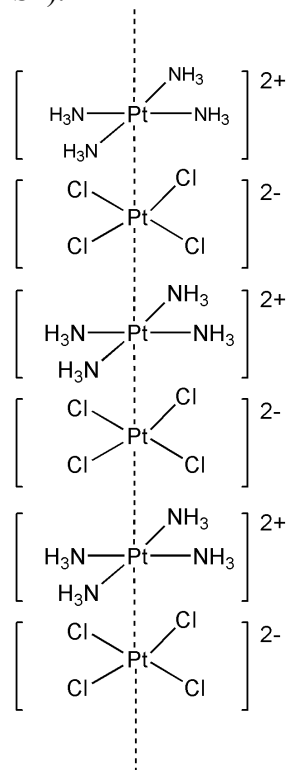


# Supplementary material to “Structural analysis of paramagnetic entities in newly designed platinum compounds with conductivity and optical properties”

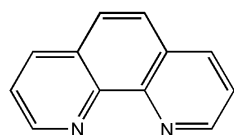
C. Finazzo, M. Fontana, S. Van Doorslaer, W. Caseri and A. Schweiger

## A. Structures

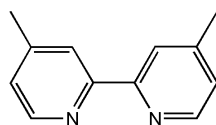
Structure of Magnus' green salt (Scheme S1) and the bidentate ligands used in this work (Scheme S2).



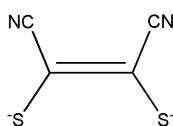
Scheme S1. Representation of the structure of Magnus' green salt.



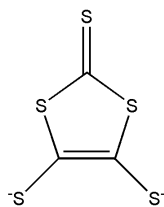
phen



mebipy



mnt



dmit

Scheme S2. Chemical structure of the bidentate ligands used in this work.

## B. Synthesis details

**Chemical Substances.**  $K_2[PtCl_4]$  was obtained from Johnson Matthew, Zurich (Switzerland), the other substances (including solvents) were purchased from Fluka, Buchs (Switzerland), or Aldrich, Buchs (Switzerland) and used as received.  $(NBu_4)_2[Pt(mnt)_2]$  was prepared as described previously<sup>2d</sup>, and  $(NBu_4)_2[Pt(dmit)_2]$  was purchased from TCI Japan. Poly(vinyl alcohol) ( $M_w = 100\ 000$  g/mol) was obtained from Polysciences, Eppelheim, Germany.

**Synthesis of  $[Pt(phen)_2](PF_6)_2$ .** The synthesis of  $[Pt(phen)_2](PF_6)_2$  followed a scheme already described in the literature<sup>S1</sup>. 1 g (2.42 mmol) of  $K_2[PtCl_4]$  was heated in 20 ml of water under stirring at 60 °C. At the same time 0.481 mg (2.42 mmol) of phenanthroline-monohydrate ( $phen \cdot H_2O$ ) were dissolved in 5 ml of DMF (dimethyl formamide) at 60 °C. The solutions were mixed and the reaction mixture was kept under reflux for 45 min at 60 °C. After 45 min a yellow precipitate formed, consisting of  $[Pt(phen)]Cl_2$  which was immediately filtered through a Teflon<sup>®</sup> filter (pore diameter 1  $\mu m$ ). The remaining solids were washed in the filter with 30 ml hexane and dried at  $10^{-2}$  mbar for 24 h, yielding 600 mg (52%) of product. The elemental analysis revealed the following contents (in % w/w, calculated values in parenthesis): C 32.87 (32.80), H 1.82 (1.93), N 6.16 (6.37), Cl 15.30 (15.94).

Thereafter 78 mg (1.74 mmol) of  $[Pt(phen)]Cl_2$  was suspended in water, and to this solution an excess of  $phen \cdot H_2O$  (0.7 g, 3.53 mmol) was added. The formed suspension was left for 18 h under reflux at 110 °C until a clear yellow suspension formed. In fact, analogous to the preparation of the perchlorate complex described in the literature<sup>6</sup> the in-situ-formed  $[Pt(phen)_2Cl_2]$  salt is soluble at this temperature in water. In order to precipitate the platinum complex, a stoichiometric amount of sodium hexafluorophosphate ( $NaPF_6$ ) was added to the chloride complex. The yellow  $[Pt(phen)_2](PF_6)_2$  precipitated and was immediately filtered through a Teflon<sup>®</sup> filter (pore diameter 1  $\mu m$ ). The remaining solids in the filter were washed with 30 ml water and dried at  $10^{-2}$  mbar for 24 h. A yield of 430 mg (35 %) was obtained. The elemental analysis revealed the following contents (in % w/w, calculated values in parenthesis): C 34.85 (34.10), H 2.05 (1.91), N 4.71 (4.63), P 7.25 (7.33), F 26.80 (26.97). Additional analytical data are discussed in the main text.

**Synthesis of  $[Pt(mebipy)_2](PF_6)_2$ .** The synthesis of  $[Pt(mebipy)_2](PF_6)_2$  followed a scheme described in the literature for a similar complex<sup>S1</sup>. 1 g (2.42 mmol) of  $K_2[PtCl_4]$  was heated in 20 ml of water under stirring at 60 °C and then cooled to room temperature. During the same time 0.481 mg (3.05 mmol) of 4,4-dimethyl-2,2-dipyridyl (mebipy) were dissolved in a separate vessel in 5 ml of DMF at 60 °C. The solutions were mixed and the mixture was kept under reflux for 45 min at 60 °C. After 45 min a yellow precipitate formed consisting of  $[Pt(mebipy)]Cl_2$ , as described in the literature for the preparation of the corresponding perchlorate complex<sup>S1</sup>. The yellow precipitate was filtered through a Teflon<sup>®</sup> filter (pore diameter 1  $\mu m$ ) and the remaining solids were washed in the filter with 30 ml hexane and dried at  $10^{-2}$  mbar for 24 h. A yield of 146 mg (63 %) was obtained. The elemental analysis revealed the following contents (in % w/w, calculated values in parenthesis): C 32.62 (32.01), H 2.61 (2.69), N 6.44 (6.22), Cl 16.19 (15.75).

Thereafter 80 mg (1.8 mmol) of  $[Pt(mebipy)]Cl_2$  were suspended in 200 ml water, and to this solution an excess of mebipy (0.7 mg, 3.5 mmol) was added. The resulting suspension was left for 18 h under reflux at 110 °C until a clear yellow suspension formed. In fact, the in-situ-formed  $[Pt(mebipy)_2]Cl_2$  is soluble at this temperature in water. In order to precipitate the platinum complex a stoichiometric amount of sodium hexafluorophosphate (30 mg) was added to the chloride complex. The yellow  $[Pt(mebipy)_2]Cl_2$  precipitated and was filtered through a Teflon<sup>®</sup> filter (pore diameter 1  $\mu m$ ). The remaining solids were washed in the filter with 30 ml  $H_2O$  and dried at  $10^{-2}$  mbar for 24 h. A yield of 400 mg (25 %) was obtained. The elemental analysis revealed the following contents (in % w/w,

calculated values in parenthesis): C 34.71 (33.72), H 3.08 (3.06), N 6.50 (6.23). Additional analytical data are discussed in the text.

**Synthesis of [Pt(phen)<sub>2</sub>][Pt(mnt)<sub>2</sub>].** A quantity of 0.192 g (0.20 mmol) of [Pt(phen)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> were dissolved in 5 ml DMF at 60 °C and then cooled to room temperature. To this solution 0.200 g (0.20 mmol) of (NBu<sub>4</sub>)<sub>2</sub>[Pt(mnt)<sub>2</sub>], dissolved in 5 ml of acetone at room temperature, were added. A deep green precipitate formed after few minutes at room temperature. The mixture was immediately filtered through a Teflon<sup>®</sup> filter (pore diameter 1 μm) and the remaining solids were washed in the filter with 30 ml hexane and dried at 10<sup>-2</sup> mbar for 24 h. A yield of 65% (134 mg) was obtained. The elemental analysis revealed the following contents (in % w/w, calculated values in parenthesis): C 37.53 (37.28), H 1.60 (1.56), N 10.71 (10.87), S 12.22 (12.44). Additional analytical data are discussed in the maintext.

**Synthesis of [Pt(phen)<sub>2</sub>][Pt(dmit)<sub>2</sub>].** 0.200 g (0.26 mmol) of [Pt(phen)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> were dissolved in 5 ml DMF at 60 °C and then cooled to room temperature. To this solution, 0.246 g (0.26 mmol) of (NBu<sub>4</sub>)<sub>2</sub>[Pt(dmit)<sub>2</sub>], dissolved in 5 ml of acetone at room temperature, were added. A black precipitate formed after few minutes at room temperature. The resulting mixture was filtered through a Teflon<sup>®</sup> filter (pore diameter 1 μm) and the remaining solids were washed in the filter with 30 ml hexane and dried at 10<sup>-2</sup> mbar for 24 h. A yield of 254 mg (85%) was obtained. The elemental analysis revealed the following contents (in % w/w, calculated values in parenthesis): C 31.52 (31.24), H 1.41 (1.64), N 4.85 (4.90), S 28.05 (28.02). Additional analytical data are discussed in the main text.

**Synthesis of [Pt(mebipy)<sub>2</sub>][Pt(mnt)<sub>2</sub>].** 0.300 g (0.345 mol) of [Pt(mebipy)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> were dissolved in 5 ml dimethylformamide at 60 °C and then cooled to room temperature. To this solution 0.340 g (0.345 mmol) of (NBu<sub>4</sub>)<sub>2</sub>[Pt(mnt)<sub>2</sub>] dissolved in 5 ml of acetone at room temperature were added. A deep red-violet precipitate formed immediately. The mixture was immediately filtered through a Teflon<sup>®</sup> filter (pore diameter 1 μm) and the remaining solids were washed in the filter with 30 ml hexane and dried at 10<sup>-2</sup> mbar for 24 h. A yield of 254 mg (80 %) was obtained. The elemental analysis revealed the following contents (in % w/w, calculated values in parenthesis): C 37.50 (37.10), H 2.55 (2.31), N 10.45 (10.78), S 12.50 (12.06). Additional analytical data are discussed in the main text.

**Synthesis of [Pt(mebipy)<sub>2</sub>][Pt(dmit)<sub>2</sub>].** 0.200 g (0.23 mmol) of [Pt(mebipy)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> were dissolved in 5 ml dimethylformamide at 60 °C. After cooling this solution to room temperature, 0.246 g (0.23 mmol) of (NBu<sub>4</sub>)<sub>2</sub>[Pt(dmit)<sub>2</sub>] dissolved in 5 ml of acetone at room temperature were added. A deep green precipitate formed after few minutes at room temperature. The mixture was immediately filtered through a Teflon<sup>®</sup> filter (pore diameter 1 μm) and the remaining solids were washed with 30 ml hexane and dried at 10<sup>-2</sup> mbar for 24 h. A yield of 202 mg (80 %) was obtained. The elemental analysis revealed the following contents (in % w/w, calculated values in parenthesis): C 31.40 (31.32), H 2.30 (2.20), N 4.66 (4.87), S 27.82 (27.85). Additional analytical data are discussed in the text.

## References

S1. Morgan, G.T.; Burstall, F.H. *J. Chem. Soc.* **1934**, 965-971

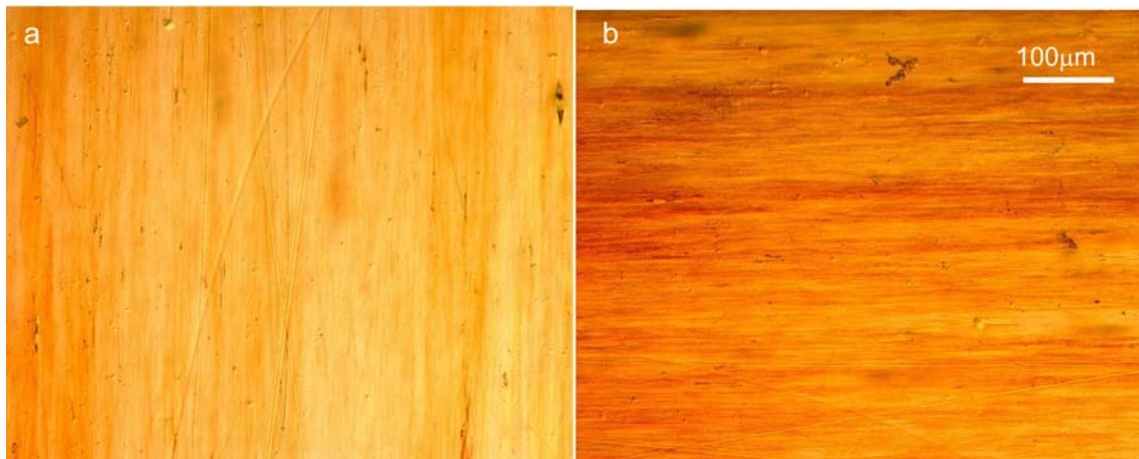
## C. IR data

**Table S1.** Selected IR Frequencies (in  $\text{cm}^{-1}$ ) of  $[\text{Pt}(\text{phen})_2][\text{Pt}(\text{dmit})_2]$ ,  $[\text{Pt}(\text{mebipy})_2][\text{Pt}(\text{dmit})_2]$  and related model compounds.

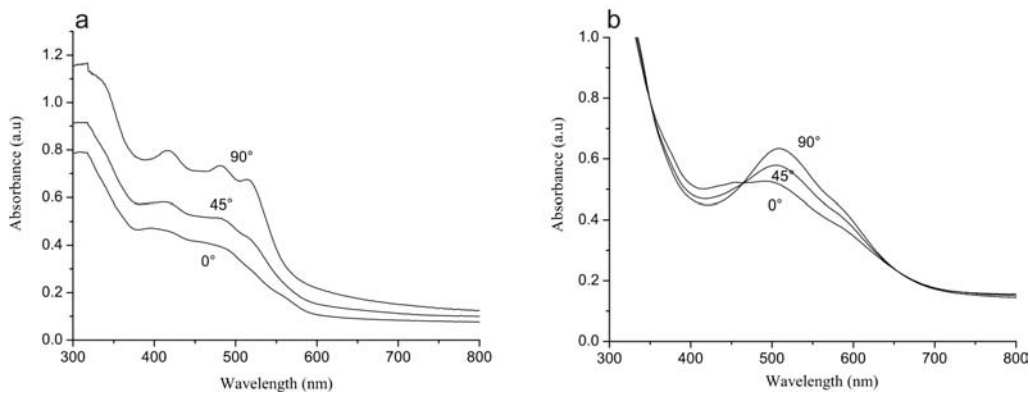
Compound	$\nu$ (C-H) aromatic	$\nu(\text{Pt-S})$
$(\text{NBu}_4)_2[\text{Pt}(\text{dmit})_2]$		468
		353
		323
$[\text{Pt}(\text{phen})_2](\text{PF}_6)_2$	3067	
	3080	
$[\text{Pt}(\text{phen})_2][\text{Pt}(\text{dmit})_2]$	3066	469
		354
		321
$[\text{Pt}(\text{mebipy})_2](\text{PF}_6)_2$	3085	
	3142	
$[\text{Pt}(\text{mebipy})_2][\text{Pt}(\text{dmit})_2]$	3060	470
		355
		323

Note that the CN stretching vibrations are evidently not present in the dmit complexes (see structure Figure 2)

## D. Dichroistic behaviour

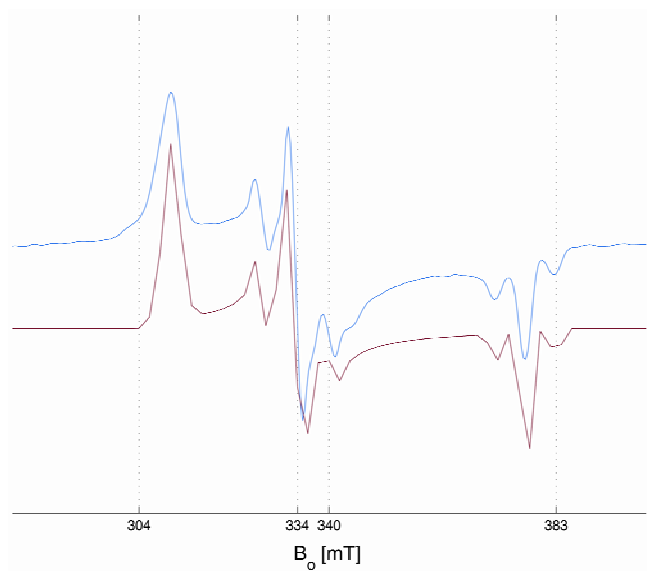


**Figure S1.** Optical micrographs of a drawn composite film (draw ratio 5) of  $[\text{Pt}(\text{mebipy}_2)][\text{Pt}(\text{mnt})_2]/\text{PVAL}$  0.6% w/w in polarized light with the polarization plane of the light (a) parallel ( $0^\circ$ ) or (b) perpendicular ( $90^\circ$ ) to the drawing axis of the composite.



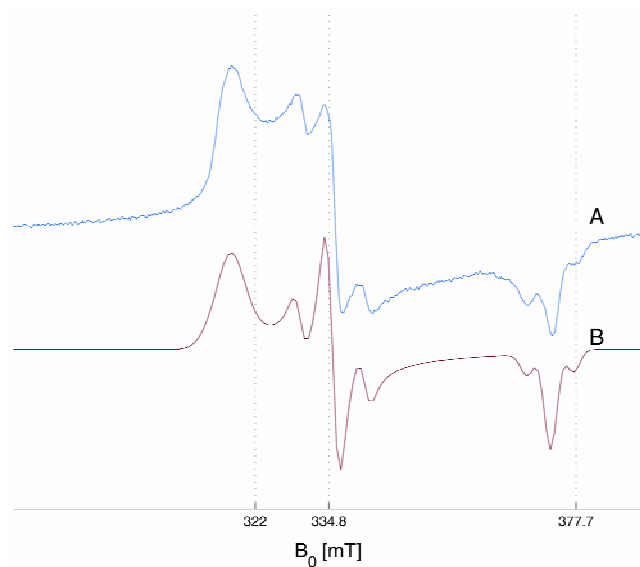
**Figure S2.** UV/VIS spectra of a drawn composite film (draw ratio 5) in polarized light of (a) PVAL and 0.6% w/w  $[\text{Pt}(\text{mebipy}_2)][\text{Pt}(\text{mnt})_2]$  and (b) PVAL and 0.6% w/w  $[\text{Pt}(\text{mebipy}_2)][\text{Pt}(\text{mnt})_2]$  or perpendicular ( $90^\circ$ ) to the drawing axis.

## E. cw EPR spectra



*Figure S3:* X-band cw EPR spectra of  $[\text{Pt}(\text{mnt})_2]^-$  in  $[\text{Pt}(\text{mebipy})_2][\text{Pt}(\text{mnt})_2]$ : experiment (A) and simulation (B). The  $B_0$ -field positions where the HYSCORE spectra are taken are marked by dashed lines.

*Figure S4:* X-band cw EPR spectrum of  $[\text{Pt}(\text{dmit})_2]^-$  in  $[\text{Pt}(\text{mebipy})_2][\text{Pt}(\text{dmit})_2]$ : experiment (A) and simulation (B). The  $B_0$ -field positions where the HYSCORE spectra are taken are marked by dashed lines.



## E. HYSORE experiments

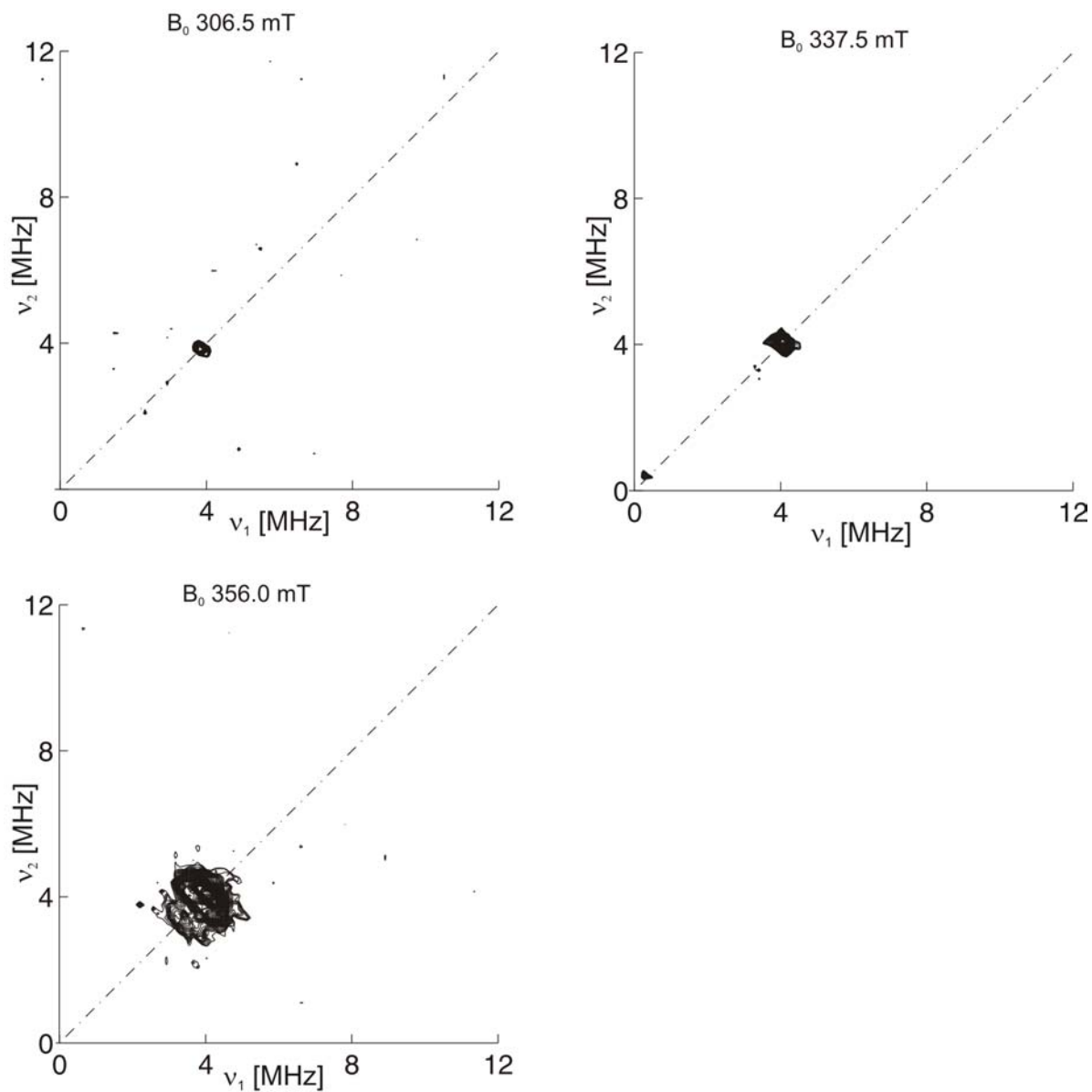


Figure S5. Experimental X-band HYSORE spectra recorded at three different field positions of  $[\text{Pt}(\text{mnt})_2]^-$  in  $(\text{NBu}_4)_2[\text{Pt}(\text{mnt})_2]$ .

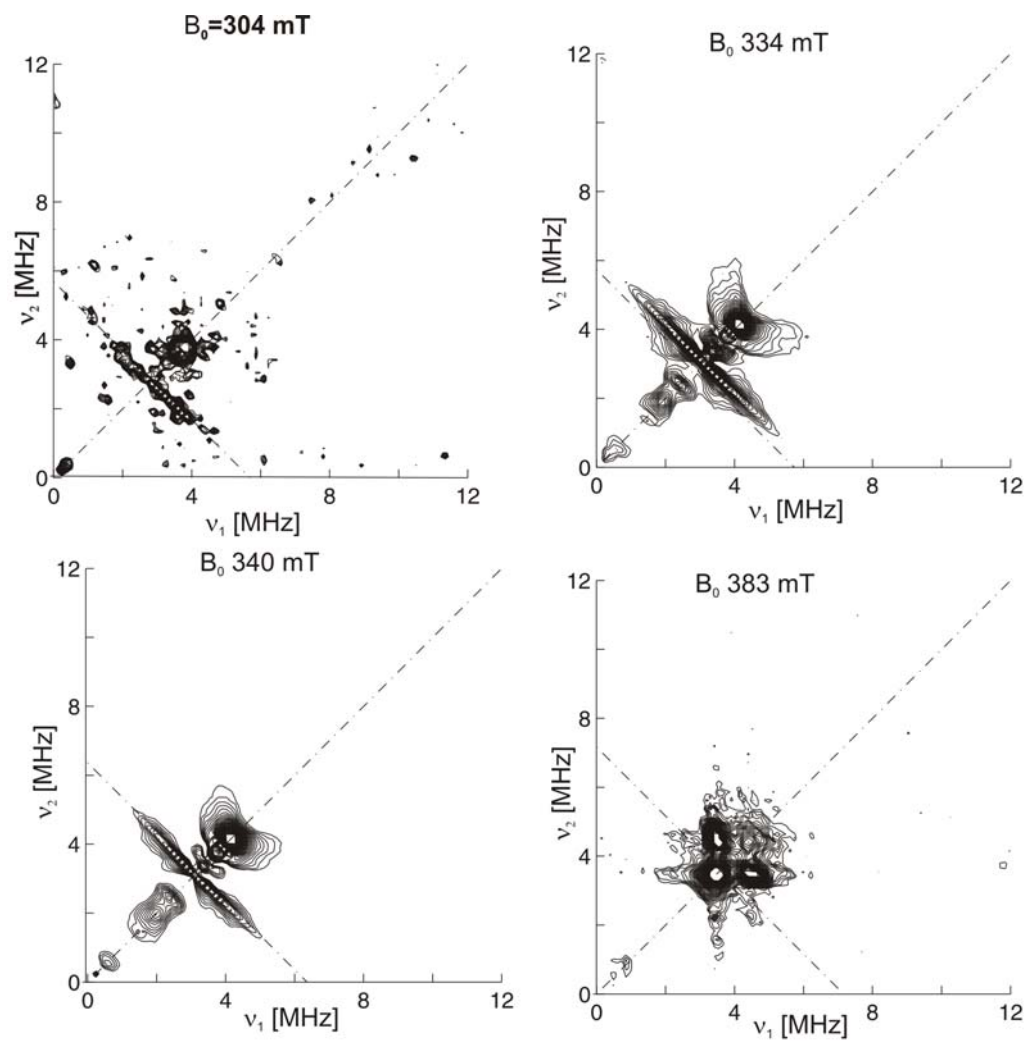


Figure S6.1



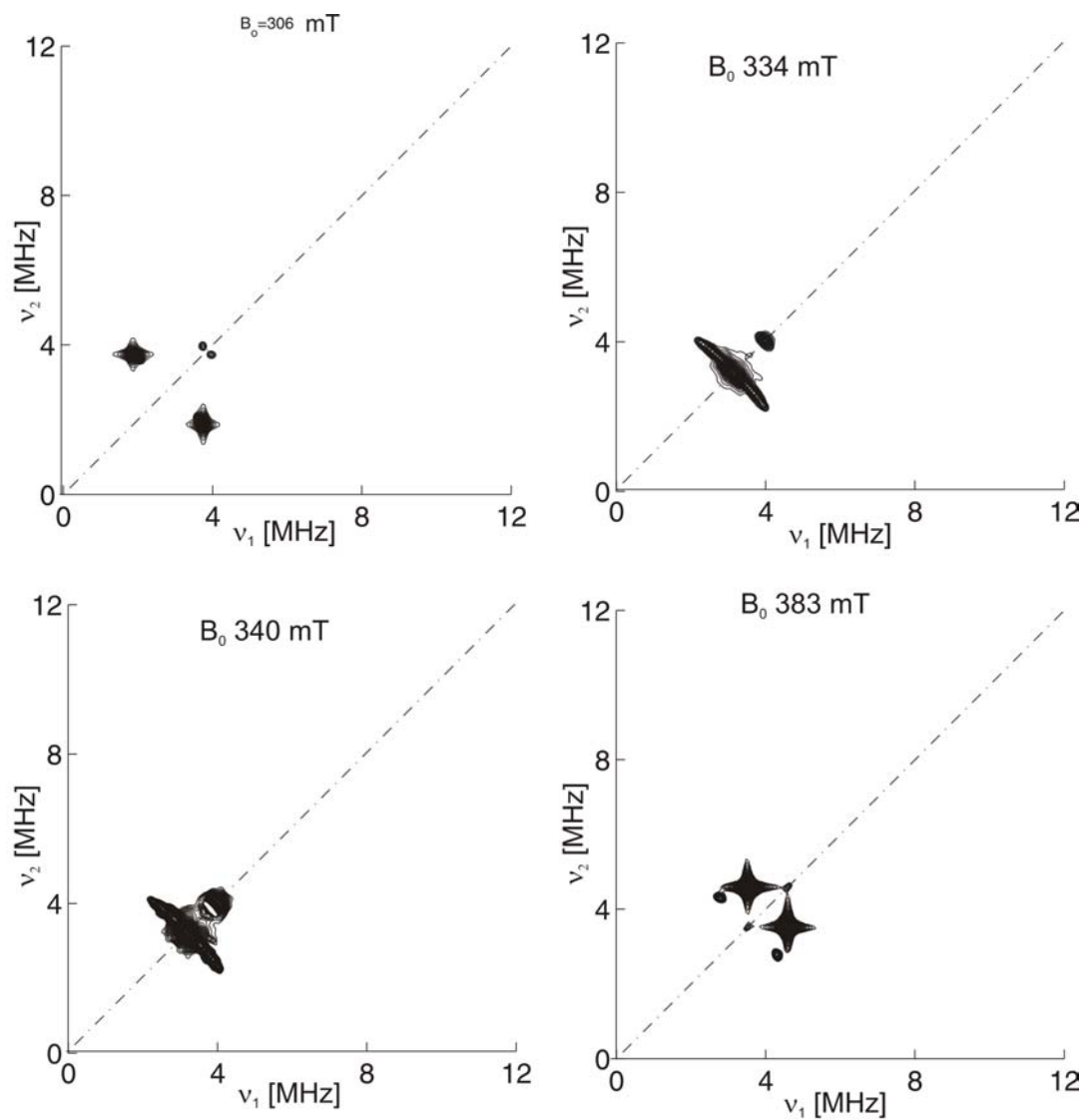


Figure S6.2

Figures S6: Experimental (S6.1) and simulated (S6.2) X-band HYSCORE spectra of  $[\text{Pt}(\text{mnt})_2]^-$  in  $[\text{Pt}(\text{mebipy})_2][\text{Pt}(\text{mnt})_2]$  recorded at four different field positions.

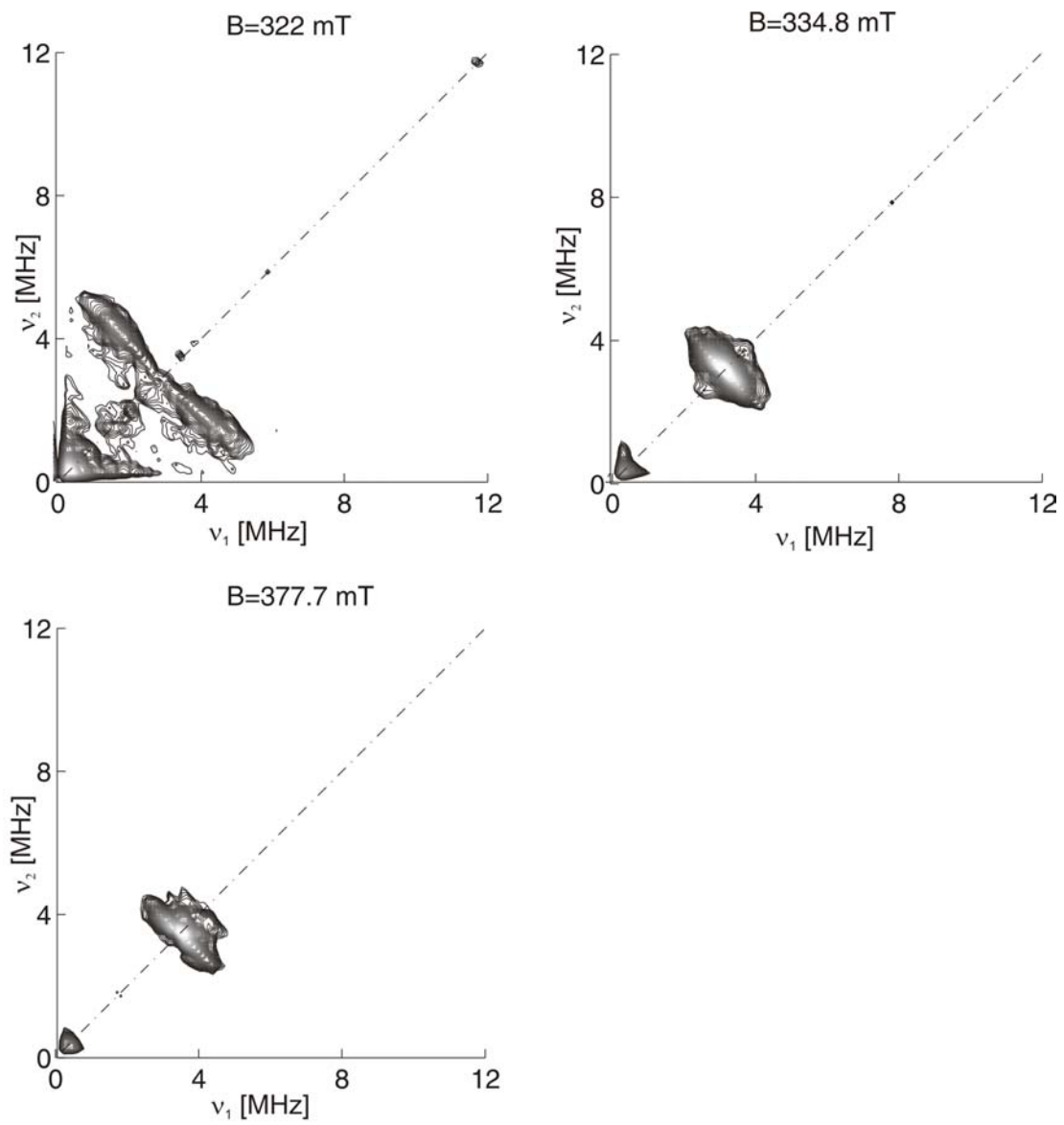


Figure S7.1

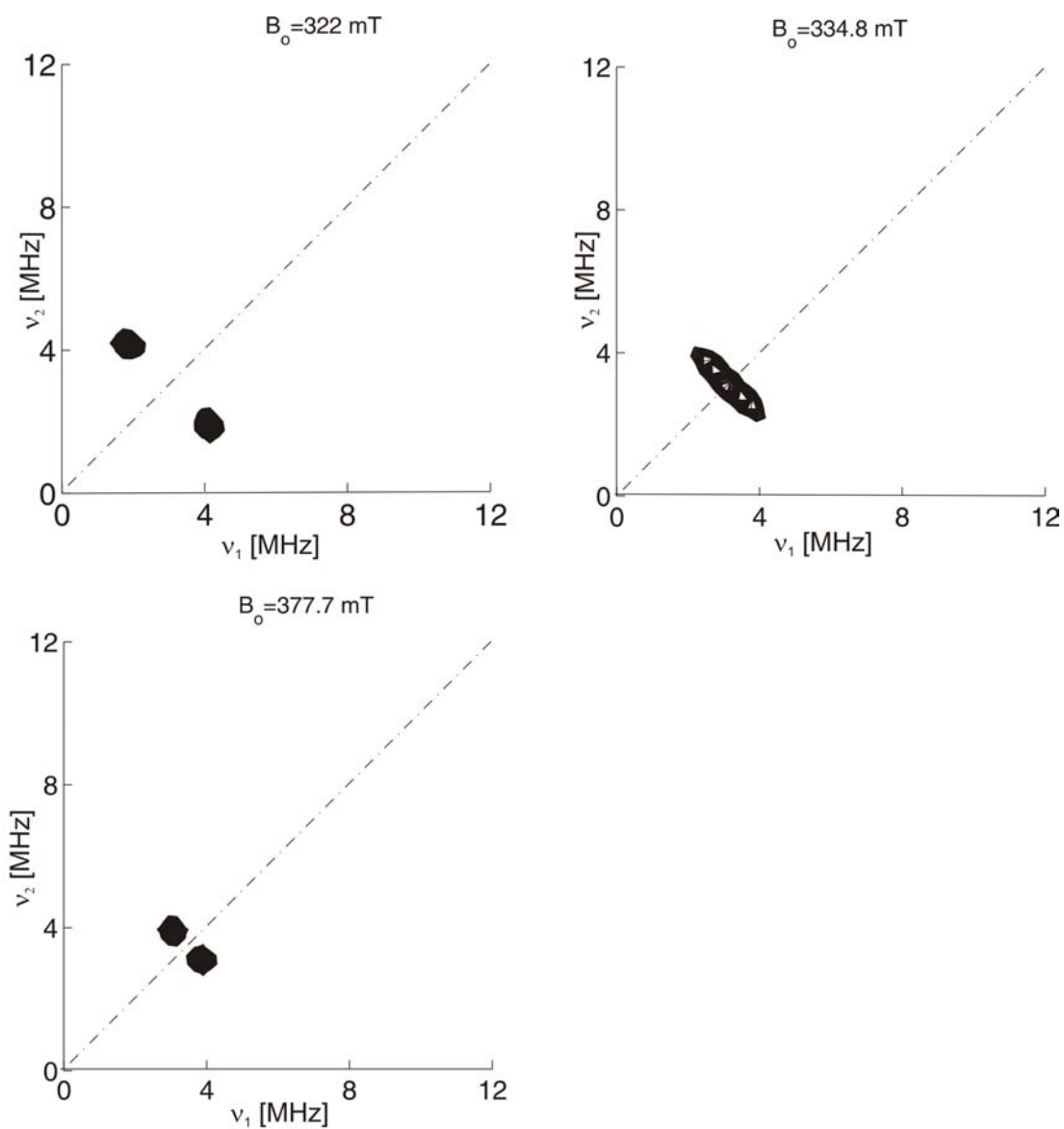


Figure 7.2

Figure S7: Experimental (S7.1) and simulated (S7.2) X-band HYSCORE spectra of  $[\text{Pt}(\text{dmit})_2]^-$  in  $[\text{Pt}(\text{mebipy})_2][\text{Pt}(\text{dmit})_2]$  recorded at three different field positions.

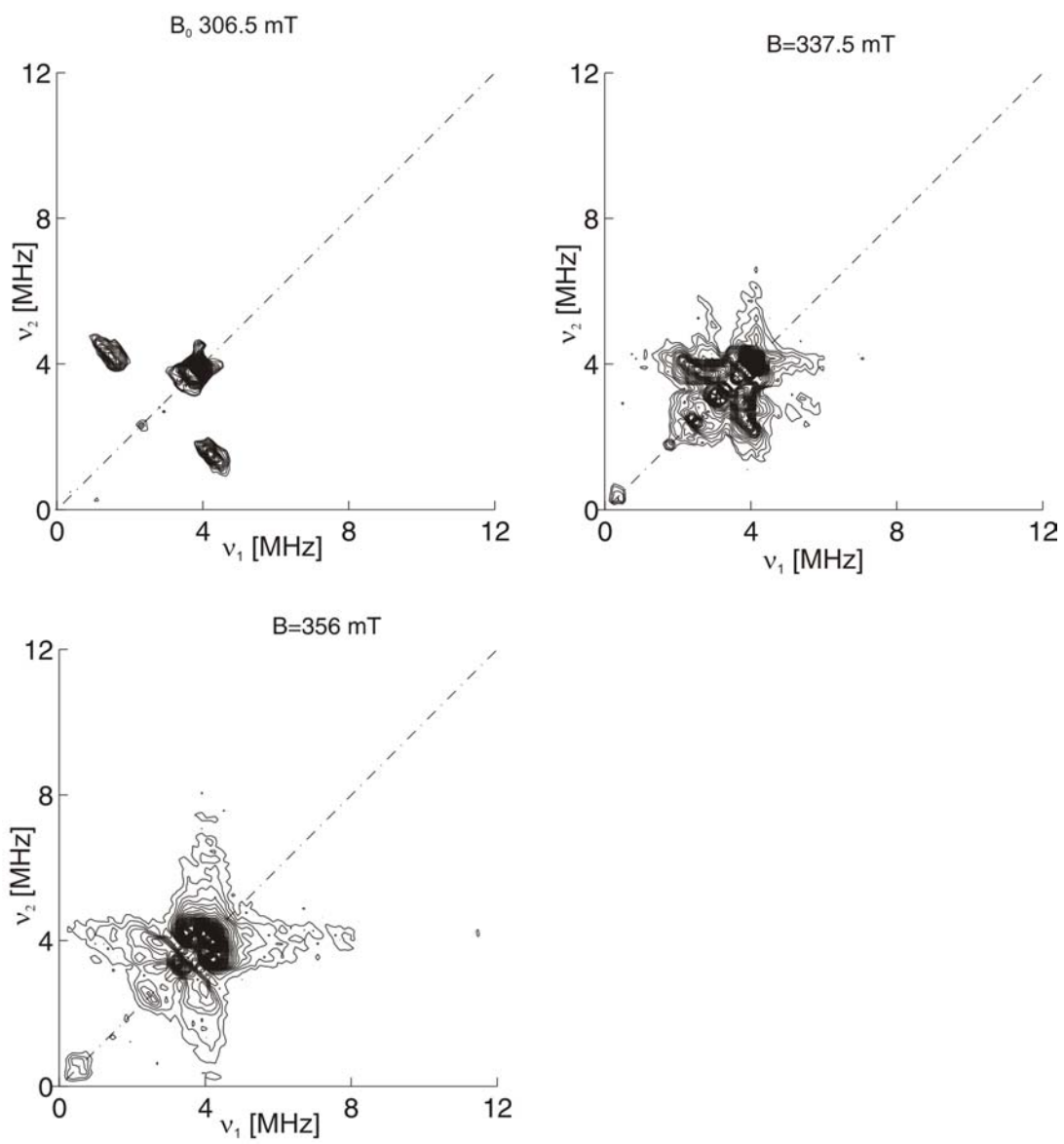


Figure S8.1

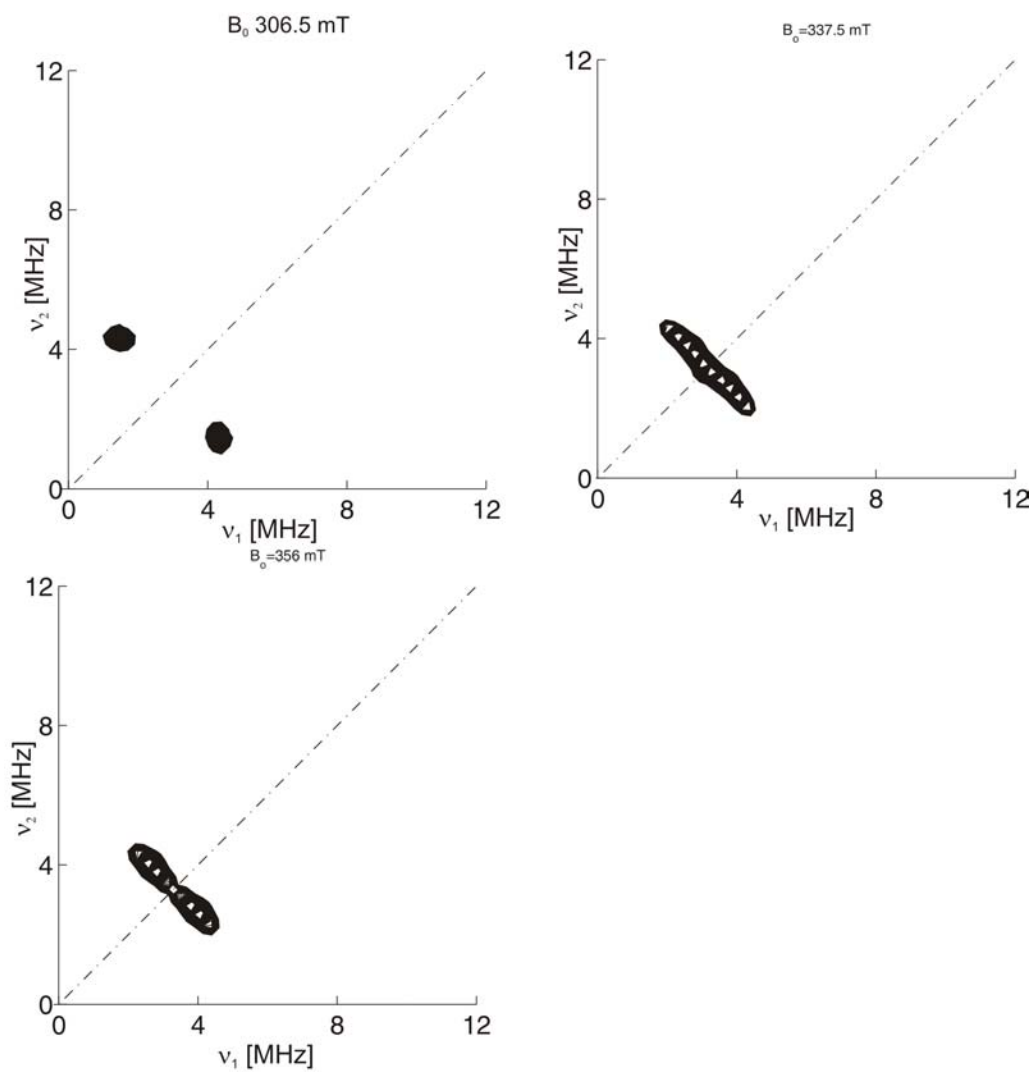


Figure S8.2

Figures S8: Experimental (S8.1) and simulated (S8.2) X-band HYSCORE spectra of  $[\text{Pt}(\text{mnt})_2]^-$  in  $[\text{Pt}(\text{phen})_2][\text{Pt}(\text{mnt})_2]$  recorded at three different field positions.