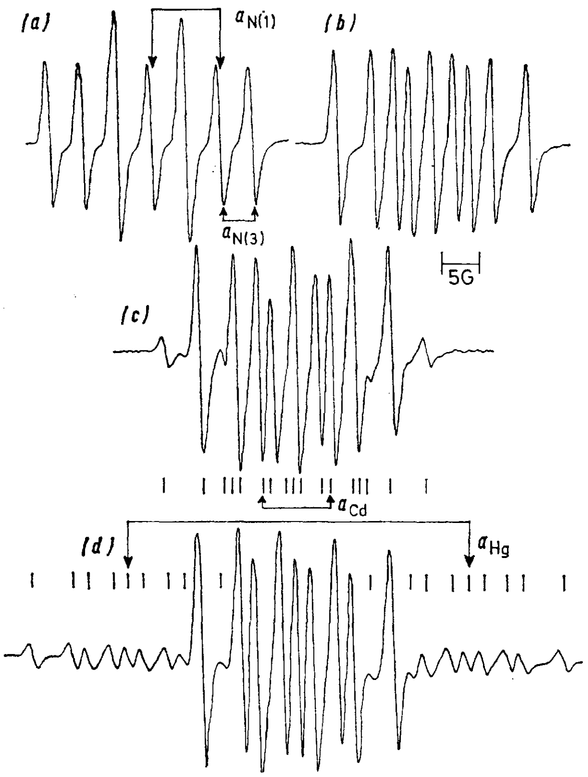

FIGURE 1 E.s.r. spectra of (*a*) 10^{-3}M-(I; R = py), (*b*) aqueous 0·5M-Zn(NO$_3$)$_2$–10^{-3}M-(I; R = py), (*c*) aqueous 0·5M-Cd(NO$_3$)$_2$–10^{-3}M-(I; R = py), and (*d*) aqueous 0·5M-Hg(NO$_3$)$_2$–10^{-3}M-(I; R = py)

Metal complexes with other ligands (I) have also been observed, but only at higher metal-ion concentrations. Table 1 lists isotropic h.f. splitting constants in aqueous and ethanol solution. Nitroxide N(1) and imine N(3) nitrogen h.f. splittings generally changed by similar percentages on co-ordination, with N(1) decreasing and N(3) increasing. Complexes were easily observable for (I; R = 2-py and 6-Brpy) under the conditions specified in Table 1, while equilibrium concentrations of complexes with (I; R = Ph and 3-BrPh) were fairly low. In ethanol, nitrogen h.f. splittings were generally smaller than in aqueous solution.

N-Oxyl nitroxides (II) react with aqueous acids to give diamagnetic products,[19] but can be protonated by trifluoroacetic acid without loss of e.s.r. signal intensity. *N*-Oxyl species (I) are weak bases that can be protonated by trifluoroacetic or aqueous acids with some decomposition at pH <0. E.s.r. spectra of the four compounds (I) were obtained in aqueous HCl from pH 7 to -1 as described for R = Ph by Ullman.[5] Nitrogen h.f. splitting constants changed continuously over the entire pH range, with N(1) decreasing and N(3) increasing with increasing acidity (Figure 2). As individual e.s.r. spectra for free and protonated radicals were not observed, spectral averaging is occurring, and pK_a = pH at the inflection point of the pH against a_N curve. Table 1 also lists pK_a values for the imidazolin-1-oxyl group of the ligands (I). We obtain pK_a = 1·6 ±

TABLE 1

E.s.r. h.f. splitting constants (in G) for N(1) and N(3) and metal-ion nuclei of ligands and metal complexes in H$_2$O and EtOH[a]

		In H$_2$O			In EtOH		
Compound	pK_a[b]	$a_{N(1)}$	$a_{N(3)}$	a_M	$a_{N(1)}$	$a_{N(3)}$	a_M
(I; R = 2-py)	−0·7	9·25	4·25		8·7	4·3	
Hg^{II}		7·6	5·2	46	7·0	5·6	45
Zn^{II}		8·0	4·9		7·4	4·8	
Cd^{II}		8·1	5·0	10·8	7·5	5·1	9·6
Ag^{I}		8·2	5·1	2·1[c]	7·5	5·2	2·1[e]
Pb^{II}		8·4	4·8		8·5	4·6	
Pb^{II}[d]		8·3	5·1	13·9	7·8	5·4	16·6[e]
(I; R = 6-Brpy)	0·6	9·4	4·4		8·6	4·2	
Hg^{II}		7·1	5·8	76	6·7	6·1	66
Zn^{II}		7·6	5·0		7·2	5·1	
Cd^{II}		8·1	5·2	9·5	7·5	5·0	10·4
Ag^{I}		8·4	5·3	2·3[c]	7·8	5·2	2·3[e]
Pb^{II}		8·9	4·6		*f*		
Pb^{II}[d]		8·6	5·1		7·5	5·2	17·1
(I; R = Ph)[g]	1·6	9·6	4·25		8·8	4·3	
Hg^{II}		6·8	5·3	77	6·5	5·4	72
Ag^{I}		8·9	5·0	$<$1·4[h]	*f*		
(I; R = 3-BrPh)[g]	1·0	9·6	4·2		8·8	4·3	
Hg^{II}		6·8	5·5	76	*f*		
Ag^{I}		8·9	5·2	$<$1·4[h]	*f*		

[a] All metals as nitrate salts except where indicated. [b] In aqueous HCl solution; all data ±0·2. [c] ^{107,109}Ag (I = ½) H.f. splitting was only observed when metal-ion and ligand concentrations were approximately equal. [d] As sat. Pb(ClO$_4$)$_2$ solution. [e] ^{207}Pb (I = ½). [f] No or little complexation was observed due to low K_f and/or low metal-salt solubility. [g] No complexation was observed for unlisted metal ions. [h] H.f. linewidth broadening of 1·4 G over pure ligand linewidth.

0·2 for (I; R = Ph) which is comparable to the value of 1·9 ± 0·1 obtained by Ullman. The observed trend in imidazoline base strength is R = Ph > 3-BrPh ⩾ 6-Brpy ≫ py.

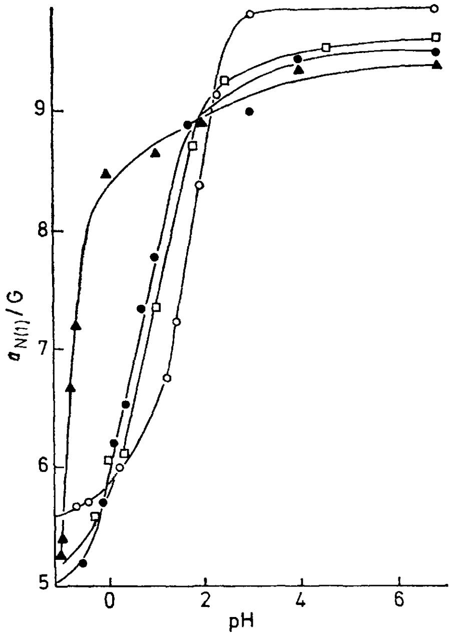

FIGURE 2 Plots of e.s.r. N(1) h.f. splitting against pH for HCl solutions of ligands (I): R = py (▲), 6-Brpy (●), Ph (○), and 3-BrPh (□)

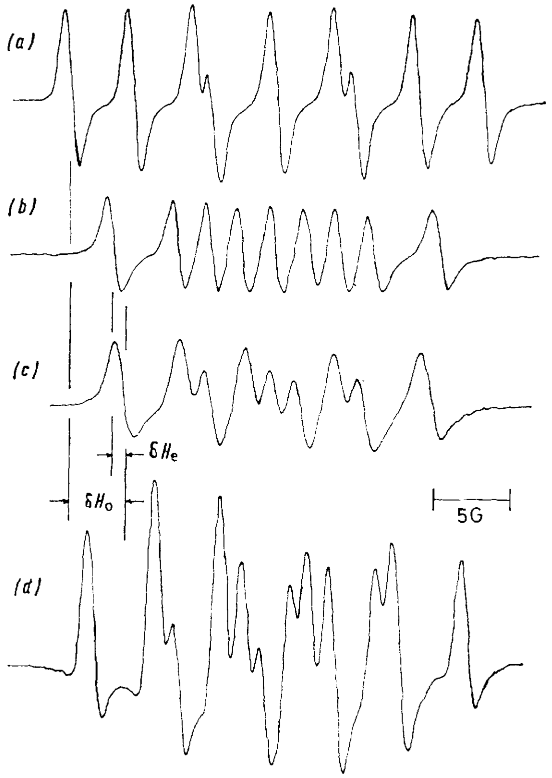

FIGURE 3 E.s.r. spectra of (I; R = py) in HCl solutions at pH values of (a) 7—10, (b) 2·0, (c) −0·7, and (d) −1·0. δH_e And δH_0 are the line separations in the presence and absence of interconversion, respectively

The contrasting protonation and complexation results are shown in Figures 3 and 4. Only 1 : 1 metal complexes were formed in aqueous and alcohol solutions. At low [M] the e.s.r. spectrum was a composite of signals due to free and complexed ligand. The ratio [M(I)] : [(I)] could be determined sufficiently well from a single e.s.r. spectrum at low radical concentration to give a K_f value with 10—20% uncertainty. Formation constants ranged from $<10^{-2}$ to 7×10^{3} l mol^{-1} in water and up to 5×10^{4} l mol^{-1} in ethanol, depending on the metal and the diamagnetic substituent R (Table 2).

Matrix ENDOR spectra in EtOH glasses at 73 K consisted of a single line (the matrix EtOH proton line) centred at the free nuclear-precession frequency at 13—14 MHz. The full width at half-height linewidths increased from 0·66 to 0·77 to 0·82 MHz for Hg(I; R = 2-py) to Pb(I; R = 2-py) to free (I; R = 2-py), respectively.

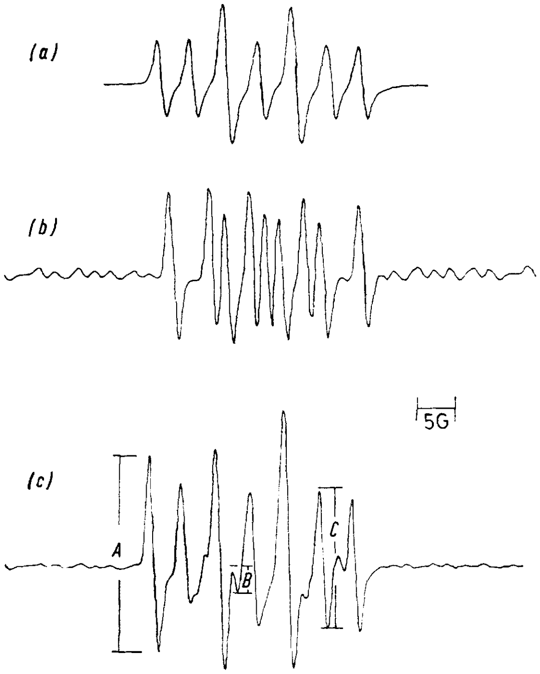

FIGURE 4 E.s.r. spectra of (a) $1{\cdot}3 \times 10^{-3}$M-(I; R = py), (b) $6{\cdot}5 \times 10^{-4}$M-(I; R = py)–4×10^{-2}M-Hg^{II}, and (c) $6{\cdot}5 \times 10^{-4}$M-(I; R = py)–4×10^{-4}M-Hg^{II}; B is a measure of [Hg(I; R = py)] because there is little spectral overlap at that field, C is a measure of [(I; R = py)], and A = [(I; R = py)] + [Hg(I; R = py)]. For Hg^{II}, ^{199}Hg h.f. lines provide an additional check of [Hg(I; R = py)]

DISCUSSION

Ligands.—The nitrogen π-spin densities for ligands (I) and (II) can be calculated from the Karplus–Fraenkel equation,[14,21] equation (1) or (2), with $Q_N^N = 26{\cdot}5$ G for the *N*-oxyl nitroxides and for N(1) of the imidazolin-1-oxyl and $Q_{N(3)}^N = 24{\cdot}3$ G. Unpaired spin density in the *N*-oxyl nitroxides is distributed equally between the two nitroxide components with $\rho_N^{\pi} = 0{\cdot}3$ and $\rho_O^{\pi} = 0{\cdot}13$ on each side.[22] These values are about half the spin

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densities found for the localized NO group in aliphatic dialkyl nitroxides.[13] Unpaired spin density in imidazolin-1-oxyl radicals is distributed unequally between the nitroxide group ($\rho_{N(1)}^{\pi} \approx 0{\cdot}38$ and $\rho_{O}^{\pi} \approx 0{\cdot}4$) and the imidazoline imine ($\rho_{N(3)}^{\pi} \approx 0{\cdot}16$), with only slight amounts of unpaired spin density on the imidazoline bridgehead carbon C(2), where $a_H = 1{\cdot}5$ G.[5]

The aromatic R groups in ligands (I) and (II) do not participate to any significant extent in the electron-spin delocalization. In the four py derivatives, the py nitrogen lone electron pair points toward the paramagnetic part of the ligand only 2 Å away in (II).[23] But judging from the absence of e.s.r. line broadening for R = py compared to R = Ph, there is no through-space spin delocalization from the *N*-oxyl nitroxide or imidazolin-1-oxyl group to the py ring nitrogen. Proton [24] and ^{13}C n.m.r. spectra [25] for (II; R = Ph or py) indicate carbon π-spin densities of at most 0·02; our results for the Br-substituted *N*-oxyl nitroxides are analogous. In the imidazolin-1-oxyl radicals the lack of unpaired spin density at the imidazoline bridgehead carbon ($\rho_{C}^{\pi} \approx 0{\cdot}06$) further precludes spin delocalization into the attached aromatic ring.

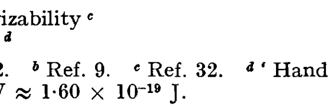
TABLE 2

Logarithms of stability constants (K_f or K_1) in solution at 25 °C

Ligand	Solvent	Co-ordinating ion H^+	Ag^{I}	Zn^{II}	Cd^{II}	Hg^{II}	Pb^{II}
(I; R = 2-py)	H_2O	−0·7 (K_2)	3·45	2·98	2·94	3·85	0·89
	EtOH		3·0	3·59	3·14	4·74	1·43
(I; R = 6-Brpy)	H_2O	+0·6	1·67	0·11	0·80	3·30	*a*
	EtOH		1·79	*a*	0·85	4·0	*a*
(I; R = 3-BrPh)	H_2O	+1·0	*a*	*a*	*a*	2·15	*a*
(I; R = Ph)	H_2O	+1·6	1·17	*a*	*a*	2·27	*a*
	EtOH					2·3	
Imidazole	H_2O [b]	7·11	3·1	2·52	2·80	16·7 (β_2)	
py	H_2O [b]	5·21	2·0	0·88	1·30	5·1	
Molar polarizability [c]			4·33	0·72	2·74	3·14	9·3
Ion i.p., eV [d]			7·5	17·9	16·9	18·7	15·0

[a] $pK_f \leqslant -2$. [b] Ref. 9. [c] Ref. 32. [d] 'Handbook of Chemistry and Physics,' 46th edn., Chemical Rubber Co., Cleveland, 1964, p. E-61; 1 eV ≈ $1{\cdot}60 \times 10^{-19}$ J.

E.s.r. spectral changes on ligand protonation or complexing depend on adduct structures. The NO group in simple aliphatic nitroxides can be considered a three-π-electron fragment, with the unpaired electron occupying the π^* LCAO molecular orbital.[4,13] Interactions with protons or metal ions occur at a ligand molecular orbital which is largely a lone-pair (p_y) oxygen orbital.[4b] Co-ordination with an electron-pair acceptor favours the polar structure (B) over the neutral resonance form (A) by an inductive effect. This has the disconcerting


(A) (B)

result, as pointed out by Hoffman,[13] that while charge density is delocalized towards the co-ordinating oxygen atom, unpaired π-spin density moves towards the nitroxide nitrogen and a_N increases. Exactly the same argument can be invoked to explain e.s.r. spectral changes in the *N*-oxyl nitroxides, where co-ordination must also occur at an NO site.

The distribution of unpaired spin density over the imine nitroxide moiety of imidazolin-1-oxyl ligands can be visualized as arising from mixing of the half-filled LCAO nitroxide π^* orbital with the empty coplanar C=N π^* orbital. Co-ordination at the NO site should lead to the same kind of spectral changes as in the dialkyl nitroxides. However, co-ordination at the imine site N(3) will lead to the reverse pattern. The electron-pair acceptor co-ordinated at N(3) attracts electron density from the nitroxide side of the imidazolin-1-oxyl ring towards the imine side by the inductive effect, thus increasing $a_{N(3)}$. If electron density is withdrawn from the nitroxide side, resonance structure (B) becomes disfavoured and $a_{N(1)}$ must decrease on co-ordination.

Ligand Protonation.—In trifluoroacetic acid, one nitroxide site of all ligands (II) except R = py is completely protonated (a_H 4·6 ± 0·2 G). The e.s.r. spectrum of the latter compound shows only slight line broadening, so that protonation on the more basic diamagnetic py site seems to prevent protonation on the adjacent (*ca.* 2 Å) nitroxide oxygen atom. In contrast, normal protonation at a nitroxide site in (II) is observed for R = 6-Brpy. The 6-Br substituent next to the py nitrogen does not by itself prevent protonation at the more basic py ring, but it does prevent sufficiently close approach by a negatively charged counterion, so that protonation at the nitroxide oxygen site becomes the energetically more favoured interaction. In none of the ligands (I) and (II) studied was there any evidence for double protonation at the radical sites. In contrast to compounds (II), simple aliphatic nitroxides are not protonated as extensively in trifluoroacetic acid and therefore are weaker bases.[26]

In contrast to the *N*-oxyl nitroxides, all imidazoline-1-oxyl radicals are protonated at the imine nitrogen

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N(3) rather than at the nitroxide oxygen. For all ligands (I) except again R = py, proton h.f. splitting of $4{\cdot}6 \pm 0{\cdot}2$ G is observed in trifluoroacetic acid, while the e.s.r. spectrum of (I; R = py) in the same medium reveals a mixture of protonated and unprotonated N(3) imine sites. The larger separation of basic sites in (I) compared to (II) (R = py) allows some protonation of the imidazoline ring after the py ring nitrogen has become protonated.

E.s.r. spectroscopy can only detect protonation equilibria that affect electron spin-density distributions. The base strength for the molecule as a whole can be determined by direct titration as shown by Harkins and Freiser for substituted benzimidazoles.[27] As shown in Table 3, only the compound (I; R = py) among ligands (I) exhibits a substantially lower $\mathrm{p}K_\mathrm{a}$ by the e.s.r. method ($-0{\cdot}7$) than by direct titration ($+2{\cdot}60$), proving that initial protonation of (I; R = py) must occur at a diamagnetic site. The imidazoline base strengths of (I) vary from a $\mathrm{p}K_\mathrm{a}$ of 1·6 to $-0{\cdot}7$ in the order R = Ph $>$ 3-BrPh $\geqslant$ 6-Brpy $\gg$ py. The order of basicities is therefore the reverse of the order of stability constants in Table 2. That steric rather than electronic factors are responsible for the decrease in imidazolin-1-oxyl $\mathrm{p}K_\mathrm{a}$ values is demonstrated by the similarities in a_N and in a_H values among the protonated ligands (I).

TABLE 3

Nitrogen h.f. splittings, mean lifetimes, and pseudo-first-order rate constants for protonation of ligands (I)

Ligand	$a_{\mathrm{N}(1)}$/G	$a_{\mathrm{N}(3)}$/G	$10^8\tau$/s	k^a/l mol^{-1} s^{-1}	$\mathrm{p}K_\mathrm{a}$	
					$a_{\mathrm{N}(3)}$ [b]	(I) [c]
$\mathrm{H_2}$(I; R = 2-py)$^{2+}$	5·3	5·3	3	3×10^6	$-0{\cdot}7$	2·6
H(I; R = 6-Brpy)$^+$	5·2	5·2	4	6×10^7	$+0{\cdot}6$	
H(I; R = 3-BrPh)$^+$	5·3	5·3	2	4×10^8	$+1{\cdot}0$	
H(I; R = Ph)$^+$	5·3	5·3	3	1×10^9	$+1{\cdot}6$	2·8

[a] Calculated from $k \approx 1/\tau[\mathrm{H^+}]$ (I. C. Smith and A. Carrington, *Mol. Phys.*, 1967, **12**, 439). [b] From Figure 2; e.s.r. titration in HCl solution. [c] For the entire ligand in HCl solution.

For the protonation of (I; R = Ph) in HCl solution,[5] nitrogen h.f. splitting constants change continuously until the limiting values of $a_{\mathrm{N}(1)} = 5{\cdot}2$ and $a_{\mathrm{N}(3)} = 5{\cdot}3$ G are reached. Proton h.f. splitting of $a_\mathrm{H} = 4{\cdot}6$ G is not observed until the pH has been lowered to <1. We obtain the same type of averaged e.s.r. spectra for R = py, 6-Brpy, and 3-BrPh, except that the onset of observable proton h.f. splitting occurs at differing pH values.

Spectral averaging between two species occurs when $1/\tau \gg 2^{\frac{1}{2}}\pi(\delta\nu)$, where τ is the mean lifetime of the two species and $(\delta\nu)$ is the line separation in Hz.[28] The mean lifetime of the exchanging species can be calculated more quantitatively by means of equation (5),[29] where

$$[(\delta H_\mathrm{e})^2 - (\delta H_\mathrm{o})^2]^{\frac{1}{2}} = 2^{\frac{3}{2}}/\tau\gamma_\mathrm{e} \qquad (5)$$

$\gamma_\mathrm{e} = 1{\cdot}76 \times 10^7$ G^{-1} s^{-1} and δH_e and δH_o are the changes in spectral positions as illustrated in Figure 3. Equation (5) is valid when the field-shifted e.s.r. line has a linewidth less than δH. The τ values for ligands (I) (Table 3) are obtained at pH values near the equivalence points of the titration curves in Figure 2, and thus reflect chemically equivalent conditions. It is interesting to note that while the τ values are essentially the same (1×10^{-8}—4×10^{-8} s), the rate constants for the protonation reactions range from 3×10^6 to 1×10^9 l mol^{-1} s^{-1} and correlate well with the base strengths of the N(3) atoms.

Changes in the e.s.r. spectra of imidazolin-1-oxyl ligands on protonation reflect electrostatic effects, and thus provide a comparison for the more complicated interactions with metal ions. In the free ligands, unpaired spin density resides mainly on the nitroxide group ($\rho_{\mathrm{N}(1)}{}^\pi$ 0·36 and $\rho_\mathrm{O}{}^\pi$ 0·47). [In this and subsequent discussion, ρ^π values were calculated from equations (1)—(4) and are therefore approximate.] On protonation, $\Delta\rho_{\mathrm{N}(1)}{}^\pi = -0{\cdot}16$ and $\Delta\rho_{\mathrm{N}(3)}{}^\pi = +0{\cdot}05$, with the observed a_H 4·6 G completely accounted for by spin polarization by a nitrogen ($Q_{\mathrm{NH}}{}^\mathrm{N}$ -21)[11] with $\rho_\mathrm{N}{}^\pi$ 0·22. If unpaired spin density on the protonated ligand is entirely distributed between N(1), N(3), and O, then unpaired spin density on the oxygen atom must increase from 0·47 to 0·58 on co-ordination at the imine nitrogen N(3). A decrease in ($\rho_{\mathrm{N}(1)}{}^\pi + \rho_{\mathrm{N}(3)}{}^\pi$) of 0·1 is indeed observed on protonation, where back bonding to the ligand does not occur. Spectral changes on complexing with metal ions thus reveal the extent to which unpaired spin density is pulled from N(1) towards N(3).

Complexing Interactions.—The changes in nitrogen h.f. splittings that occur on complexing of imidazolin-1-oxyl ligands parallel the e.s.r. spectral changes in the protonation studies. The observed increase in $a_{\mathrm{N}(3)}$ and decrease in $a_{\mathrm{N}(1)}$ on complexing, and the appearance of metal h.f. coupling ($I \neq 0$), leads to the conclusion that co-ordination with metal ions in solution must also occur at the imine nitrogen N(3) (Table 1). The relative simplicity of the observed e.s.r. spectra (Figure 1) indicates lack of electron spin–spin coupling in ligand–ligand interactions, and indicates 1 : 1 metal–ligand stoicheiometry for these complexes. E.s.r. spectra at 77 K of $\mathrm{Ag^+}$, $\mathrm{Hg^{2+}}$, and $\mathrm{Pb^{2+}}$ frozen solutions containing excess of ligand lack the characteristic powder spectral features of 1 : 2 radical complexes observed by Clopath and v. Zelewsky in MTHF (2-methyltetrahydrofuran)

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glass for the α-di-imine radical-anion complex [Mg(glir)$_2$] [glir = glyoxal bis-(*N*-t-butylimine) radical anion].[35]

In contrast to the protonation behaviour of ligands (I), spectral averaging does not occur on complexing, so that the complexes are long lived ($\tau \gg 10^{-7}$ s) on the e.s.r. time scale. Nevertheless, ligand exchange does occur: addition of Hg^{2+} to solutions of other complexes causes the immediate appearance of the Hg^{2+}-complex spectrum. But addition of Hg^{2+} to (I; R = py) solution causes the collapse of the ligand ^1H n.m.r. signals, so that ligand exchange might be occurring on the n.m.r. time scale.

Formation constants K_f reflect the effect of the diamagnetic substituents R. In aqueous solution, K_f values for (I; R = py) are one to three orders of magnitude higher than those for the (I; R = Ph) whose basicity is slightly higher. Sterically hindered (I; R = 6-Brpy) (py nitrogen partially blocked) gives K_f values that are much lower than those of (I; R = py). The data in Table 2 are consistent with chelation of the py and the imidazoline imine nitrogen atoms of (I; R = py) with metal ions, analogous to the known diamagnetic complexes of 2-(2-pyridyl)imidazoline,[20] while the other ligands co-ordinate in unidentate fashion. For each individual ligand, formation constants increase in the order $Pb < Zn \leqslant Cd < Ag \ll Hg$. This order arises from a combination of steric and electronic factors and is consistent with the behaviour of other imine ligands [9,30-32] (Table 2).

E.s.r. spectral changes largely mirror electronic effects, while K_f values reflect the overall energy changes of the bonding interaction including those due to steric effects. The fractional change in N(1) and N(3) spin density on complexing should correlate with the strength of the interaction, as is the case with the simple aliphatic nitroxides.[13] Tables 1 and 2 indeed indicate a good correlation between K_f and Δa_N for a particular ligand. For every ligand, Δa_N is largest for Hg^{2+}, smallest for Pb^{2+} (if complexing can be observed at all), with Zn^{2+}, Cd^{2+}, and Ag^+ intermediate and in the proper order.

The importance of chelation as a determinant of electronic demands placed on a ligand is demonstrated by the comparison of a_N and a_M values for the bidentate (I; R = py) and unidentate (I; R = 6-Brpy). Although K_f values are much higher for the chelated (I; R = py) complexes, changes in a_N on co-ordination are much larger for the unidentate complexes of (I; R = 6-Brpy). Co-ordination of the py group makes that nitrogen lone pair available to the metal ion, and so eases the electronic requirements placed on the co-ordinating imidazoline ring. For example, $a_{N(1)}$ and $a_{N(3)}$ in (I; R = py) change by 18 and 22% on co-ordination with Hg^{2+}, while the analogous changes for (I; R = 6-Brpy) are 25 and 33%, respectively. More dramatically, ^{199}Hg ($I = \frac{1}{2}$) h.f. splitting of the e.s.r. line increases from 46 G for (I; R = py) to 76 G for (I; R = 6-Brpy). The other unidentate ligands (I; R = Ph and 3-BrPh) exhibit a_N splittings similar to those of (I; R = 6-Brpy) in their Hg^{2+} h.f. splittings (see below). The above observations graphically illustrate the enthalpy contribution to the chelate effect. Similarly, solvent and anion co-ordination also affect the electronic distribution in the imidazoline ring, as seen by the data in Table 1.

Metal–ligand bonding interactions can be gauged by the extent of unpaired spin and electron delocalization beyond the paramagnetic imidazoline ring. Extensive spin delocalization in (I; R = py) from the imidazoline N(3) to the nitrogen atom of the diamagnetic py ring *via* orbitals of the intervening metal atom should result in py ^{14}N ($I = 1$) e.s.r. line broadening. But even in the Hg complex h.f. linewidths are unchanged from the free ligand, so that unpaired π-spin density does not bridge the N(3)–Hg–N(py) gap. But π-bonding with the py ring should be favoured over that to the imidazoline [9,33] and there are no low-lying Hg π-orbitals. In contrast, h.f. lines for the Pt^{II} adduct with (I; R = py) are three times as broad as the ligand lines.[10]

Insight into bonding to the metal ion comes from the coupling of ligand unpaired spin density with the non-zero nuclear spin of the metal, as described by equation (4). But as Q^M values are usually not known, correlations of a_M with ρ_M^{π} must remain speculative. As shown in Table 1, a_M does not change significantly with (I) for a given metal atom except for Hg^{II}. If metal h.f. splitting originates predominantly from spin polarization from $\rho_{N(3)}^{\pi}$, then a_M should change proportionately with the latter quantity. In complexes of Hg^{2+} a_M changes by 65% in going from (I; R = py) to (I; R = 6-Brpy), while $\rho_{N(3)}^{\pi}$ differs by only 11%. It seems highly likely that the increase in a_M for the unidentate (I; R = 6-Brpy) ligand is indeed caused by an increase in unpaired spin density on Hg.

Matrix ENDOR linewidth measurements provide evidence for some slight unpaired electron delocalization on co-ordination. The unpaired electron wavefunction radius $\bar{a}$ for Hg(I; R = py), Pb(I; R = py), and (I; R = py) in EtOH glass at 73 K extends 3·6, 3·2, and 3·1 Å, respectively, into the frozen matrix, as determined from line-shape analysis. The change in $\bar{a}$ on co-ordination is statistically significant, but is too small to be due to extensive unpaired electron-density delocalization onto the metal. Larger changes in electron delocalization are exemplified by Ag^0 radicals in differing matrices: $\bar{a}$ for Ag^0 in non-co-ordinating MTHF glass is 1·5 Å, but is 3·3 Å in co-ordinating frozen aqueous solution.[18] For the (I; R = py) complexes, the slight increase in $\bar{a}$ on co-ordination can be adequately explained by the increasing spin density on the nitroxide oxygen atom at the periphery of the ligand [stabilization of resonance form (A)].

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Due to the fleeting nature of the interaction, complexing of $^{7}Li^{+}(I = 3/2)$ by (I) or (II) could not be detected by e.s.r. spectroscopy. Dynamic nuclear polarization (DNP), a double-resonance n.m.r.–e.s.r. technique, revealed the existence of Li^{+} complexes with lifetimes ranging from 1×10^{-10} s for (II; R = Ph) to 1×10^{-8} s in chelated interactions with (I) and (II) (R = py) in EtOH. These results have been presented elsewhere but are quoted here to demonstrate the extension of magnetic-resonance techniques to the study of intermolecular complexing or collisions of free-radical ligands at the diffusion limit in solution.[34]

Free-radical ligands should further enhance the value of magnetic-resonance techniques in studies of bonding in catalytic systems featuring very transitory interactions for which traditional spectroscopic techniques are no longer applicable.[2e,4e,35]

EXPERIMENTAL

Reagent-grade metal nitrate salts, distilled water, and gold-label ethanol were used to make up the required solutions. Solutions of the nitroxides were air stable for periods up to 3 months. Starting aldehydes were obtained from Aldrich, Inc., except for 6-bromopyridine-2-carbaldehyde which was prepared as previously described.[36] 2,3-Bishydroxylamino-2,3-dimethylbutane dihydrogen sulphate (hdbs) was obtained from Eastman–Kodak. The phenyl and 3-bromophenyl derivatives of (I) and (II) were prepared by literature methods.[5]

For room-temperature e.s.r. measurements, solutions were pipetted into capillary tubes and were left open to air. Evacuation produced no changes in the e.s.r. spectra. Samples measured at 77 K were in the form of frozen spheres, which were prepared by dropwise addition of solution to liquid nitrogen. E.s.r. spectra of the solutions at room temperature were recorded on a Varian 4500 spectrometer. Samples measured at 77 K were recorded on a Varian E-4 spectrometer. Noise due to nitrogen bubbles was prevented by bubbling helium gas through the liquid nitrogen in the tail section of an immersion Dewar. The ENDOR spectrometer used was a Varian E-700 model which has been fully described elsewhere.[16] ^{1}H N.m.r. spectra were obtained in HR mode on a Varian HA-100 100 MHz spectrometer. Chemical analyses were made by Galbraith, Inc., Knoxville, Tenn., U.S.A.

4,4,5,5-*Tetramethyl*-2-(2-*pyridyl*)-Δ^{2}-*imidazoline*-1,3-*diol*.—Potassium hydroxide powder (1·7 g, 30 mmol) was added to a suspension of hdbs (3·67 g, 15 mmol) in absolute alcohol (100 cm^3). The white suspension was stirred for 1 h, and pyridine-2-carbaldehyde (1·69 g, 15 mmol) in absolute alcohol (25 cm^3) was added dropwise over 5 min. The white to yellow suspension was stirred for 24 h and filtered. The precipitate was washed with absolute alcohol (25 cm^3) to remove traces of base and used directly in the next step. The intermediate can be isolated as white crystals (2·25 g, 65%) by extraction of the solid mixture with boiling $CHCl_3$.

4,4,5,5-*Tetramethyl*-2-(2-*pyridyl*)-Δ^{2}-*imidazolin*-1-*oxyl* 3-*Oxide* (II; R = py).—The crude solid product of the above reaction was stirred with PbO_2 (20 g) in dry benzene (250 cm^3) for 1 h at room temperature. Filtering and evaporation of the dark blue benzene solution gave the crystalline *radical* in quantitative yield. Soluble in organic solvents and water, stable to air, the radical is easily decomposed by traces of KOH.

TABLE 4

Analytical and m.p. data for diamagnetic precursors to the radicals

	Analyses */%			M.p.
Radical	C	H	N	(θ_c/°C)
(II; R = py)	61·0	8·15	17·7	193—196
	(60·75)	(8·05)	(17·7)	(decomp.)
(I; R = py)	66·05	8·20	18·9	150—152
	(65·75)	(7·80)	(19·15)	(decomp.)
(II; R = 6-Brpy)	45·55	5·85	13·35	193—196
	(45·6)	(5·75)	(13·3)	(decomp.)
(I; R = 6-Brpy)	48·6	5·25	14·3	179—180
	(48·35)	(5·40)	(14·1)	(decomp.)

* Calculated values are given in parentheses.

4,4,5,5-*Tetramethyl*-2-(2-*pyridyl*)-Δ^{2}-*imidazolin*-3-*oxyl*.—Conc. HCl (7·5 cm^3) in absolute alcohol (25 cm^3) was added dropwise over 15 min to a stirred solution of (II; R = py) (3 g) in absolute alcohol (100 cm^3). The resulting greenish blue solution was warmed on a steam-bath for 1 h, and then cooled in an ice-bath. The pale yellow solution was slowly neutralized with saturated Na_2CO_3 solution to an orange end-point. All solvent was stripped on a rotary evaporator, the residue being taken up in $CHCl_3$ (100 cm^3) and stirred for 15 min with Na_2SO_4. Filtration and evaporation of all solvent gave yellow crystals in a pale brown oil. Chromatography of this material with alumina ($CHCl_3$ eluant) gave a yellow oil (1·2 g, 43%) which solidified to yellow *crystals* after 24 h. The compound is soluble in polar solvents, benzene, and water, and forms chelated complexes with transition-metal ions:[10] $\nu_{max.}$ (Nujol) at 3 280 cm^{-1} (NH); δ ($CDCl_3$) 1·30 (s, 2 Me), 1·43 (s, 2 Me), 5·17 (s, NH), 7·33 [t, H(4) of py], 7·84 [t, H(5) of py], and 8·6 p.p.m. [d, H(3) of py].

4,4,5,5-*Tetramethyl*-2-(2-*pyridyl*)-Δ^{2}-*imidazoline*-1-*oxyl* (I; R = py).—The above solid was taken up in benzene (250 cm^3) and stirred for 30 min with PbO_2 (20 g). The resulting solution was filtered, condensed to 25 cm^3, and chromatographed on neutral alumina. A red-orange oil was obtained in quantitative yield which solidified to red *crystals* after standing for 1 week: δ ($CDCl_3$) —1 to 1·7 (m, 4 Me) and 6·5—8·7 p.p.m. [m, H(3)—H(6) of py].

2-(6-*Bromo*-2-*pyridyl*)-4,4,5,5-*tetramethyl*-Δ^{2}-*imidazoline*-1,3-*diol*.—This was prepared analogously to the 2-py derivative as a white *solid* (48%) sparingly soluble in hot $CHCl_3$.

2-(6-*Bromo*-2-*pyridyl*)-4,4,5,5-*tetramethyl*-Δ^{2}-*imidazolin*-1-*oxyl* 3-*Oxide* (II; R = 6-Brpy).—Prepared analogously to the 2-py derivative and is moderately soluble in organic solvents.

2-(6-*Bromo*-2-*pyridyl*)-4,4,5,5-*tetramethyl*-Δ^{2}-*imidazoline* 3-*Oxide*.—This was prepared analogously to the 2-py

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derivative as yellow *crystals* (31%) moderately soluble in organic solvents: $\nu_{max.}$ (Nujol) at 3 280 cm^{-1} (NH); δ ($CDCl_3$) 1·33 (s, 2 Me), 1·40 (s, 2 Me), 4·97 (s, NH), 7·42—7·83 [m, H(4) of py], and 9·3, 9·4 p.p.m. [d, H(3), H(5) of py].

2-(6-*Bromo*-2-*pyridyl*)-4,4,5,5-*tetramethyl*-Δ^2-*imidazolin*-1-*oxyl* (I; R = 6-Brpy).—This was prepared analogously to the 2-py derivative as an orange *solid* moderately soluble in organic solvents, sparingly soluble in H_2O: δ ($CDCl_3$) −1 to +1 (m, 4 Me) and 5—7 p.p.m. [m, H(3)—H(5) of py].

We thank Professor L. Kevan, Wayne State University, for permission to run matrix ENDOR spectra in his laboratory, Professor R. D. Bates, jun., and Dr. E. F. Ullman for helpful discussions, and Mr. A. J. Montedoro for experimental assistance.

[4/1937 *Received, 23rd September*, 1974]