Structural and magnetic studies of copper (II) complexes of verdazyl radicals

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Supplemental Information

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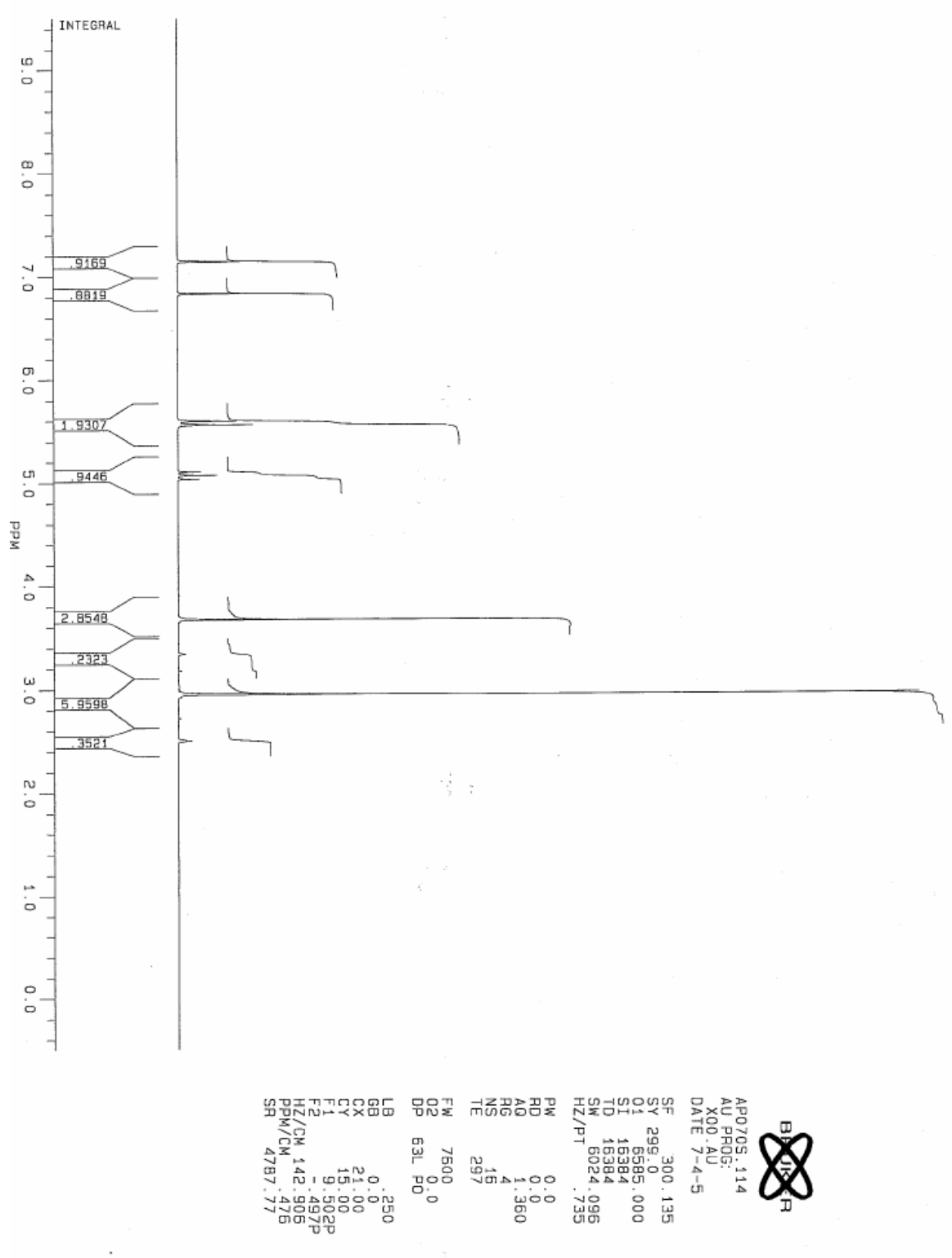

Figure S1. ^{1}H NMR of **5** in *d6*-DMSO

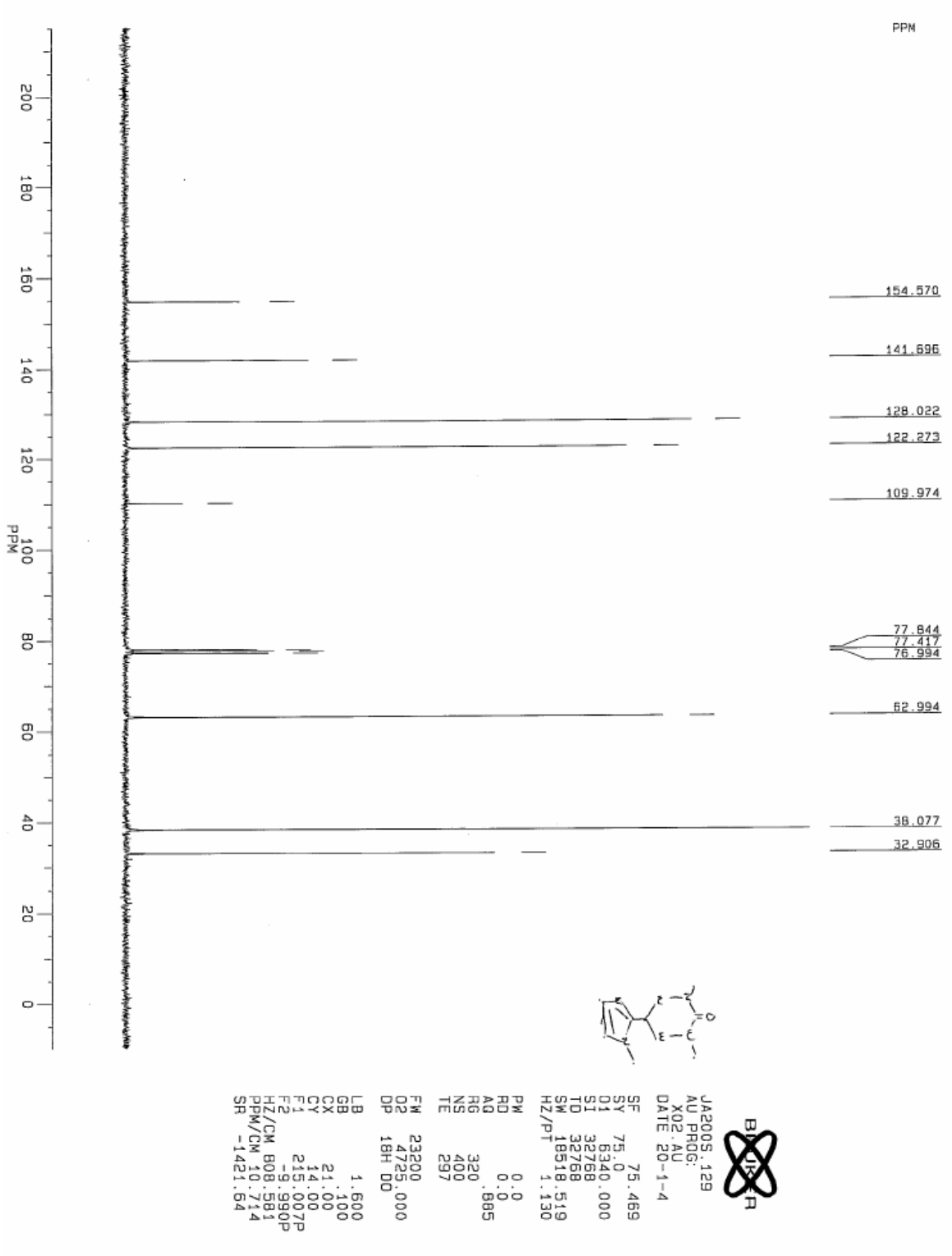

Figure S2. ^{13}C NMR of **5** in $CDCl_3$

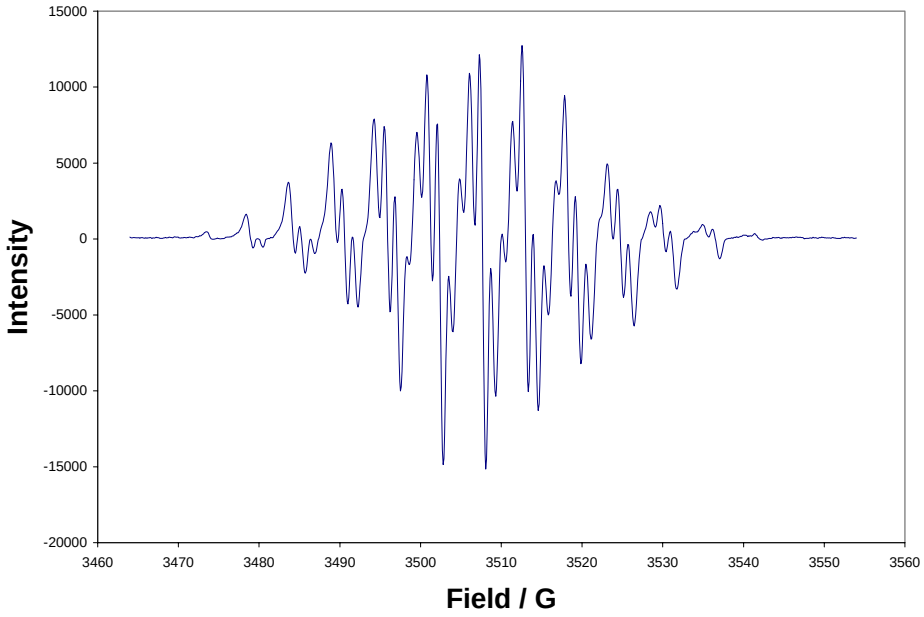

Figure S3. EPR of **4** in CH_2Cl_2 at RT (g = 2.0037, a_{N1} = 6.5 G, a_{N2} = 5.3 G, a_H = 5.3 G)

Details of Magnetic Modeling:

Goodness of fit $R = \Sigma[\chi_{obs} - \chi_{calc}]^2/\Sigma[\chi_{obs}]^2$

Verdazyl (4)

The antiferromagnetic intermolecular interactions between radicals were modeled using the Bonner-Fisher chain model[1] based on the following Hamiltonian.

$$\mathbf{H} = -J\Sigma\mathbf{S}_{rad}\cdot\mathbf{S}_{rad+1}$$

The magnetic susceptibility is thus given by:

$$\chi = \frac{Ng^2\beta^2}{kT}\frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3}$$

where x = |J|/kT

Fitting of χ with g = 2.00 fixed gave ρ = 0.95, J = -3.33 cm^{-1} and R = 0.0011.

Cu(2)Cl_2 (6)

The antiferromagnetic intramolecular interaction in complex **6** was modeled using the Bleaney-Bowers dimer model[2] based on the following Hamiltonian.

$$\mathbf{H} = -J\mathbf{S}_{Cu}\cdot\mathbf{S}_{rad}$$

The magnetic susceptibility is thus given by:

$$\chi = \frac{2Ng^2\beta^2}{kT[3+\exp(-J/kT)]}$$

The interdimer interactions observed in the crystal structure of **6** were accounted for using a molecular field correction.[3]

$$\chi' = \frac{\chi}{1-(2zJ'/Ng^2\beta^2)\chi}$$

A term for a Curie-Weiss impurity was also incorporated to yield an expression similar to that found above. Fitting of χT with g = 2.1 fixed gave values ρ = 0.97, J = -203.99 cm^{-1}, 2zJ' = -520.95 cm^{-1}, and θ = -2.31 K, R = 0.011.

Cu(pyvd)(hfac)$_2$ (8)

An analogous approach was taken to that of compound **6**. Fitting of χT with g = 2.1 fixed gave values ρ = 0.99, J = 5.00 cm^{-1}, 2zJ' = -7.57 cm^{-1}, θ = 1.50 K, and R = 0.0011. The value of J was optimized by first fitting a truncated portion of the data, removing the high and low temperature linear portions of the data. It should be noted that the exact value of J has little impact on the overall curvature, and values between 2 and 10 cm^{-1} can be used to model this data effectively.

Cu(NMe-imdvd)(hfac)$_2$ (9)

A four-spin model[4] was employed based on the following spin arrangement:

$$S_{Cu1} \overset{J_2}{\text{---}} S_{rad1} \overset{J_1}{\text{---}} S_{rad2} \overset{J_2}{\text{---}} S_{Cu2}$$

The corresponding Hamiltonian is as follows:

$$\mathbf{H} = -2J_1\mathbf{S}_{rad1}\cdot\mathbf{S}_{rad2} - 2J_2(\mathbf{S}_{rad1}\cdot\mathbf{S}_{Cu1} + \mathbf{S}_{rad2}\cdot\mathbf{S}_{Cu2})$$

The related expression for susceptibility is given by:

$$\chi = \frac{Ng^2\beta^2}{kT}\frac{A}{B}$$

$$A = 10\exp(-E_1/kT) + 2\exp(-E_2/kT) + 2\exp(-E_3/kT) + 2\exp(-E_4/kT)$$

$$B = 5\exp(-E_1/kT) + 3[\exp(-E_2/kT) + \exp(-E_3/kT) + \exp(-E_4/kT)] + \exp(-E_5/kT) + \exp(-E_6/kT)$$

$$E_1 = -J_2 - J_1/2$$

$$E_2 = J_2 - J_1/2$$

$$E_3 = J_1/2 + (J_2^2 + J_1^2)^{1/2}$$

$$E_4 = J_1/2 - (J_2^2 + J_1^2)^{1/2}$$

$$E_5 = J_2 + J_1/2 + (4J_2^2 - 2J_2J_1 + J_1^2)^{1/2}$$

$$E_6 = J_2 + J_1/2 - (4J_2^2 - 2J_2J_1 + J_1^2)^{1/2}$$

A second term was once again introduced in order to account for paramagnetic impurities displaying Curie-Weiss impurity. It should also be noted that our data was based on molecular units containing two spins rather than a true four spin system, therefore the expression for χ was multiplied by one half. The overall equation used to model susceptibility was:

$$\chi' = (\rho)\frac{Ng^2\beta^2}{2kT}\frac{A}{B} + (1-\rho)\frac{2Ng^2\beta^2}{k(T-\Theta)}$$

Fitting of χT with g = 2.1 fixed gave values $\rho = 0.95$, $J_1 = -39.51$ cm^{-1}, $J_2 = 6.06$ cm^{-1}, $\theta = 0.59$ K, and R = 0.00058. The curvature from 25-150 K shows dependence on J_1 almost exclusively with the value of J_2 and θ having a larger influence on the low temperature data. It should be noted that J_2 has little impact on the overall curvature, and values between 2 and 10 cm^{-1} can be used to model this data.

References

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