Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Structure determination of bound nitrogen-based adducts with copper (II) acetylacetonato; an EPR, ENDOR and DFT study.

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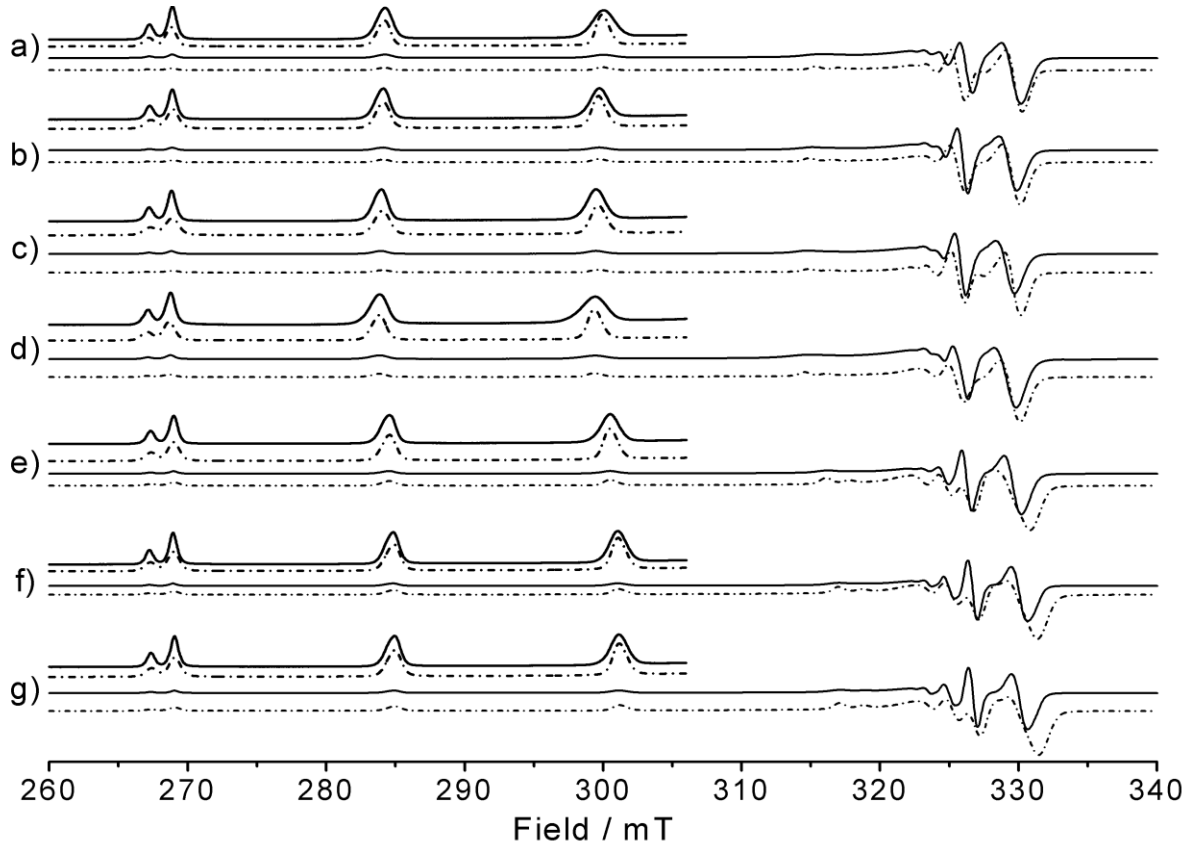
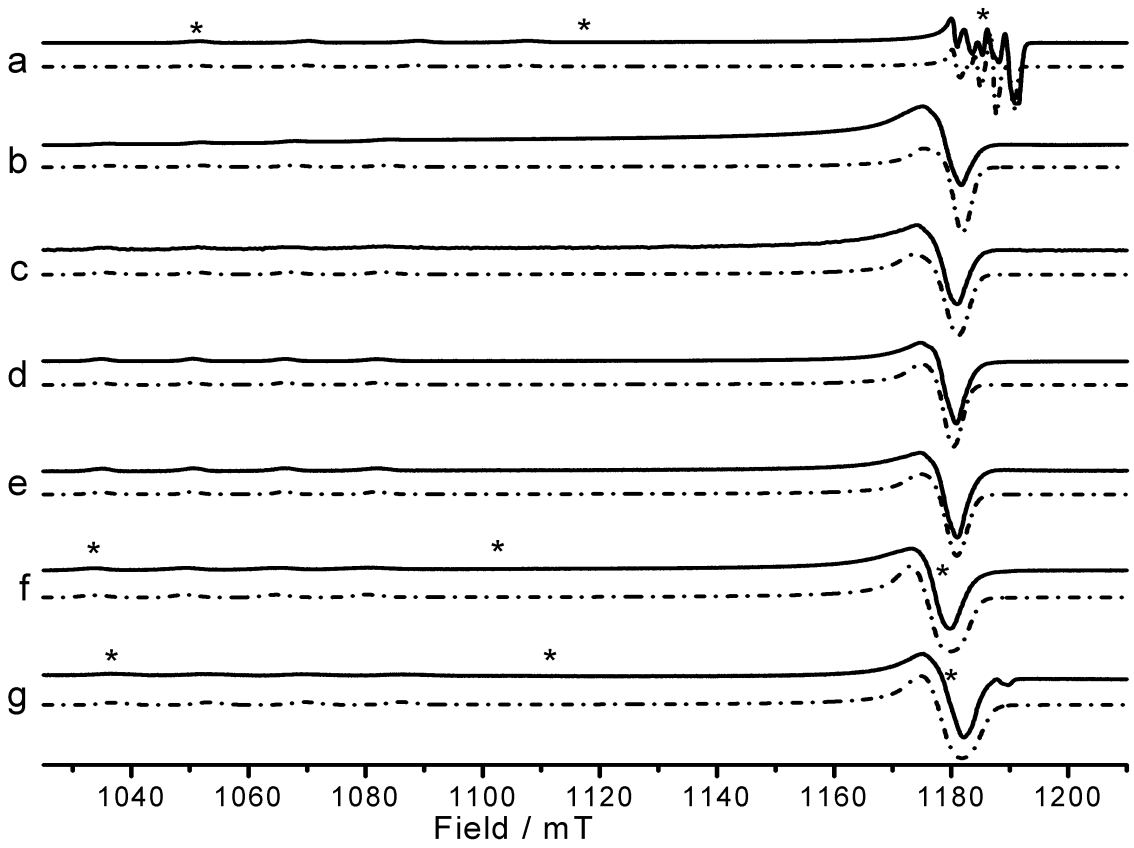
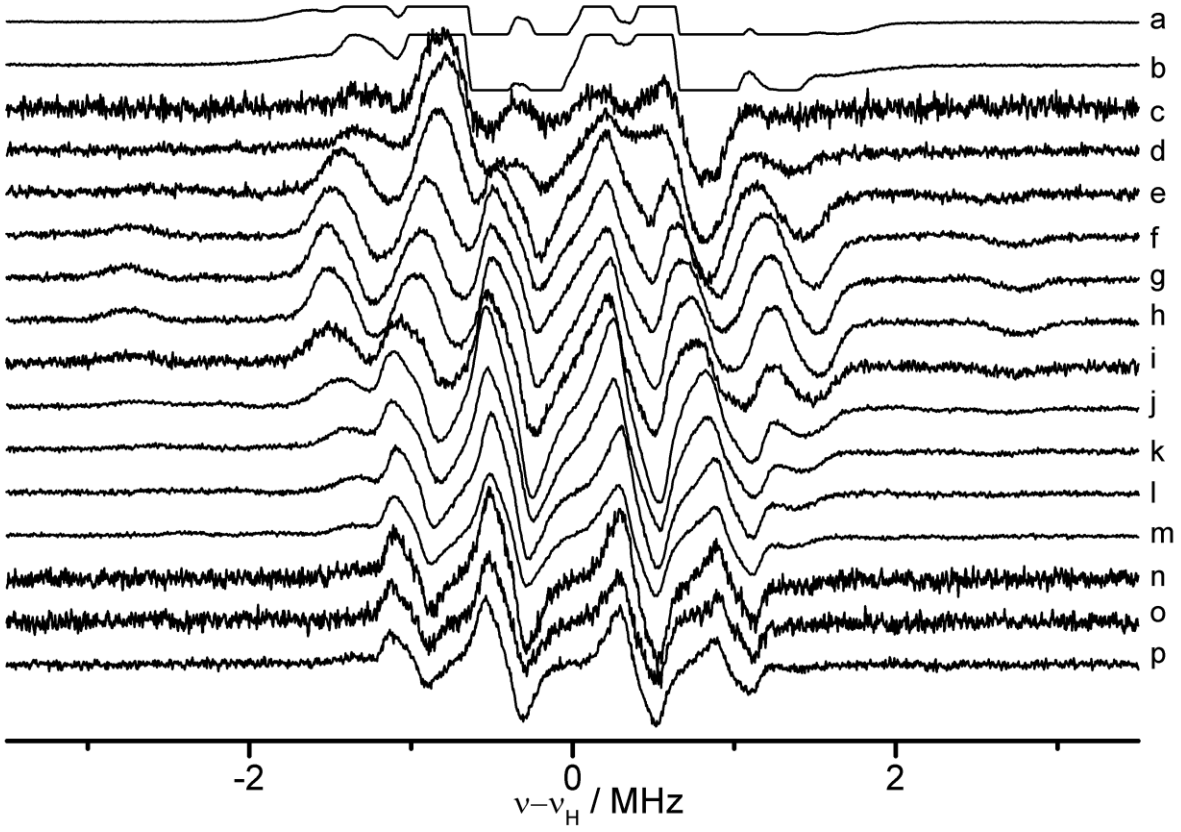
Electronic Supplementary Information



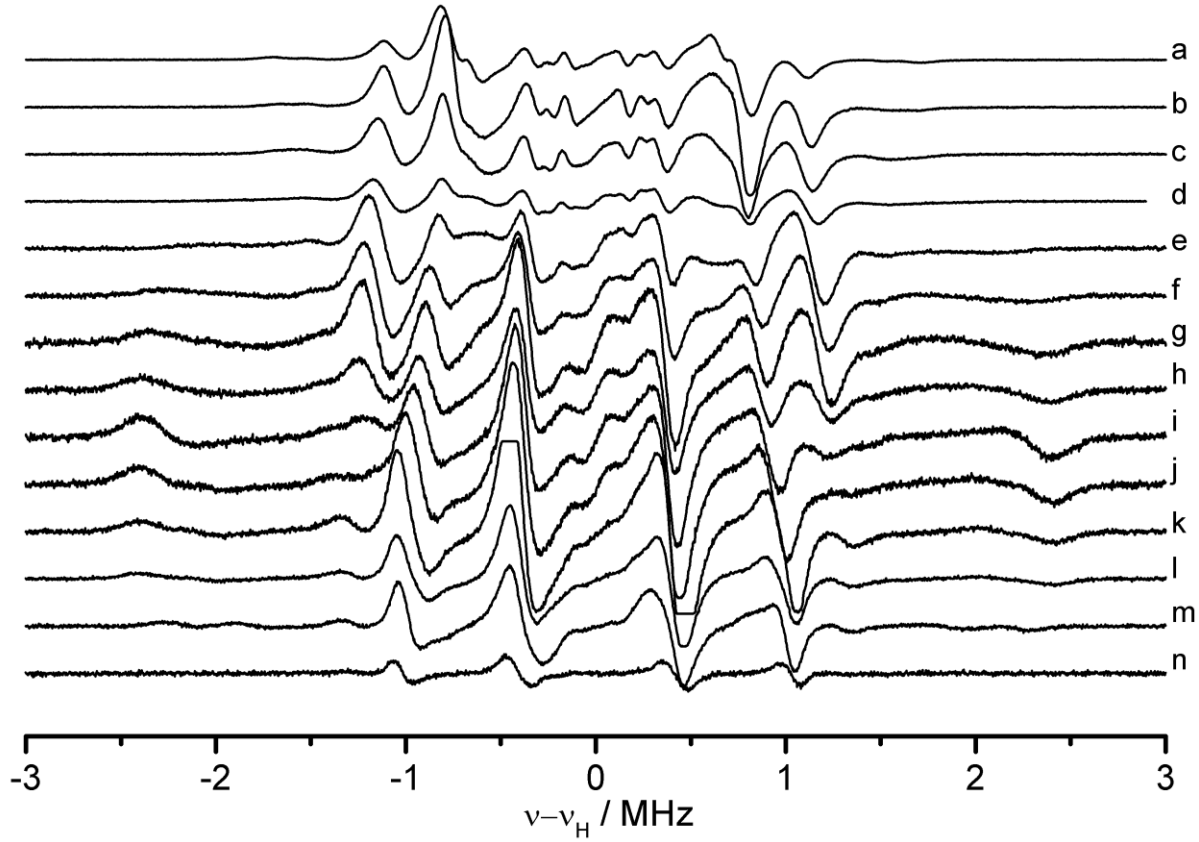
SI-Fig. 1 CW X-band EPR spectra (recorded at 140 K) of a) [Cu(acac)$_2$]-(2-methylpyridine) b) [Cu(acac)$_2$]-(3-methylpyridine) c) [Cu(acac)$_2$]-(4-methylpyridine) d) [Cu(acac)$_2$]-(2-amino-4-methylpyridine) e) [Cu(acac)$_2$]-(pyridazine) f) [Cu(acac)$_2$]-(pyrimidine) g) [Cu(acac)$_2$]-(pyrazine). The corresponding simulations are shown with the dashed lines.



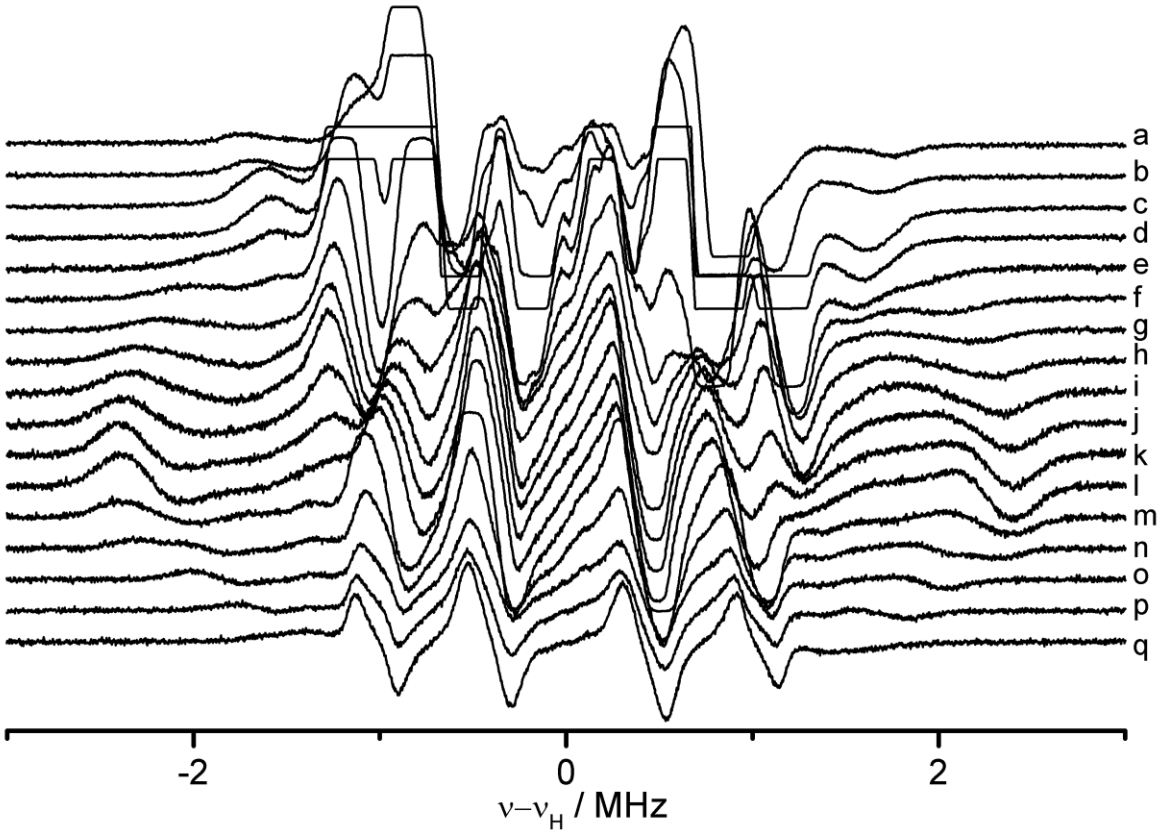
SI-Fig. 2 CW Q-band EPR spectra (recorded at 140 K) of a) $[Cu(acac)_2]$ b) $[Cu(acac)_2]$-(pyridine) c) $[Cu(acac)_2]$-(2-methylpyridine) d) $[Cu(acac)_2]$-(3-methylpyridine) e) $[Cu(acac)_2]$-(4-methylpyridine) f) $[Cu(acac)_2]$-(2-amino-4-methylpyridine) g) $[Cu(acac)_2]$-(2-amino-6-methylpyridine). The corresponding simulations are shown with the dashed lines. Field positions for ^1H ENDOR measurements are indicated with *.



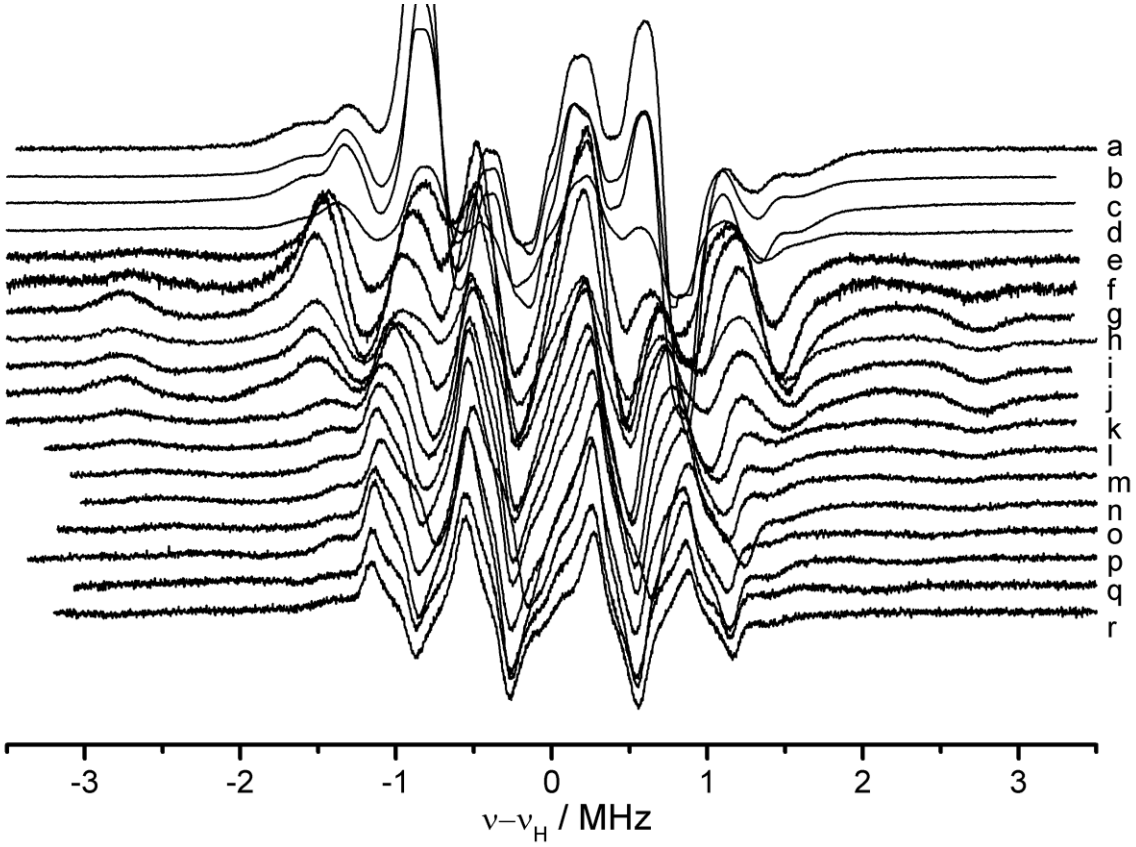
SI-Fig. 3 CW Q-band ^{1}H ENDOR spectra (10 K; 200 kHz RF modulation) of the [Cu(acac)$_2$](2-methylpyridine) adduct dissolved in dry $CDCl_3/C_6D_5CD_3$ (1:1), recorded at the field positions a) 1191.4, b) 1188.5, c) 1186.0, d) 1185.0, e) 1175.0, f) 1159.2, g) 1143.5, h) 1120.7, i) 1109.2, j) 1094.9, k) 1086.4, l) 1077.8, m) 1070.6, n) 1060.7, o) 1054.9, and p) 1044.9 mT.



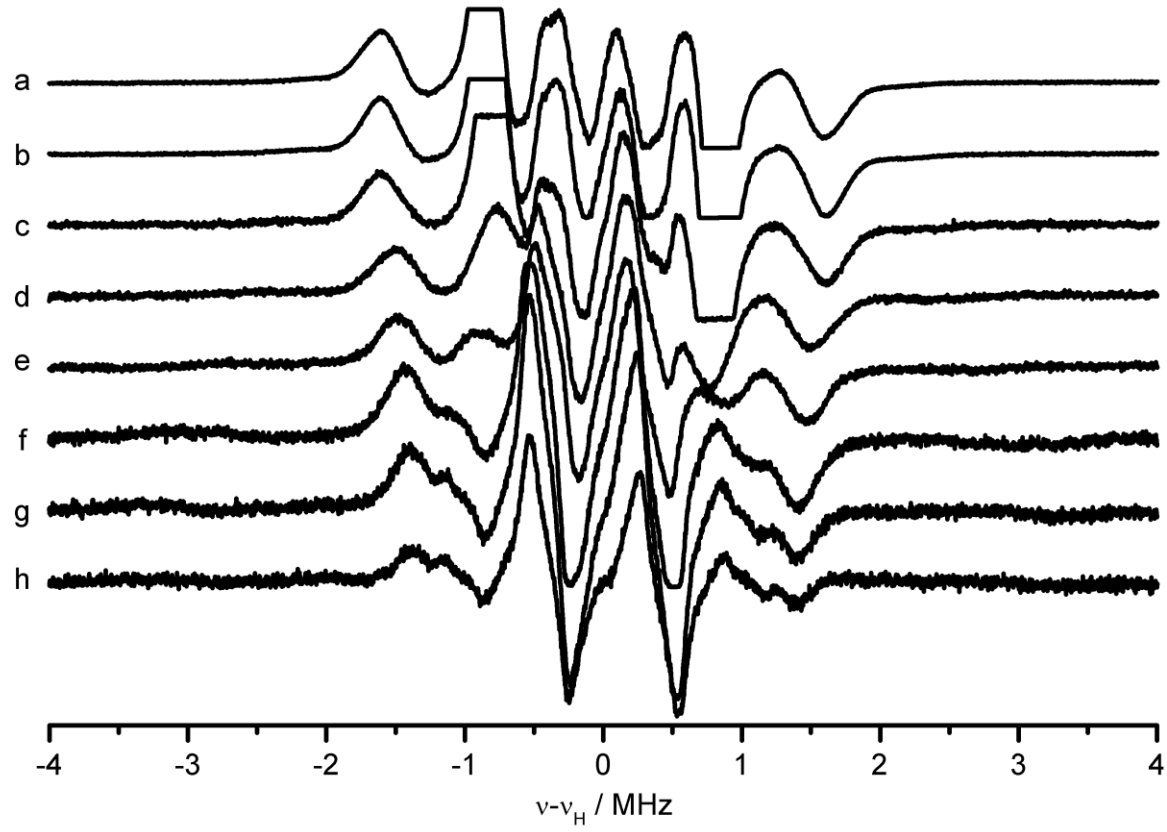
SI-Fig. 4 CW Q-band ^{1}H ENDOR spectra (10 K; 200 kHz RF modulation) of the [Cu(acac)$_2$](3-methylpyridine) adduct dissolved in dry $CDCl_3/C_6D_5CD_3$ (1:1), recorded at the field positions a) 1192.1, b) 1185.0, c) 1177.8, d) 1170.7, e) 1162.1, f) 1149.3, g) 1140.7, h) 1132.1, i) 1119.2, j) 1106.3, k) 1092.1, l) 1082.4, m) 1067.8 and n) 1043.5 mT.



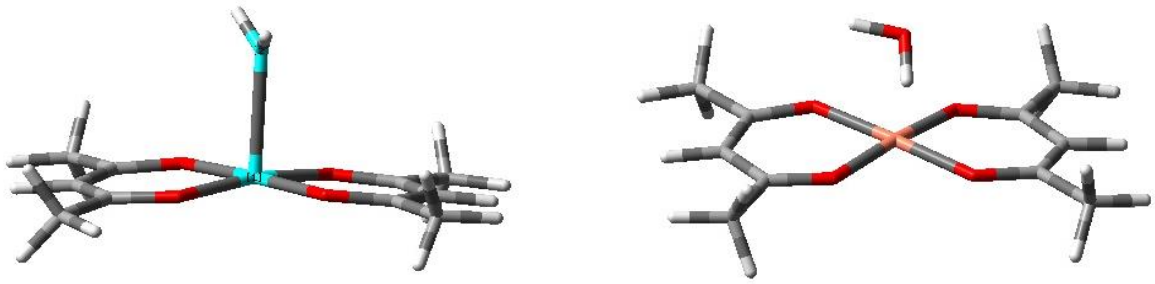
SI-Fig. 5 CW Q-band ^{1}H ENDOR spectra (10 K; 200 kHz RF modulation) of the $[Cu(acac)_2]$(4-methylpyridine) adduct dissolved in dry $CDCl_3/C_6D_5CD_3$ (1:1), recorded at the field positions a) 1192.1, b) 1189.2, c) 1185.0, d) 1179.2, e) 1170.7, f) 1162.1, g) 1153.5, h) 1144.9, i) 1139.2, j) 1130.6, k) 1122.1, l) 1113.5, m) 1093.5, n) 1072.1, o) 1054.9, p) 1049.2 and q) 1044.9 mT.



SI-Fig. 6 CW Q-band ^{1}H ENDOR spectra (10 K; 200 kHz RF modulation) of the [Cu(acac)$_2$](2-amino-4-methylpyridine) adduct dissolved in dry $CDCl_3/C_6D_5CD_3$ (1:1), recorded at the field positions a) 1190.7, b) 1186.4, c) 1183.5, d) 1172.1, e) 1159.2, f) 1147.8, g) 1136.4, h) 1134.0, i) 1125.0, j) 1112.1, k) 1100.7, l) 1092.1, m) 1076.4, n) 1070.0, o) 1066.4, p) 1059.2, q) 1052.1 and r) 1043.5 mT.



SI-Fig. 7 CW Q-band ^{1}H ENDOR spectra (10 K; 200 kHz RF modulation) of the [Cu(acac)$_2$](d$_2$-2-amino-6-methyl-pyridine) adduct dissolved in dry $CDCl_3/C_6D_5CD_3$ (1:1), recorded at the field positions a) 1181.8, b) 1177.4, c) 1168.9, d) 1154.6, e) 1134.8, f) 1092.1, g) 1066.2 and h) 1048.9 mT.



SI-Fig. 8 DFT generated structures representing the end-on (left) and side-on (right) coordination mode of H_2O to [Cu(acac)$_2$]. The side on configuration was 8.7 kJ mol^{-1} more stable.

SI-Table 1 Summary of DFT calculated spin Hamiltonian parameters

Molecular structure	Functional	Cu basis set	Ligand basis set	g_1	g_2	g_3	A_1	A_2	A_3	REF
Trans [a]	PBE0	CP	EPR(II)	2.069	2.068	2.219	-72	-76	-861	TW
Trans	B38LYP	CP	IGLO(II)	2.0835	2.0828	2.2824	69	74	-557	1
Cis [b]	B38LYP	CP	IGLO(II)	2.0839	2.0848	2.2889	73	76	-550	1
Sq. plr[c]	BP86	CP	DB4	-	-	2.127	-	-	475	2
Sq. plr	B3LYP	CP	DB4	-	-	2.190	-	-	554	2

All *A* values given in MHz. [a] Pyridine ring bisects between acac units; [b] Pyridine ring bisects across acac units; [c] Molecular structure of mono adduct not specified.

References

1. K. J. de Almeida, T. C. Ramalho, Z. Rinkevicius, O. Vahtras, H. Ãgren and A. Cesar, *J. Phys. Chem. A,* 2011, **115**, 1331-1339; (b) Z. Rinkevicius, K. J. de Almeida and O. Vahtras, *J. Chem. Phys.*, 2008, **129**, 064109-064117; (c) K. J. de Almeida, A. Cesar, Z. Rinkevicius, O. Vahtras and H. Ågren, *Chem. Phys. Lett.*, 2010, **492**, 14-18.
2. W. M. Ames and S. C. Larsen, *J. Phys. Chem. A*, 2009, **113**, 4305-4312.