

ENDOR Spectroscopy of Bis(pentane-2,4-dionato)copper(II) and Bis(hexafluoropentane-2,4-dionato)copper(II)

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A single-crystal ENDOR study of $[\text{Cu}(\text{pd})_2]$ in $[\text{Pd}(\text{pd})_2]$ (pd = pentane-2,4-dionato) has been carried out. Tensors for all protons in the molecule have been determined together with one, the largest in magnitude, associated with the γ -proton of a neighbouring $[\text{Pd}(\text{pd})_2]$ molecule. Frozen-solution ENDOR spectra of $[\text{Cu}(\text{pd})_2]$ and of the hexafluoro derivative have also been determined and hyperfine coupling to protons and fluorine assigned.

There have been three single-crystal studies by e.s.r. of $[\text{Cu}(\text{pd})_2]$ (pd = pentane-2,4-dionato).^{1,2} Both were carried out using $[\text{Pd}(\text{pd})_2]$ as the host lattice, and their results are in broad agreement. The complexes $[\text{Cu}(\text{pd})_2]$ and $[\text{Pd}(\text{pd})_2]$ are isomorphous, having space group $P2_1/n$.^{3,4} The only ENDOR study on $[\text{Cu}(\text{pd})_2]$ has been carried out by Kirste and van Willigen⁵ on the complex coprecipitated with $[\text{Pd}(\text{pd})_2]$ and in frozen solution. We have recently carried out a detailed single-crystal ENDOR study of the related complex $[\text{Cu}(\text{tmhd})_2]$ (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionato).⁶ In this paper, we report on a detailed single-crystal proton ENDOR study of $[\text{Cu}(\text{pd})_2]$ in $[\text{Pd}(\text{pd})_2]$ and of ENDOR measurements on $[\text{Cu}(\text{hfpd})_2]$ (hfpd = hexafluoropentane-2,4-dionato) in frozen solution.

Experimental

The complexes $[\text{Cu}(\text{pd})_2]$ and $[\text{Pd}(\text{pd})_2]$ were prepared by standard methods.^{7,8} Doped single crystals of $[\text{Pd}(\text{pd})_2]$ with ca. 1% $[\text{Cu}(\text{pd})_2]$ were grown from CH_2Cl_2 -toluene by slow evaporation. $[\text{Cu}(\text{hfpd})_2]$ was prepared by the method of Bertrand and Kaplan.⁹ ENDOR spectra were recorded on a Bruker ER 200D spectrometer with an ER 250 ENDOR accessory at 25 K using an Oxford Instruments ESR-900 continuous flow cryostat. Single-crystal ENDOR spectra were recorded in three approximately orthogonal but arbitrary planes at 5° intervals.

The data were processed using the computer program ESR64 that diagonalises the 16×16 Hamiltonian matrix. ESR64 is a function subroutine of the minimisation program EOLIJBF.¹⁰ It minimises the error function (1) by varying * the elements of

$$h \left[\frac{1}{N} \sum_{i=1}^N (v_{\text{obs.}}^i - v_{\text{calc.}}^i)^2 \right]^{\frac{1}{2}} \quad (1)$$

the g tensor and the copper hyperfine and quadrupole tensors. In the analysis of e.s.r. data, v is the microwave frequency; in the analysis of the ENDOR spectra, it is the radio frequency. The summation runs over all e.s.r. or ENDOR transitions in all spectra which are measured in the three planes.

Results and Discussion

E.S.R. Spectra.—The resulting principal g values and hyperfine and quadrupole tensors are listed in Table 1 together with their relative angles; the tensors are also compared with those of Maki and McGarvey¹ and Kita *et al.*² We were unable to define the direction of the principal values of the tensors because the

parameters for the second site would not minimise using our minimisation function. However, the values and relative directions of the principal values of the tensor from both sites were internally consistent. Both Kita *et al.*² and Maki and McGarvey¹ found that the directions of g_z and A_z are inclined slightly off the normal to the plane of the molecule, 5.8 and 4.0, and 9.5° and 8.0° respectively. Less reliance can be put on the latter pair of angles since Maki and McGarvey¹ used the cell parameters for $[\text{Cu}(\text{pd})_2]$ rather than $[\text{Pd}(\text{pd})_2]$, the structure of which had not been carried out at the time of their work. Figure 1 shows the relative orientation of the g , A , and P tensors. The g tensor is very closely axial, and as such it is not possible to define the directions of g_x and g_y ; they can in theory be in any direction in the xy plane from symmetry considerations of the two molecular sites in the crystal; we found that the principal values of the A tensor in the xy plane bisected the O—Cu—O angle as was found in the study of $[\text{Cu}(\text{tmhd})_2]$.⁶ The magnitudes of the g and A tensors were similar to those of Maki and McGarvey,¹ and Kita *et al.*,² although we found that the quadrupole tensor was different. We do not place any

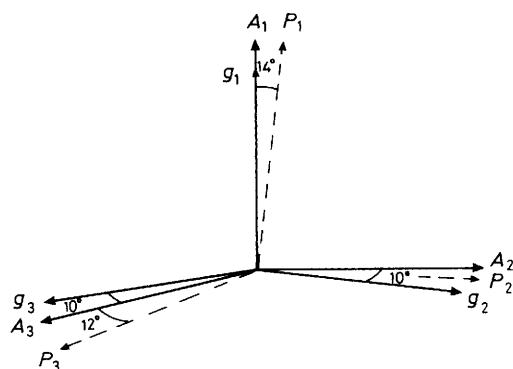


Figure 1. The relative orientation of the tensors in $[\text{Cu},\text{Pd}(\text{pd})_2]$

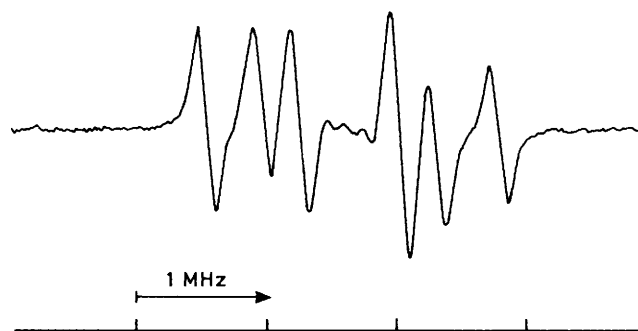


Figure 2. A typical ENDOR spectrum of $[\text{Cu},\text{Pd}(\text{pd})_2]$

* For the applications of the program ESR64, see, for example, M. L. H. Paulissen and C. P. Keijzers, *J. Mol. Struct.*, 1984, **113**, 267.

Table 1. E.s.r. results for the complex $[\text{Cu}(\text{pd})_2]$. The quadrupole and hyperfine couplings are given in units of 10^{-4} cm^{-1}

	Ref. 2	Ref. 1	This work	Angles (relative to laboratory frame) ^a		
g_1	2.259	2.266	2.264	46	135	94
g_2	2.052	2.053	2.056	70	76	24
g_3	2.050	2.053	2.050	129	132	66
A_1^b	-214.5	-160.0	-198.94	44	134	95
A_2^b	-27.0	-19.0	-25.36	65	71	32
A_3^b	-24.6	-19.0	-15.78	124	130	58
P_1	2.45		-5.11	127	117	49
P_2	-1.54		3.39	46	135	81
P_3	-0.68		1.45	67	56	42

^a This work. ^b Includes the isotropic component.

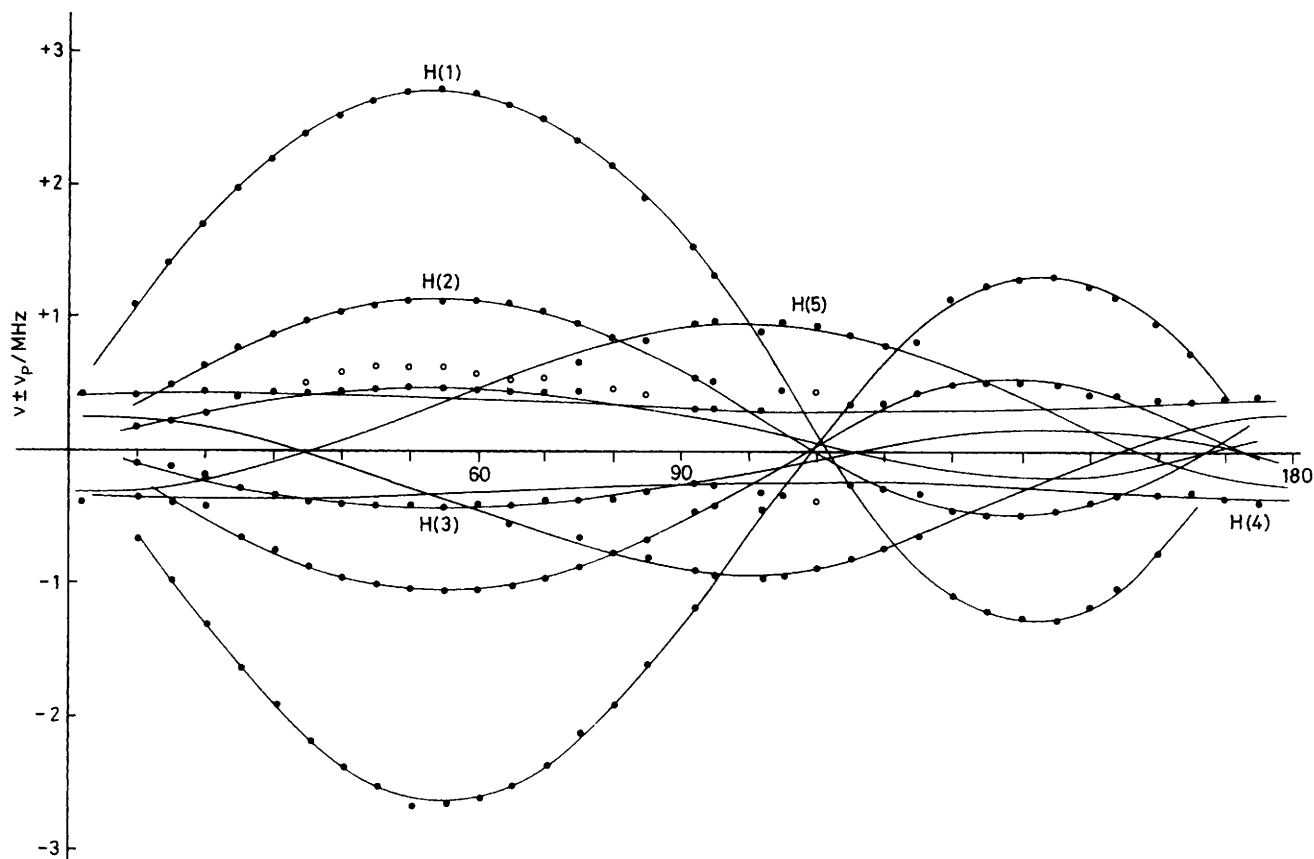


Figure 3. Angular variation of the proton ENDOR spectrum of $[\text{Cu}, \text{Pd}(\text{pd})_2]$. The points are the experimental data and the curves are those fitted by the minimisation routine. The open circles are data points that could not be fitted by the minimisation routine

reliance on the magnitude or direction of the P tensor since the method of calculation of it is notoriously inaccurate.

ENDOR Spectra.—A typical ENDOR spectrum is shown in Figure 2; the linewidths were *ca.* 25 kHz. The angular variation of the ENDOR frequencies in one of the three measured planes is shown in Figure 3; here the experimental frequencies have been scaled to a free proton frequency of 13 MHz.

The ENDOR data were analysed for each proton individually using the spin-Hamiltonian (2). The curves shown

$$\mathcal{H} = \mu_B B \cdot g \cdot S - g_H \mu_N B \cdot I^H + I^H \cdot A^H \cdot S + I^{\text{Cu}} \cdot A^{\text{Cu}} \cdot S + I^{\text{Cu}} \cdot Q^{\text{Cu}} \cdot I^{\text{Cu}} - g_{\text{Cu}} \mu_N B \cdot I^{\text{Cu}} \quad (2)$$

are those that could be fitted to the data using the minimisation routine described above.

All four proton tensors together with one for an interaction with a neighbouring host molecule were extracted. By observing three separate tensors H(3), H(4), and H(5), for the methyl groups, all equivalent by symmetry, it follows that they are not rotating, nor is there any disorder as was found for $[\text{Cu}(\text{tmhd})_2]$.⁶

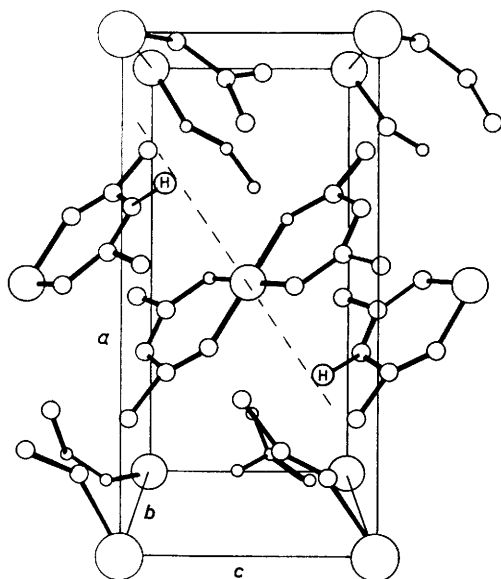
The form of the γ -proton [H(2)] tensor is unusual, although the principal direction of the tensor is almost coincident with the copper tensor as expected. It has the format expected for a proton in a π -radical, but clearly this is not the mechanism of spin transfer in this case. The isotropic hyperfine coupling is very small (0.121 MHz, Table 2) and shows little direct delocalization. That which does reach it comes by various mechanisms: direct delocalisation, dipolar interactions, polarization of electrons in the π -ring system, and mixing-in of

Table 2. Experimental hyperfine tensors from the fitting of curves to the single-crystal data of $[\text{Cu}(\text{pd})_2]$

	A/MHz	Angles (relative to laboratory frame)			
H(1-N)	A_1	5.008	36	125	98
	A_2	-2.432	70	75	25
	A_3	-2.577	119	141	66
	A_{iso}	0.082			
γ -H(2)	A_1	1.977	33	120	78
	A_2	0.647	78	48	44
	A_3	-2.624	120	124	48
	A_{iso}	0.121			
H(3)(Me)	A_1	1.726	51	126	60
	A_2	-0.163	41	52	104
	A_3	-1.564	100	58	34
	A_{iso}	-0.067			
H(4)(Me)	A_1	1.351	17	76	102
	A_2	0.326	107	54	139
	A_3	-1.676	92	38	52
	A_{iso}	0.451			
H(5)(Me)	A_1	1.502	70	87	21
	A_2	-0.701	70	23	101
	A_3	-0.801	151	67	73
	A_{iso}	0.014			

Table 3. Proton coupling (MHz) when the ENDOR spectrum is taken at the $M_I = +\frac{3}{2}$ parallel feature

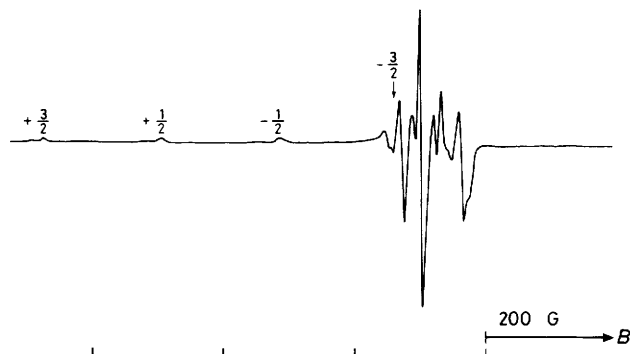
	Me	γ -H(2)	Distal H(1-N)	CF_3
$[\text{Cu}(\text{pd})_2]$				
Single crystal		1.98	5.09	
Powder	0.85	2.08	5.20 (+ 4.80)	
Frozen solution	0.80	2.12	—	
$[\text{Cu}(\text{hfpd})_2]$		2.03	—	1.60
				1.3
				0.79

**Figure 4.** The unit cell of a crystal of $[\text{Cu}(\text{pd})_2]$ showing the interaction with the γ -H of a neighbouring molecule

excited-state ($d_{xz,yz}$) orbitals which can genuinely provide a mechanism for π -delocalisation. Separating these components would not be easy. The tensor is very similar to the corresponding one found in $[\text{Cu}(\text{tmhd})_2]$.⁶

Table 4. Proton couplings (MHz) taken from the ENDOR spectrum of $[\text{Cu}(\text{pd})_2]$ when the magnetic field is at the $M_I = +\frac{1}{2}$ perpendicular feature

		Frozen solution	Powder
U-U	H(1-N) (\parallel)	—	5.24
V-V	H(1-N) (\perp)	—	2.45
W-W	H(2) (\parallel)	2.01	—
X-X	CH ₃ and H(2)	1.51	1.36
Y-Y		0.59	0.75
Z-Z		0.2	—

**Figure 5.** E.s.r. spectrum of a frozen solution of $[\text{Cu}(\text{pd})_2]$ in CH_2Cl_2 -toluene showing where the ENDOR spectra are taken ($G = 10^{-4}$ T)

The largest tensor comes from a proton [H(1-N)] on a neighbouring molecule. The orientation of the two different $[\text{Pd}(\text{pd})_2]$ molecules in the unit cell (Figure 4) is such that the γ -proton of one is almost vertically below the metal atom of the other. The vector makes an angle of 10.7° with the normal to the plane of the molecule containing the metal atom. We find that the angle between the Cu tensor and this H(1-N) tensor is 9° , very close to the above figure. The actual Cu-H(1-N) distance is 3.08 Å, and using the point dipole approximation, a coupling of 5.41 MHz is predicted, sufficiently close to the 5.09 MHz found experimentally.

Frozen Solution and Powder ENDOR Spectra.—The e.s.r. spectrum of a frozen solution of $[\text{Cu}(\text{pd})_2]$ in CH_2Cl_2 -toluene is shown in Figure 5. The ENDOR spectra of finely powdered crystals of $[\text{Cu}, \text{Pd}(\text{pd})_2]$ and of a frozen solution of $[\text{Cu}(\text{pd})_2]$ in CH_2Cl_2 -toluene are shown in Figures 6 and 7. The spectrum in Figure 6 was recorded by sitting on the Cu $M_I = +\frac{3}{2}$ (\parallel) e.s.r. line (of Figure 5) and that in Figure 7 was recorded by sitting on the Cu $M_I = +\frac{1}{2}$ (\perp) line (of Figure 5). The ENDOR spectra taken on the $M_I = +\frac{3}{2}$ (\parallel) line are 'single-crystal like' and the hyperfine couplings observed relate directly to the experimental proton coupling tensors in the single crystal.

The spectra in Figure 6 are relatively simple and have lines in common. The pair of lines marked P-P, separated by 2.08 MHz in the powdered crystal and 2.12 MHz in the frozen solution (Table 3), arise from coupling to the γ -H of the complex and are the A_1 component of this proton hyperfine tensor. In the single crystal, it had a value of 2.098 MHz. The pairs of lines Q-Q, separated by 0.85 MHz in the powdered crystal and by 0.80 MHz in the frozen solution, must arise from the methyl protons. In the single-crystal ENDOR measurement (at 25 K) each of the three protons of the methyl group was clearly observed, thus showing that the methyl group was not rotating. The single line in the powder and in frozen solution shows that the methyl is rotating freely. This is confirmed by calculating the hyperfine coupling expected for each methyl proton along the molecular z axis (g_1) and averaging.¹¹ The expected couplings along z for

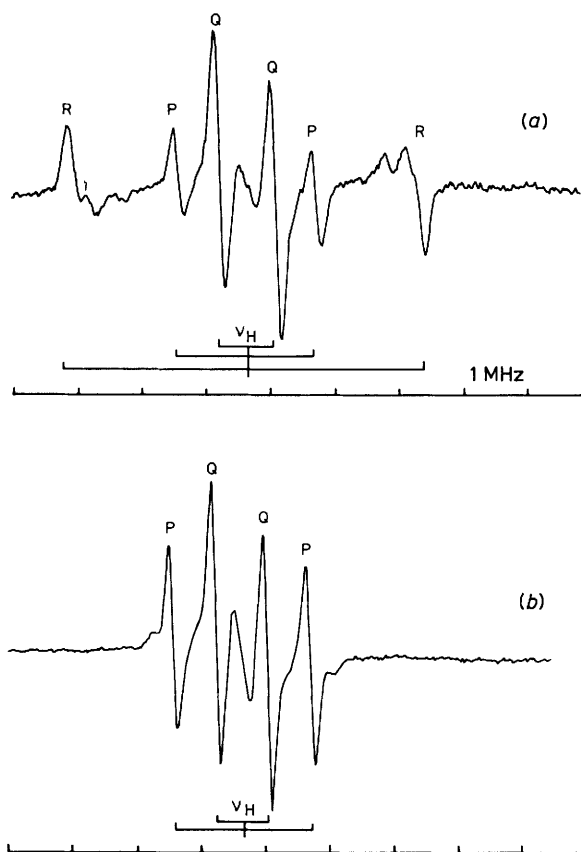


Figure 6. ENDOR spectrum taken on the Cu $M_I = +\frac{3}{2}$ (\parallel) line of (a) [Cu,Pd(pd)₂] powder and (b) a frozen solution of [Cu(pd)₂] in CH₂Cl₂-toluene

H(3), H(4), and H(5) are 0.75, 1.77, and 0.14 MHz which averages to 0.89 MHz, very similar to the powder and frozen-solution couplings of 0.85 and 0.80 MHz; rotating methyl groups are common even at low temperatures.¹² In the single crystal, rotation is prevented by crystal lattice forces, but in the frozen solution this is greatly reduced. For rotation to occur in the powder, there must be distortions and dislocations in the lattice to reduce the lattice forces. At similar temperatures, disorder of the methyl groups was found in [Cu(tmhd)₂].⁶ The central line in the ENDOR spectrum at the free proton nuclear frequency arises from long-range protons.

In the powdered crystal, strong features R, separated by 5.20 MHz, are not present in the frozen solution spectrum. These lines arise from coupling to the distal proton H(1-N) on the neighbouring [Pd(pd)₂] molecules of the host lattice and match the coupling from the single-crystal measurements $A_{\parallel} = 5.09$ MHz. A weaker pair of lines close to R-R, separated by 4.80 MHz, presumably arise from the same neighbouring protons of the host molecule which are in a slightly different position because of the strains generated by the mechanical powdering of the crystals or by disordered molecules.

Analysis of the ENDOR spectrum when the field is set in the perpendicular region of the spectra is very much more difficult because of the complicated angular dependence of the ENDOR signals and the appearance of extra turning points. When the field is set on the Cu $M_I = +\frac{1}{2}$ (\perp) line, it coincides also with the Cu $M_I = -\frac{3}{2}$ (\parallel) line (Figure 5). Thus the perpendicular spectrum will include components of the parallel spectrum in it. In Figure 7(a), remnants of the parallel features R-R of the distal proton H(1) are observed (U-U), separated by

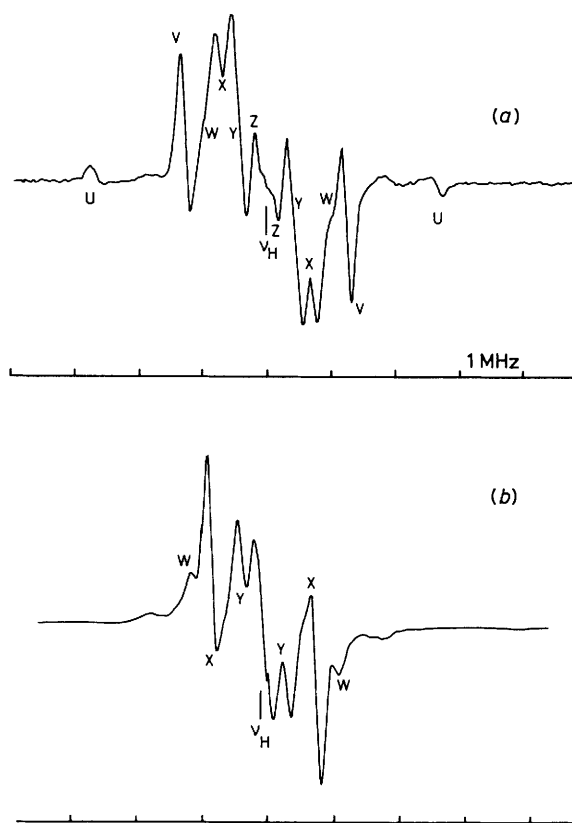


Figure 7. ENDOR spectrum taken on the Cu $M_I = +\frac{1}{2}$ (\perp) line of (a) [Cu,Pd(pd)₂] powder and (b) a frozen solution of [Cu(pd)₂] in CH₂Cl₂-toluene

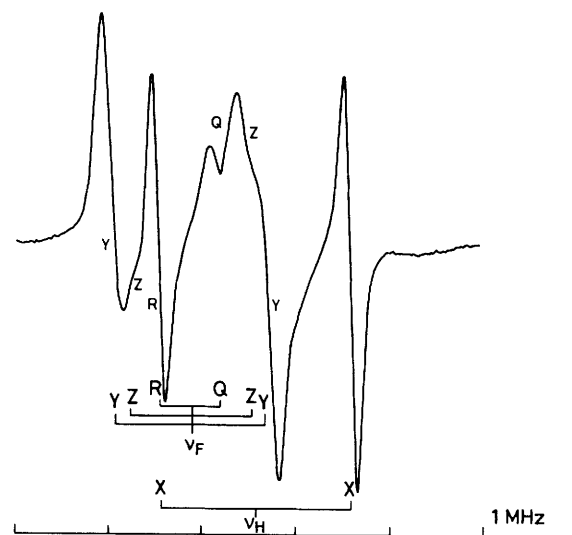


Figure 8. ENDOR spectrum taken on the Cu $M_I = +\frac{3}{2}$ (\parallel) line of a frozen solution of [Cu(hfpd)₂] in CH₂Cl₂

5.24 MHz, and lines V-V, separated by 2.45 MHz (Table 4), correspond with the perpendicular component of the same proton (2.43 and 2.58 MHz in the single crystal). These lines are absent in the frozen-solution spectrum [Figure 7(b)]. Lines W-W in both Figure 7(a) and 7(b), separation *ca.* 2.01 MHz, can be assigned to the γ -H(2) proton parallel features. The remaining

lines X-X, Y-Y, and Z-Z, all well resolved, are difficult to assign and must include extra turning points in the perpendicular ENDOR spectrum derived from the methyl and γ -H(2) protons. Although Kirste and van Willigen⁵ try to assign these lines, their assignments must be in doubt because of this.

The ENDOR spectrum of [Cu(hfpd)₂] in CH₂Cl₂ is shown in Figure 8. This spectrum is taken on the Cu $M_I = +\frac{3}{2}$ (\parallel) line. Pairs of lines centred on the free proton and free fluorine nuclear frequencies are observed. Two pairs of lines, Y-Y and Z-Z, are centred on ν_F and there is the probability of another pair Q-R. These arise from the three fluorines of the CF₃ groups which are not rotating. A pair of lines X-X centred on ν_H is from the γ -H(2) proton and has a coupling (2.03 MHz) almost identical to the corresponding proton in [Cu(pd)₂]. We were unable to grow single crystals of [Cu,Pd(hfpd)₂] suitable for a single-crystal study.

Conclusions

The detection and analysis of proton hyperfine couplings in the ENDOR spectra of copper complexes having relatively few protons in their ligands is possible when dilute single crystals are used. In contrast, much information is lost if frozen solutions are used although a number of proton ENDOR lines may be observed and assigned.

It is interesting to note that in the case of the compound [Cu(hfpd)₂], the CF₃ groups are not rotating, whilst in the

corresponding compound [Cu(pd)₂], the methyl groups are rotating. Presumably steric reasons predominate.

Acknowledgements

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