# Spin Density Delocalization from a Stable Free-radical Ligand onto Diamagnetic Metal Ions

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*Summary* The novel air-stable, free-radical di-imine ligand 4,4,5,5-tetramethyl-2-(2-pyridyl)-$\Delta^2$-imidazoline-1-oxyl forms stable 1 : 1 complexes with bivalent, Zn, Cd, and Hg; upon complexation, e.s.r. ligand hyperfine couplings increase from 4·25 G to 5·2 G for the co-ordinating imine nitrogen, decrease from 9·25 G to 7·6 G for the nitroxide nitrogen, and metal hyperfine splitting of 9·6 G and 46 G is observed due to $I = \frac{1}{2}$ isotopes of Cd and Hg, respectively.

PARAMAGNETIC ligands capable of spin delocalization onto diamagnetic metals are quite rare. Some metal complexes containing unpaired spins have been prepared with *o*-semiquinones,[1,2] bipyridyl radical anion,[3] and dithiolene ligands[4] by oxidation–reduction reactions on precursor complexes, but spin-delocalized chelate complexes of metal ions with solvent- and air-stable free-radical ligands have not been reported. Such complexes are of obvious interest for studies on metal–ligand bonding, spin labelling of metals in enzymes, and transfer of spin from the radical ligand *via* the metal to other parts of the ligand framework.

We have prepared the air-stable free radical 4,4,5,5-tetramethyl-2-(2-pyridyl)-$\Delta^2$-imidazoline-1-oxyl, m.p. 30—35 °C, which is soluble in water and in organic solvents. This orange pyridyl iminonitroxide radical L is obtained quantitatively by $PbO_2$ oxidation of the fully characterized diamagnetic precursor 4,4,5,5-tetramethyl-2-(2-pyridyl)-$\Delta^2$-imidazoline 3-oxide, m.p. 150—152 °C (decomp.); $\nu_{max}$ (Nujol) 3280 cm$^{-1}$ (NH); $\delta$ ($CDCl_3$): 1·36 (s, 2 × Me), 1·43 (s, 2 × Me), 5·17 (s, NH), 7·33 (t, py-4-H), 7·84 (t, py-5-H), 8·6 (d, py-3-H), and 9·3 (d, py-6-H).

TABLE

Observed hyperfine splittings in G for $10^{-3}$M aqueous solutions of L and metal nitrates.

| | *a*[N(1)] | *a*[N(3)] | *a*(M,$I = \frac{1}{2}$) |
|---|---|---|---|
| L | 9·25 | 4·25 | — |
| ZnL | 8·0 | 4·9 | — |
| CdL | 8·1 | 5·0 | 9·6 |
| HgL | 7·6 | 5·2 | 46 |

The four-step synthesis of L is analogous to that reported by Ullman[5] for the 2-phenyl derivative. In contrast to the latter, L forms strong 1 : 1 complexes with bivalent Zn, Cd, and Hg, as shown by the e.s.r. data in the Table.

The simplified Karplus–Fraenkel expression[6] $a(\mathrm{N}) = ca.\ Q(\mathrm{N})\rho(\mathrm{N})$ [$\rho(\mathrm{N})$ = nitrogen spin density] indicates that $\rho[\mathrm{N}(1)]$ decreases by *ca.* 20% upon complexation, and $\rho[\mathrm{N}(3)]$ increases by a similar amount. This effect is interpreted as due to electron delocalization from the ligand towards the metal. Electron spin delocalization onto the metal itself is demonstrated by the observation of additional hyperfine splittings due to $^{111,113}$Cd and $^{199}$Hg $I = \frac{1}{2}$ isotopes. The Hg complex spectrum is shown in the Figure. The intensities of metal hyperfine lines are consistent with relative isotopic abundances. [As expected, the $^{201}$Hg ($I = \frac{3}{2}$) spectrum is hidden under the $I = 0, \frac{1}{2}$ lines, except for weak shoulders just beyond the outermost lines of the $^{199}$Hg ($I = \frac{1}{2}$) hyperfine structure.]

While the large metal hyperfine splittings observed for Cd and Hg are indicative of considerable spin delocalization and strong bonding between L and Group IIB metals, solution e.s.r. spectra did not reveal any interaction between L and alkali metals or alkaline earths.

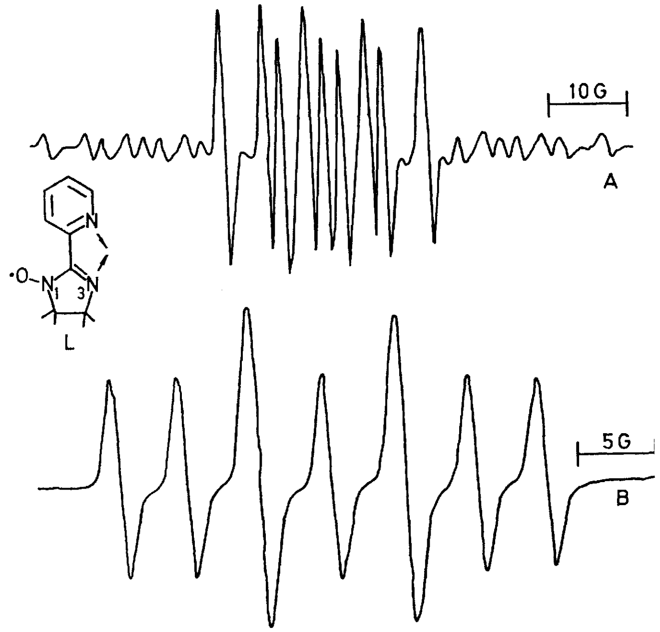

FIGURE. First derivative e.s.r. spectrum of (A) HgL complex and (B) 4,4,5,5-tetramethyl-2-(2-pyridyl)-$\Delta^2$-imidazoline-1-oxyl ligand (L), $10^{-3}$M in H$_2$O.

(*Received*, 16*th July* 1973; *Com.* 1031.)

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