

Valence Tautomerism in a Cobalt-Verdazyl Coordination Compound.

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I. Synthetic Details

General Experimental Details

1,3-di-(2'-pyridyl)-5-isopropyl-6-oxo-4H-tetrazine was synthesized as previously described. Cobalt triflate was synthesized from cobalt metal and triflic acid in acetonitrile. NMR spectra are referenced to internal solvent peaks.

$[\text{Co}(\text{dipyvd})_2]^+\text{PF}_6^-$

1,3-di-(2'-pyridyl)-5-isopropyl-6-oxo-4H-tetrazine (120 mg, 0.4 mmol) was dissolved in 5 mL acetonitrile. To this was added a solution of cobalt(II) triflate (87 mg, 0.2 mmol) in 1 mL acetonitrile. The solution immediately turned greenish brown and then turned deep green upon stirring in air for ~10 min. The solution was evaporated and the deep green residue redissolved in 10 mL methanol. To this was added excess ammonium hexafluorophosphate dissolved in methanol, followed by the addition of 5 mL water. The resulting deep green precipitate was removed by filtration and dried under vacuum. (127 mg, 0.16 mmol, 80%) The precipitate was purified by diffusion of ether into an acetonitrile solution to give very dark green needle shaped crystals containing one equivalent of diethyl ether solvate. $^1\text{H-NMR}$ (300 MHz; CD_3CN): δ 8.42 (dd, $J = 5.7, 0.5$ Hz, 1H), 8.17-8.09 (m, 2H), 8.06 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.98 (td, $J = 7.6, 1.3$ Hz, 1H), 7.70 (ddd, $J = 8.8, 7.2, 1.6$ Hz, 1H), 7.50 (ddd, $J = 7.6, 5.7, 1.7$ Hz, 1H), 6.86 (ddd, $J = 7.2, 6.2, 1.1$ Hz, 1H), 5.04 (quintet, $J = 6.6$ Hz, 1H), 3.43 (q, $J = 7.0$ Hz, 4H, Et_2O solvate) 1.53 (d, $J = 6.6$ Hz, 6H), 1.14 (t, $J = 7.0$ Hz, 6H, Et_2O solvate). ^{13}C NMR (CD_3CN) 155.0, 154.92, 153.14, 150.55, 147.26, 146.24, 141.43, 140.92, 128.74, 124.14, 120.45, 114.81, 65.83 (Et_2O), 48.33, 20.20, 15.18 (Et_2O solvate); IR(ATR) 1685 cm^{-1} (C=O); UV-vis (CH_3CN) λ_{max} 632 nm ($\epsilon=1350$); ESMS $m/z=649$; calcd. for $\text{C}_{34}\text{H}_{40}\text{CoF}_6\text{N}_{12}\text{O}_3\text{P}$: C, 47.01; H, 4.64; N, 19.35; found: C 47.44 H 3.99 N 19.49.

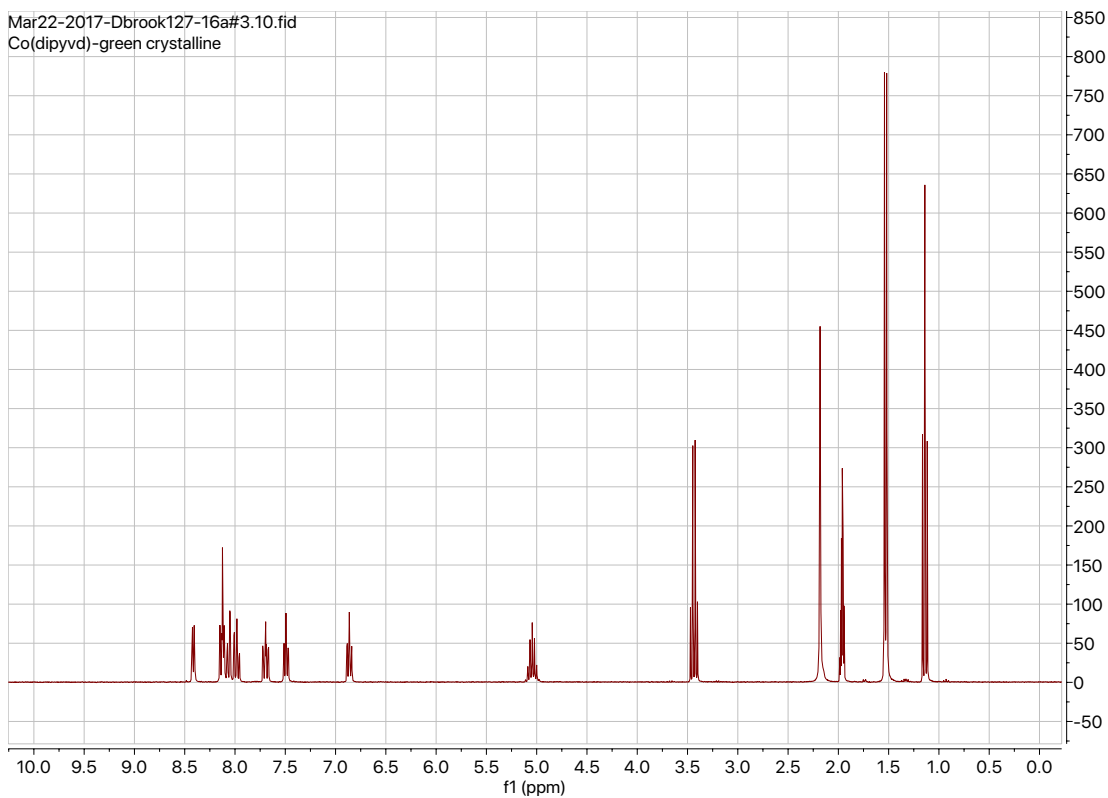
A crystal for study by X-ray diffraction was grown by layering n-octane onto a solution of this material in dichloromethane. Data was collected through the Service Crystallography at the Advanced Light Source (SCrALS) program at Lawrence Berkeley National Laboratory. Intensity data were collected at 150K on a D8 goniostat equipped with a Bruker PHOTON-II detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to $\lambda=0.7749\text{\AA}$. For data collection 2-s frames were measured at 0.5° intervals of ω . The data frames were collected using the program APEX3²² and processed using the SAINT²³ routine within APEX3. The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS.²⁴ Solution and refinement used the program Olex2 along with the SHELX software suite. Crystal data: $\text{C}_{31}\text{H}_{32}\text{Cl}_2\text{CoF}_6\text{N}_{12}\text{O}_2\text{P}_1$, Monoclinic, $a=11.2862(6)$, $b=17.875(1)$, $c=20.4254(12)$, $\beta=86.479(2)$, $V=4112.79$, $Z=2$, space group $P2_1/a$ (No. 14). 151425 reflections were measured, of which 9047 were unique. ($R_{\text{int}}=0.045$). Solution and refinement gave $R(F)=0.054\%$ ($F > 2\sigma(F)$) $R_w(F^2)=0.1745$ (all reflections). Details of data collection, solution, and refinement are included in the supporting information in .cif format.

[Co(dipyvd)₂]²⁺(PF₆⁻)₂

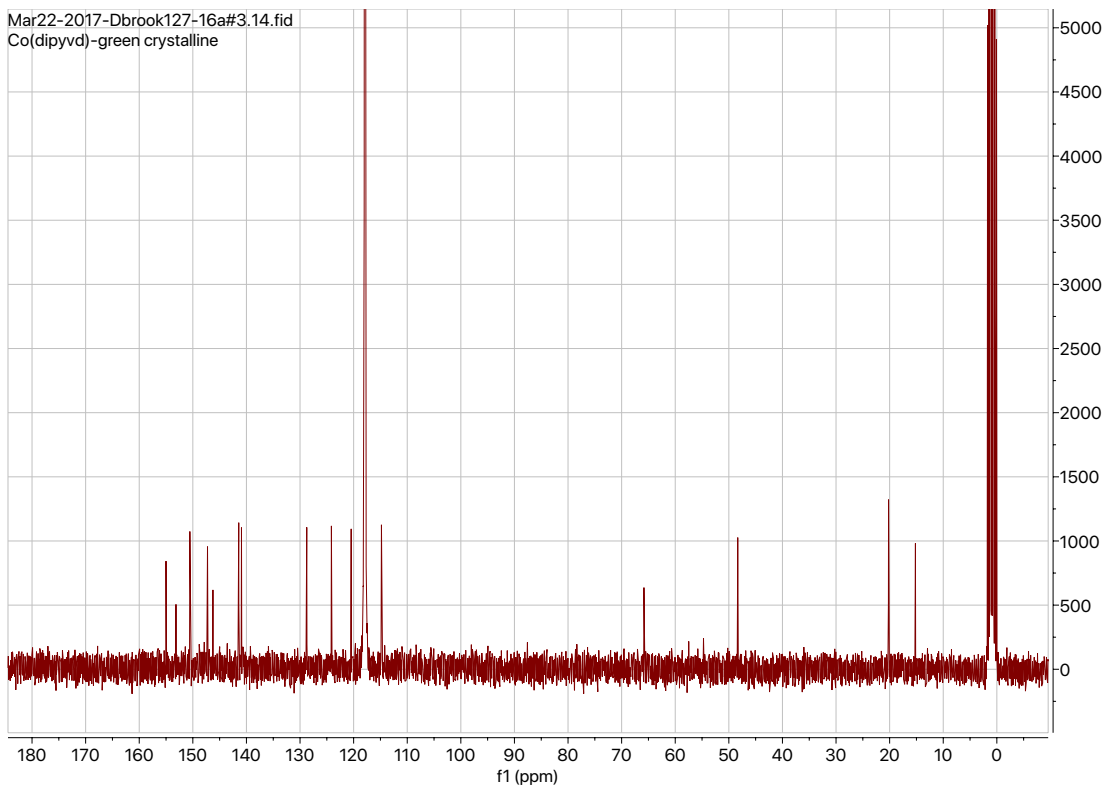
[Co(dipyvd)₂]⁺PF₆⁻•Et₂O (150 mg, 0.17 mmol) was dissolved in 5 mL dichloromethane. To the resulting solution was added a solution of AgPF₆ (50 mg, 0.19 mmol) in 1 mL dichloromethane. A dark green precipitate formed immediately and was removed by filtration. The precipitate (177 mg, 0.16 mmol 95%) containing both [Co(dipyvd)₂]²⁺(PF₆⁻)₂ and metallic silver, was characterized before further purification: Elemental analysis gave: C 33.99, H 2.60, N 15.49 consistent with 1.2 equivalents of silver (calcd. for C₃₀H₃₀CoN₁₂O₂•(PF₆)₂•Ag_{1.2}: C 33.71, H 2.83, N 15.72). X-ray powder diffraction (Cu K_α radiation) confirmed the presence of metallic silver and gave diffraction lines consistent with a tetragonal unit cell (*a*=15.84 Å, *c*=15.37 Å); IR (ATR) 1725 cm⁻¹ (C=O stretch); magnetic susceptibility was recorded on this mixture from 5-300K. The precipitate was redissolved in acetone and filtered to remove silver. Ether was allowed to diffuse into the acetone solution precipitating a crystalline product. IR(ATR) 1725 (C=O) cm⁻¹; χT (298K)=1.4; HRMS *m/z*=649.1941, calculated for [C₃₀H₃₀CoN₁₂O₂]⁺: *m/z*=649.1947; anal. calcd for C₃₀H₃₀CoN₁₂O₂•(PF₆)₂: C 38.35, H 3.22, N 17.89; found: C 38.59, H 3.05, N 17.35; A single crystal was isolated and characterized by X-ray diffraction giving cell dimensions consistent with the earlier precipitate. Data was collected through the Service Crystallography at Advanced Light Source (SCrALS) program at Lawrence Berkeley National Laboratory. Intensity data were collected at 150K on a D8 goniostat equipped with a Bruker PHOTON-II detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to λ =1.0333 Å. For data collection 1 s frames were measured at 0.5° intervals of ω . The data frames were collected using the program APEX3²² and processed using the SAINT²³ routine within APEX3. The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS.²⁴ Solution and refinement used the program Olex2 along with the SHELX software suite. Crystal data: C₃₀H₃₀CoF₁₂N₁₂O₂P₂, Tetragonal, *a*=15.7805(4), *c*=15.4465(14), *V*=3846.6(4), *Z*=4, space group *P*-42₁*c* (No. 114). 40042 reflections were measured, of which 3945 were unique. (*R*_{int} = 0.0392). Solution and refinement gave *R*(*F*)=0.0465 (*F*> 2 σ (*F*)) *wR*(*F*²)=0.1323 (all reflections). Details of data collection, solution, and refinement are included in the supporting information in .cif format.

II. ^1H and ^{13}C NMR of $[\text{Co}(\text{dipyvd})_2](\text{PF}_6)$ in acetonitrile- d_3

Mar22-2017-Dbrook127-16a#3.10.fid
Co(dipyvd)-green crystalline



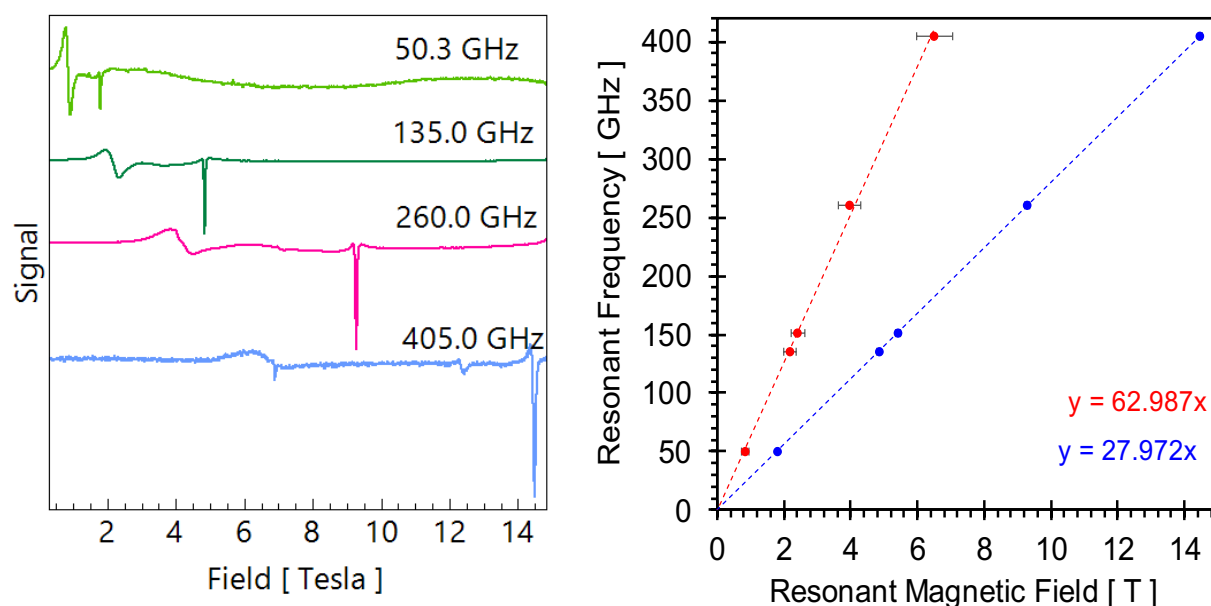
Mar22-2017-Dbrook127-16a#3.14.fid
Co(dipyvd)-green crystalline



III. HF EPR spectra of $[\text{Co}(\text{dipyvd})_2](\text{PF}_6)_2$

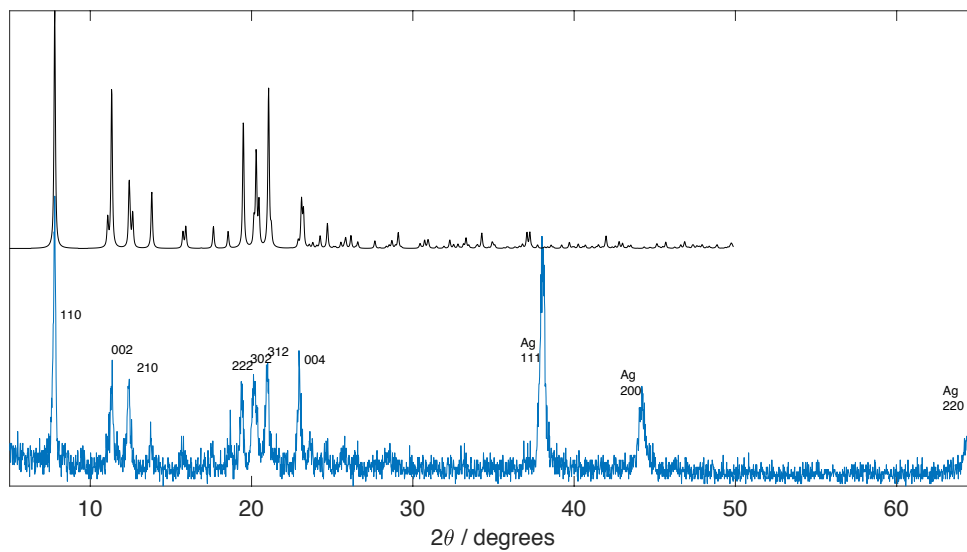
The frequency-dependent, high-field EPR spectra of $[\text{Co}(\text{dipyvd})_2](\text{PF}_6)_2$ were recorded at 5 K using a home-built, transmission-type spectrometer which does not require a resonant cavity.¹ This instrument is operated by the EMR facility at the NHMFL. The instrument is fitted with an Oxford Instruments, liquid helium-cooled superconducting magnet which was used to generate magnetic fields of up to 17 T. Microwaves with frequencies ranging from 50 to 450 GHz were generated using a phase-locked Virginia Diodes source that produced a base frequency of 13 ± 1 GHz, which was subsequently multiplied using a cascade of frequency multipliers. "The simulation of the X-band EPR spectra and the EPR figures were obtained using the SpinCount program written by Prof. Mike Hendrich at Carnegie Mellon University."

¹ Hassan, A.; Pardi, L.; Krzystek, J.; Sienkiewicz, A.; Goy, P.; Rohrer, M.; Brunel, L.-C. Ultrawide Band Multifrequency High-Field EMR Technique: A Methodology for Increasing Spectroscopic Information. *J. Magn. Reson.* **2000**, *142* (2), 300–312



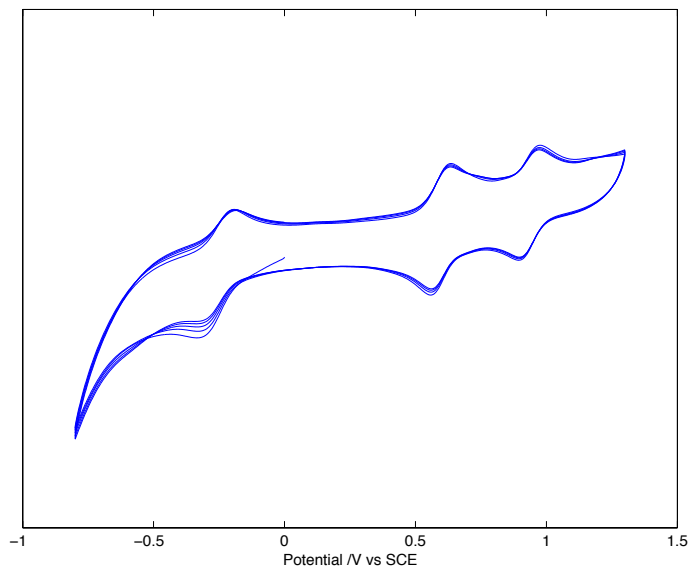
Left: Frequency-dependent spectra recorded at 5 K for a neat powder spectrum of **1**. The modulation - induced phase distortion of the 135- 450 GHz spectra was corrected using a Hilbert transform procedure. *Right:* The magnetic field vs. microwave frequency dependence of the observed resonances. The horizontal error bars indicate the FWHM linewidth of the observed resonance. The linear fits of these dependencies yield an effective g-value of 4.500 (for the red curve) and 1.998 (for the blue curve), respectively.

IV. Calculated and Observed X-ray powder diffraction patterns



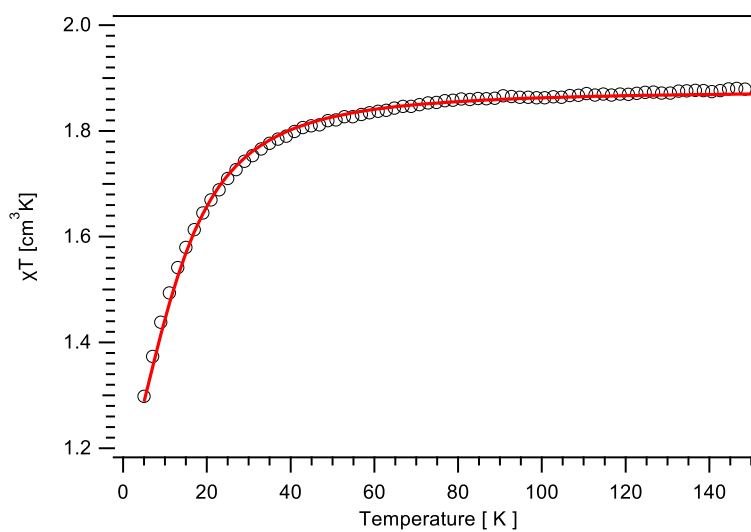
Top: Calculated X-ray powder diffraction pattern (Cu-K α) for solid $[\text{Co}(\text{dipyvd})_2](\text{PF}_6)_2$ based on the single crystal X-ray diffraction data. Bottom: Observed powder pattern for freshly synthesized samples of $[\text{Co}(\text{dipyvd})_2](\text{PF}_6)_2$, co-precipitated with metallic silver.

V. Cyclic voltammetry



Cyclic voltammetry of $[\text{Co}(\text{dipyvd})_2]^{n+}$ in acetonitrile with 0.1 M Bu_4NPF_6 as supporting electrolyte. Potentials were measured with respect to a Ag/AgCl pseudoreference electrode calibrated with ferrocene. Potentials are reported vs SCE assuming the ferrocene/ferrocenium couple is at 0.4 V vs SCE.

VI Fit of the low-temperature magnetic susceptibility data recorded for $[\text{Co}(\text{dipyvd})_2](\text{PF}_6)_2$



Best fit of the χT data obtained using a single-site, $S = 3/2$ spin-Hamiltonian. The theoretical red trace was obtained using $D = 16 \text{ cm}^{-1}$, $E/D = 0.05$, $g_{\text{iso}} = 2.0$, and $\text{TIP} = 200 \cdot 10^{-6} \text{ cm}^3$