

Observation of Nitrogen Hyperfine Splitting in the Electron Spin Resonance Spectra of 1:1 Copper(II) β -Diketonate Adducts with Nitrogen Donors

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Summary The e.s.r. spectra for 1:1 nitrogen donor adducts of Cu^{II} bisacetylacetonate and Cu^{II} bishexafluoroacetylacetonate are reported: the 1:1 adducts of Cu(hfacac)₂ with pyridine and quinuclidine are unique in exhibiting ¹⁴N hyperfine splitting in the e.s.r. spectrum.

NEUTRAL four-co-ordinate Cu^{II} chelates such as Cu^{II} bisacetylacetonate, [Cu(acac)₂], function as acceptors and form five-co-ordinate complexes (1:1 adducts) with donors such as pyridine. X-Ray structure determinations of Cu(acac)₂-quinoline¹ and Cu(*N*-phenyl salicylalimine)₂-pyridine² have shown that these complexes have the square-pyramidal type framework with the neutral donor (*e.g.* pyridine) occupying the axial position (Figure 1A). We report that the e.s.r. spectra for the 1:1 adducts of Cu^{II} bishexafluoroacetylacetonate, [Cu(hfacac)₂], with pyridine and quinuclidine (C₇H₁₃N) exhibit ¹⁴N hyperfine splitting, which is incompatible with axial ligation (Figure 1A), but is consistent with several structure types (Figure 1B and C) which are unusual for this class of five-co-ordinate complexes.

E.s.r. studies of copper(II) β -diketonates and the 1:1 five-co-ordinate adducts with donors have invariably resulted in $g_{xy} > g_x \sim g_y$ which has been used to place the single odd electron in the d_{xy} molecular orbital.^{3,4} In the case of axial ligation, the σ and π orbitals of the axial donor are orthogonal to the Cu^{II} d_{xy} orbital in the idealized C_{2v} adduct

structure (Figure 1A). The odd electron will thus have only a small probability of penetrating to the nitrogen nucleus of the donor, and ¹⁴N hyperfine splitting is not expected to be observable in the e.s.r. spectra for this class of complexes.

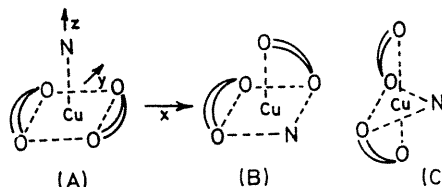


FIGURE 1. Schematic representations of structure types for 1:1 Cu(chelate)₂-nitrogen donor adducts.

The e.s.r. spectrum of the 1:1 pyridine adduct of [Cu(acac)₂] in frozen dichloromethane shows no resolvable ¹⁴N hyperfine splitting (Figure 2A) (Table). Nitrogen-14 n.m.r. contact-shift studies for the pyridine adduct of Cu(acac)₂ in neat pyridine were carried out as a check on the e.s.r. results. The resulting isotropic ¹⁴N coupling constant of $+0.70 \pm 0.10$ G is too small to be resolved in the e.s.r. spectrum. Small pyridine proton contact shifts are also consistent with these observations.⁵

The e.s.r. spectrum for the g_z region of $\text{Cu}(\text{hfacac})_2$ -pyridine in Nujol glass at 90 K is given in Figure 2B. Hyperfine structure is most apparent on the $M_1 = -\frac{3}{2}$

transition. Nitrogen hyperfine structure is clearly resolved in the CH_2Cl_2 frozen solution (Figure 2C) (Table). The splitting of each of the four ^{63}Cu resonances in the g_z region

TABLE

E.s.r. parameters for the g_z transitions of Cu^{II} β -diketonates and 1:1 nitrogen donor adducts in frozen solution media at 90K^{a,b}

Complex	Solvent	g_z	$A_z(^{63}\text{Cu})^c$ (Gauss)	$A(^{14}\text{N})$ (Gauss)
$\text{Cu}(\text{acac})_2$	CH_2Cl_2	2.261	181	—
$\text{Cu}(\text{acac})_2 \cdot \text{pyridine}$	CH_2Cl_2	2.291	146	—
$\text{Cu}(\text{hfacac})_2$	Nujol	2.270	175	—
	CH_2Cl_2	2.263	171	—
$\text{Cu}(\text{hfacac})_2 \cdot \text{pyridine}$	Nujol	2.302	145	9 ± 2
	CH_2Cl_2	2.303	142	8.6 ± 0.5
$\text{Cu}(\text{hfacac})_2 \cdot \text{quinuclidine}$	Nujol	2.295	146	ca. 8
	CH_2Cl_2	2.302	145	7.7 ± 0.5

^a Second-order effects are found to be negligible in the g_z regions and the reported parameters are the result of a first-order analysis of the spectra.

^b $g_z > g_x \sim g_y \sim 2.05$ — 2.06 is observed for every complex reported. Large second-order effects, quadrupole effects, forbidden bands, $^{63},^{65}\text{Cu}$ and ^{14}N coupling complicate the analysis of the g_x, g_y region. Complete spectral simulation is in progress.

^c ^{63}Cu hyperfine is resolved in all cases and is observed to be close to the theoretical value $A^{63}\text{Cu}/A^{65}\text{Cu} = 1.07$.

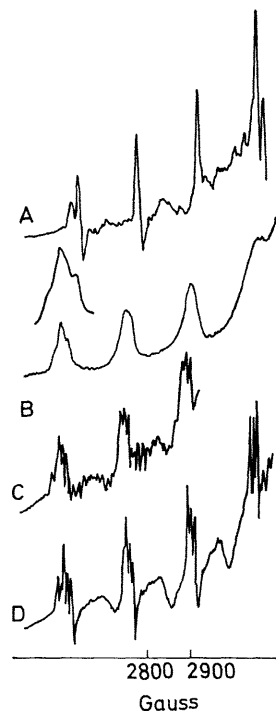


FIGURE 2. *E.s.r. spectra ($\nu = 9140$ MHz) for the g_z region in frozen solutions of (A) $\text{Cu}(\text{acac})_2 \cdot \text{pyridine}$ in CH_2Cl_2 ; (B) $\text{Cu}(\text{hfacac})_2 \cdot \text{pyridine}$ in Nujol; (C) $\text{Cu}(\text{hfacac})_2 \cdot \text{pyridine}$ in CH_2Cl_2 ; (D) $\text{Cu}(\text{hfacac})_2 \cdot \text{quinuclidine}$ in CH_2Cl_2 .*

into three equal intensity components is ascribed to the coupling of the single ^{14}N ($I = 1$) nucleus in the 1:1 adduct. The 1:1 quinuclidine adduct of $\text{Cu}(\text{hfacac})_2$ is also found to exhibit three equal-intensity ^{14}N hyperfine components on each of the ^{63}Cu components in the g_z region (Figure 2D).

The e.s.r. g values ($g_z > g_x \sim g_y$) for these mono-adducts are consistent with the odd electron occupying the d_{xy} molecular orbital. The presence of nitrogen hyperfine indicates that the nitrogen donor orbitals make a large contribution to the odd electron m.o. in these adducts, and thus identifies the d_{xy} as an important acceptor level of Cu^{II} in binding the neutral nitrogen donor.

Muetterties and Schunn have listed the possible structure types for five-co-ordinate species of the form $[\text{MX}_4\text{Y}]$.⁶ The two structural types that could be compatible with the e.s.r. results are shown in Figure 1B and C. A square pyramid with the neutral donor occupying a basal position is one possibility (Figure 1B) and a trigonal bipyramid with nitrogen donor in an equatorial position and elongated axial bonds is a second possibility (Figure 1C). At present we favour the basally ligated square-pyramid type (Figure 1B), for trigonal-bipyramidal complexes such as $[\text{Cu}(\text{dipyridyl})_2\text{I}]^+$ have dz^2 ground states.^{7,8} The basally ligated square pyramid has precedent in the structure reported for the five-co-ordinate 1:1 adduct of bis-(α -nitroacetophenato)copper(II) with 2-methylpyridine.⁹

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