Electronic Supporting Information

Pushing T_C to 27.5 K in a Heavy Atom Radical Ferromagnet

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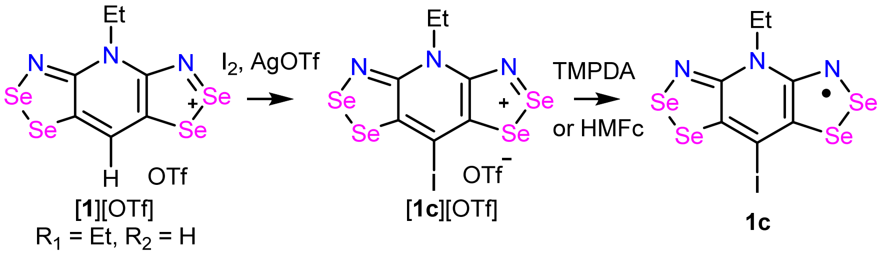
Contents (12 pages in total)

Synthetic Details

General Methods and Procedures. The reagents iodine, silver trifluoromethanesulfonate (triflate) and *N*,*N*,*N*′,*N*′-tetramethylphenylenediamine (TMPDA) were obtained commercially. Hexamethylferrocene[1] (HMFc) and 4-ethyl-4*H*-bis[1,2,3]diselenazolo[4,5-*b*:5′,4′-e]pyridin-2-ium triflate[2] [**1**][OTf] (R = H) were prepared according to literature methods. HMFc was sublimed in vacuo and recrystallized from acetonitrile before use, and TMPDA was purified by sublimation in vacuo. The solvents acetonitrile (MeCN) and dichloroethane (DCE) were of reagent grade, and MeCN was dried by distillation from P_2O_5 and CaH_2. Infrared spectra (Nujol mulls, KBr optics) were recorded on a Nicolet Avatar FTIR spectrometer at 2 cm^{-1} resolution. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ 85018.

Scheme 1



Preparation of [1c][OTf] (Scheme 1). A solution of [**1**][OTf] (R_1 = Et, R_2 = H) (1.00 g, 1.68 mmol), iodine (1.32 g, 5.2 mmol) and silver triflate (1.32 g, 5.2 mmol) in 100 mL MeCN was heated to 90 °C with stirring in a sealed glass pressure vessel. After 40 hr the reaction flask was cooled to room temperature and its contents decanted into a second flask, from which the solvent and excess iodine were removed in vacuo. Addition of 25 mL of a hot mixture (1:4) of MeCN/DCE to the residual solid afforded a powdery precipitate and a brown solution. The solid was filtered off and washed twice with another 25 mL of the (1:4) MeCN/DCE mixture, then dried in vacuo. The solid was boiled into 75 mL MeCN, and the fine white precipitate of AgI was removed by filtration. The filtrate was boiled down to 25 mL, then cooled to -20 °C overnight. Filtration of this

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[1] S. Zürcher, J. Petrig, M. Perseghini, V. Gramlich, M. Wörle, D. von Arx and A. Togni. *Hel. Chim. Acta*, 1999, **82**, 1324.

[2] C. M. Robertson, A. A. Leitch, K. Cvrkalj, R. W. Reed, D. J. T. Myles, P. A. Dube and R. T. Oakley, *J. Am. Chem. Soc.*, 2008, **130**, 8414.

mixture afforded crude [**1c**][OTf], yield 680 mg (0.94 mmol, 56%) as black microcrystalline solid. Triple recrystallization from MeCN afforded purple-black shards, mp > 250 °C, suitable for reduction work. IR (Nujol mull, KBr, cm^{-1}): 1415 (m), 1351 (s), 1270(s), 1237(vs), 1222 (s), 1171 (s), 1155 (s), 1084 (w), 1024 (m), 983 (w), 725 (m), 692 (m), 635 (s), 578 (s), 517 (w). Anal. Calcd for $C_8H_5F_3IN_3O_3SSe_4$: C, 13.29; H, 0.70; N, 5.81; Found: C, 13.47; H, 1.00; N, 5.72.

Preparation of 1c (Scheme 1). *Method 1, for single crystal growth:* Degassed solutions (four freeze-pump-thaw cycles) of HMFc (8.0 mg, 0.29 mmol) in 12 mL of MeCN and [**1c**][OTf] (15.0 mg, 0.21 mmol) in 12 mL of MeCN were allowed to diffuse together slowly at room temperature over a period of 16 h. The solvent was decanted to leave fine, metallic black needles of **1c** suitable for X-ray work. *Method 2, bulk material for magnetic measurements*: Degassed (4 freeze-pump-thaw cycles) solutions of TMPDA (50.0 mg, 3.10 mmol) in 40 mL MeCN and [**1c**][OTf] (0.200 g, 2.80 mmol) in 200 mL MeCN were combined and after 30 min the gold-brown microcrystalline precipitate of **1c** was filtered off, washed with 4 × 20 mL MeCN, and dried in vacuo; yield 0.125 g (2.20 mmol, 71 %), dec > 120 °C. IR (Nujol mull, KBr, cm^{-1}): 1435 (s), 1393 (m), 1368 (m), 1348 (m), 1308 (m), 1308 (s), 1218 (vs), 1162 (w), 1084 (w), 1049 (w), 988 (w), 865 (vw), 813 (w), 680 (vs), 558 (s), 500 (m), 421 (w), 412(w). Anal. Calcd for $C_7H_5IN_3Se_4$: C, 14.65; H, 0.88; N, 7.32. Found: C, 14.89; H, 1.01; N, 7.50.

Magnetic Susceptibility Measurements.

Ambient pressure DC magnetic susceptibility (χ) measurements on **1c** were performed over the temperature range 2-300 K on a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were made using Pascal's constants.[3] AC susceptibility measurements were performed on an Oxford Instruments MagLab EXA.

High pressure piston cylinder cell (PCC) AC magnetic susceptibility measurements on **1c** were performed over the pressure range 0-1.6 GPa in a SQUID magnetometer. The crystals were mixed with Apiezon J as pressure transmitting medium. Pressure was estimated from the load value, and the relationship between the pressure value at low temperature and the load applied at room temperature had been investigated through the observation of the superconducting transition of lead. Diamond anvil cell (DAC) AC magnetic susceptibility measurements were carried out using techniques and procedures described previously.[4] The pressure in the DAC experiments was estimated by the fluorescence of ruby, which was held in the sample cavity with the sample.

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[3] (a) R. L. Carlin, *Magnetochemistry*, Springer-Verlag, New York, 1986. (b) G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532.

[4] (a) M. Mito, *J. Phys. Soc. Jpn., Suppl. A*, 2007, **76**, 182. (b) M. Mito, M. Hitaka, T. Kawae, K. Takeda, T. Kitai and N. Toyoshima, *Jpn. J. Appl. Phys.*, 2004, **40**, 6641.

Ambient Pressure Single Crystal Crystallography.

A small needle of **1c** was mounted on a glass fiber. Diffraction data were collected at 296 K using omega and phi scans with a Bruker kappa APEX II CCD detector and Mo Kα ($\lambda = 0.71073$ Å) radiation. Data reduction and structure solution were performed using Bruker APEX2 software[5] and SADABS.[6] The deposition number for this structure is CCDC 1501479.

High Pressure Powder Crystallography.

High pressure X-ray diffraction experiments on **1c** were performed at BL10XU, SPring-8, using synchrotron radiation ($\lambda = 0.413581$ Å) and powdered samples mounted in a diamond anvil cell, with helium as the pressure transmitting medium. The diffraction data were collected at ambient temperature (293 K) and as a function of *increasing* pressure. A series of data sets (from 0-10 GPa) were indexed with DICVOL,[7] as provided in DASH 3.01.[8] It was evident that the compound was isostructural with **1a**,**b** at all pressures, and the space group $P\bar{4}2_1m$ was selected. Starting with a model based on the molecular coordinates for **1c** taken from the (296 K) ambient pressure single crystal data set, the structures were solved and refined in DASH using a rigid body restriction. The solutions were further refined by Rietveld methods[9] using the GSAS program package.[10] Final Rietveld indices R_p and R_{wp} are listed in Table S1. Data from $2\theta = 3$-$12°$ were refined with fixed atomic positions and isotropic thermal parameters with values generated during the DASH refinement. Atomic positions were not further refined and, as a result, standard deviations for atomic coordinates are not available. The pressure setting of 0.0 GPa in Table S1 and S2 refers to the single crystal data collected at ambient pressure.

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[5] *APEX2*, Bruker AXS Inc., Madison, WI, 2007.

[6] *SADABS*, Bruker AXS Inc., Madison, WI, 2001.

[7] A. Boultif and D. Louer, *J. Appl. Crystallogr.*, 2004, **37**, 724.

[8] W. I. F. David, K. Shankland, J. van de Streek, E. Pidcock, W. D. S. Motherwell and J. C. Cole, *J. Appl. Crystallogr.*, 2006, **39**, 910.

[9] H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.

[10] A. C. Larson and R. B. Von Dreele, *General Structure Analysis System (GSAS*), Los Alamos National Laboratory Report LAUR 86-748, 2000.

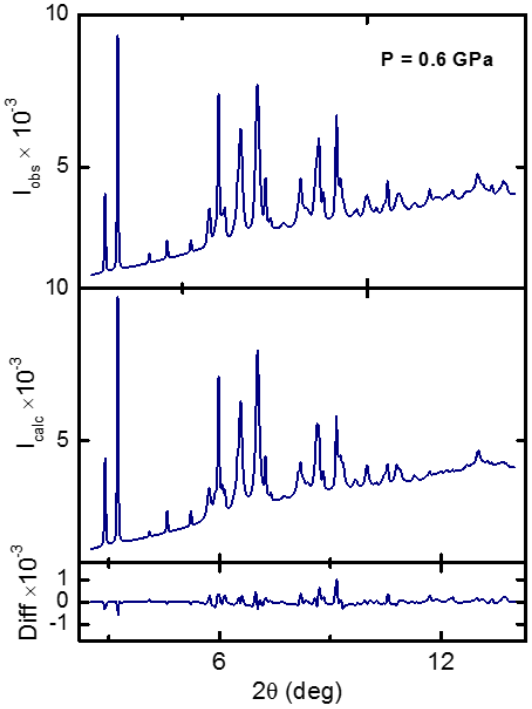
Table S1A Crystal Data for **1c**

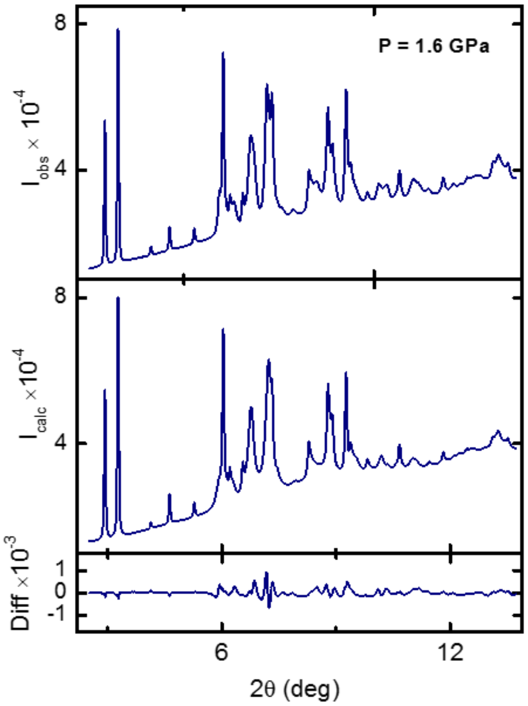
P, GPa	0.0 GPa	0.6 GPa	1.6 GPa	3.0 GPa	3.6 GPa	4.0 GPa
formula	$C_7H_5IN_3Se_4$	$C_7H_5IN_3Se_4$	$C_7H_5IN_3Se_4$	$C_7H_5IN_3Se_4$	$C_7H_5IN_3Se_4$	$C_7H_5IN_3Se_4$
M	573.88	573.88	573.88	573.88	573.88	573.88
a, Å	16.4704(6)	16.3764(7)	16.2024(8)	16.0383(14)	15.9987(15)	15.9908(13)
c, Å	4.2345(2)	4.1533(5)	4.0040(9)	3.8839(17)	3.8700(21)	3.8382(22)
V, Å^3	1148.71(10)	1113.86(15)	1051.11(25)	999.0(4)	990.6(5)	981.5(6)
D_{calc} (g cm^{-1})	3.318	3.422	3.626	3.815	3.848	3.883
space group	$P\bar{4}2_1m$	$P\bar{4}2_1m$	$P\bar{4}2_1m$	$P\bar{4}2_1m$	$P\bar{4}2_1m$	$P\bar{4}2_1m$
Z	4	4	4	4	4	4
temp (K)	296(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.413581	0.413581	0.413581	0.413581	0.413581
solution method	direct methods	powder data	powder data	powder data	powder data	powder data
R, R_w (on F^2)	0.0509, 0.0711	0.0238, 0.0333	0.0288, 0.0386	0.0436, 0.0561	0.0435, 0.0576	0.0408, 0.0538

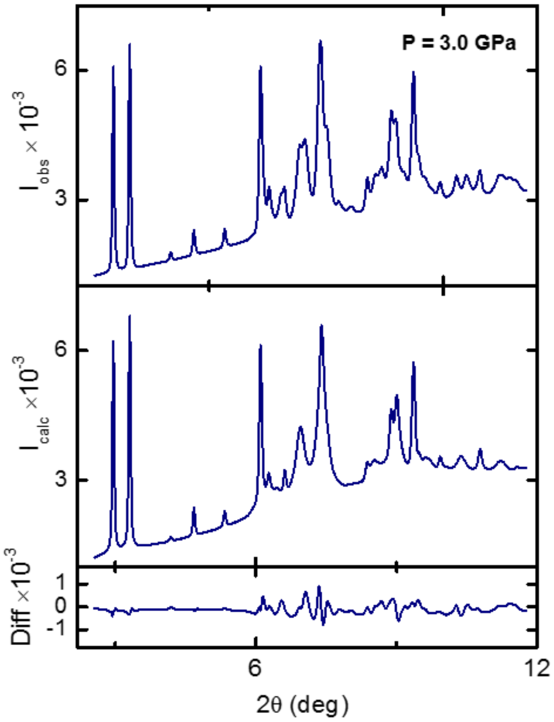
Table S1B Crystal Data for **1c**

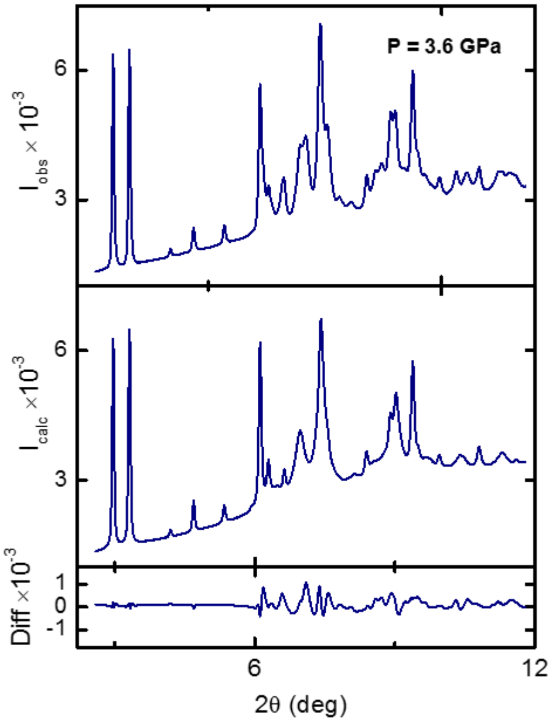
P, GPa	5.0 GPa	5.5 GPa	7.1 GPa	7.5 GPa	8.0 GPa	8.8 GPa
formula	$C_7H_5IN_3Se_4$	$C_7H_5IN_3Se_4$	$C_7H_5IN_3Se_4$	$C_7H_5IN_3Se_4$	$C_7H_5IN_3Se_4$	$C_7H_5IN_3Se_4$
M	573.88	573.88	573.88	573.88	573.88	573.88
a, Å	15.9014(14)	15.8651(16)	15.7336(18)	15.7128(16)	15.6976(15)	15.6831(15)
c, Å	3.7814(24)	3.7650(26)	3.7167(27)	3.6914(26)	3.6631(23)	3.6436(24)
V, Å^3	956.2(6)	947.7(7)	920.1(7)	911.4(7)	902.6(6)	896.2(6)
D_{calc} (g cm^{-1})	3.986	4.022	4.142	4.182	4.223	4.253
space group	$P\bar{4}2_1m$	$P\bar{4}2_1m$	$P\bar{4}2_1m$	$P\bar{4}2_1m$	$P\bar{4}2_1m$	$P\bar{4}2_1m$
Z	4	4	4	4	4	4
temp (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.413581	0.413581	0.413581	0.413581	0.413581	0.413581
solution method	powder data	powder data	powder data	powder data	powder data	powder data
R, R_w (on F^2)	0.0411, 0.0542	0.0456, 0.0593	0.0500, 0.0658	0.0437, 0.0580	0.0427, 0.0590	0.0433, 0.0593

High Pressure PXRD Reitveld Refinement Profiles (GSAS)









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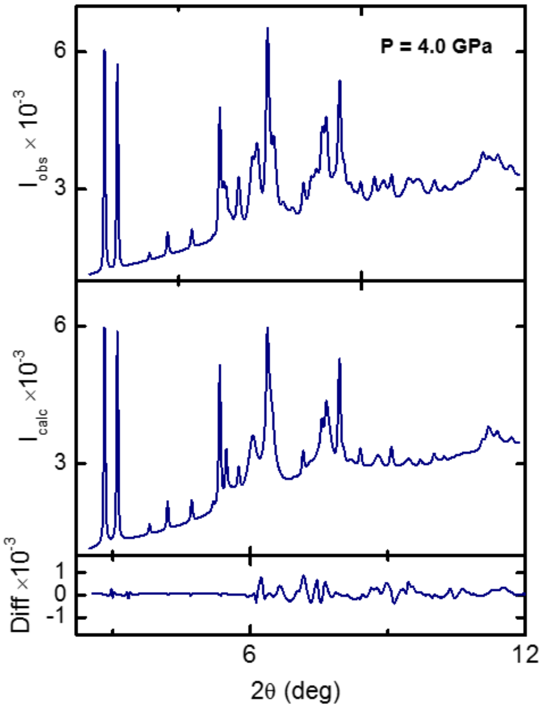
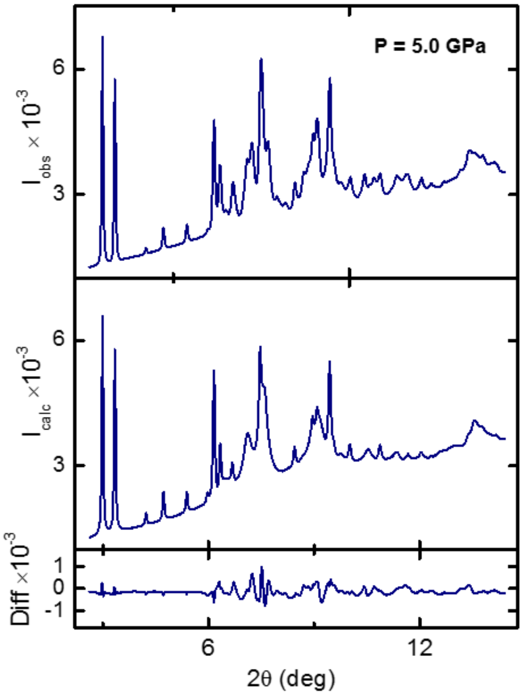
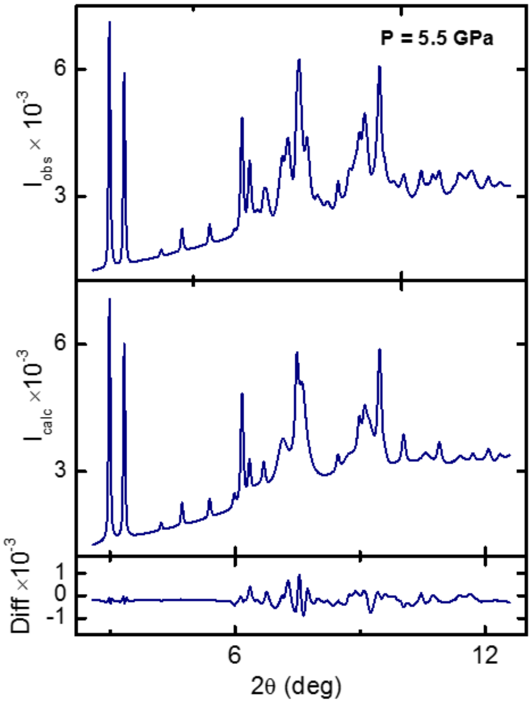
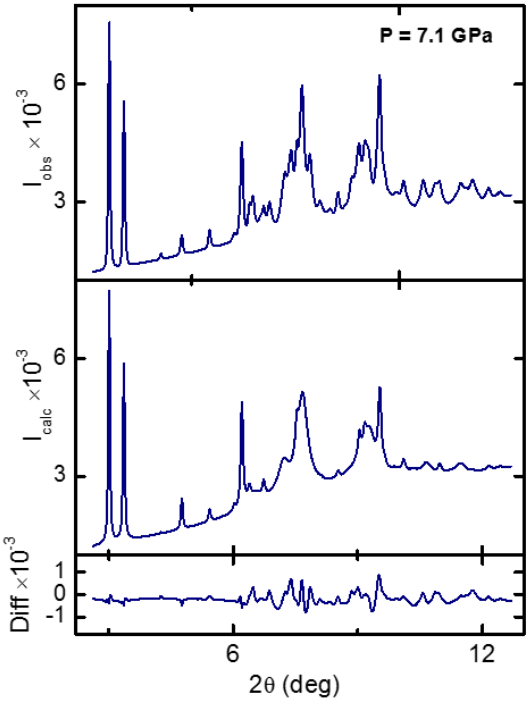
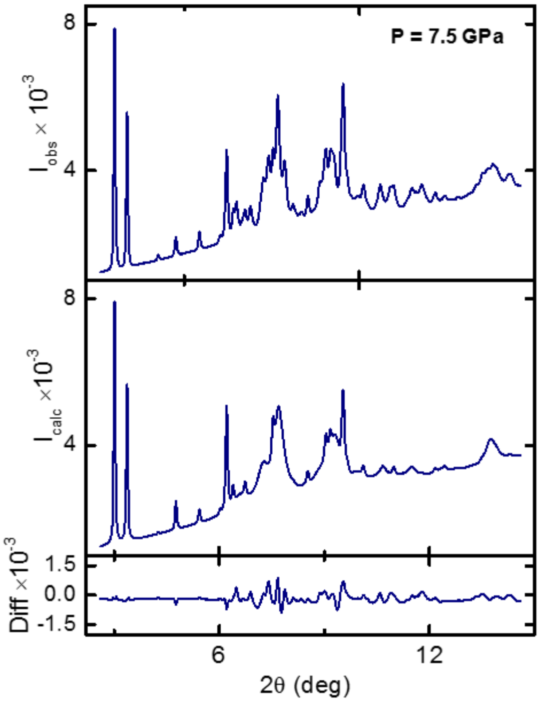


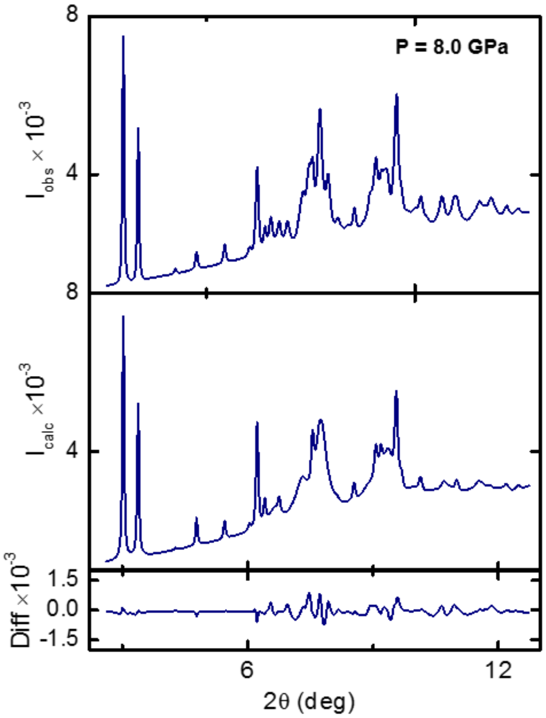


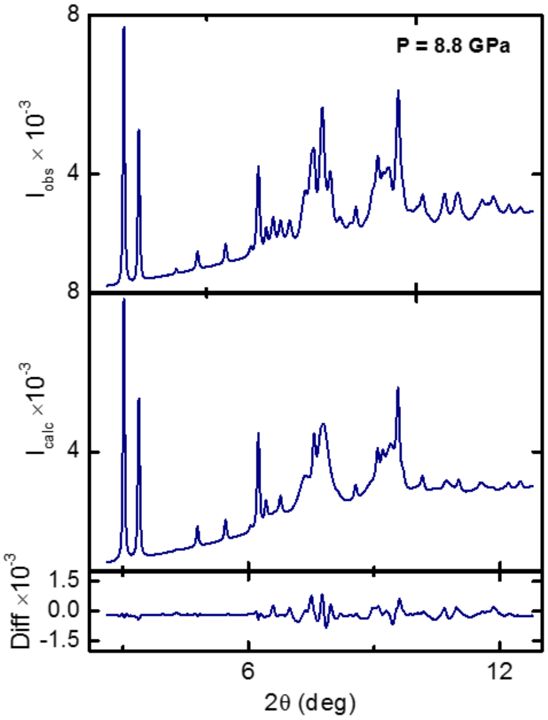




High Pressure PXRD Reitveld Refinement Profiles (GSAS) - continued

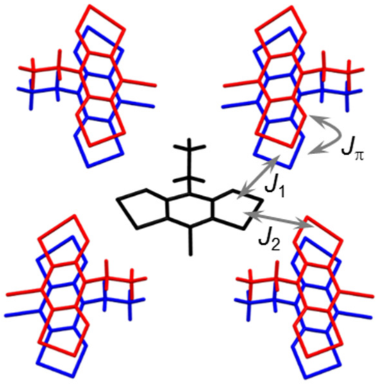






Exchange Energy Calculations.

DFT-BS calculations of magnetic exchange energies were performed with the Gaussian 09 suite of programs,[11] using the (U)B3LYP hybrid functional and a polarized, split-valence basis set with double-ζ (6-31G(d,p)) functions on all atoms save iodine, for which a 3-21g basis set was employed. Pairwise exchange energies J_π, J_1 and J_2, illustrated below and defined in magnitude and sign in terms of the Hamiltonian $H_{ex} = -2\ J_{ij}\ \{S_i \bullet S_j\}$, were calculated using the broken symmetry method.[12] Accordingly, the exchange energy J for any pair of interacting radicals can be estimated from the total energies of the triplet (E_{TS}) and broken-symmetry singlet (E_{BSS}) states and the respective expectation values $<S^2>$, as shown below. Tight convergence criteria were employed. Coordinates for the model 1D calculations (Fig. 3) of J_π as a function of the π-stack slippage (dy) and plate-to-plate separation (δ) were performed using coordinates of a model **1** ($R_1 = R_2 = H$) obtained from UB3LYP/6-31G(d,p) calculations optimized in C_{2v} symmetry. Coordinates for the calculation of J_π, J_1 and J_2 as a function of pressure shown in Table S2 were taken from the high pressure crystallographic data on **1c**.



Pairwise exchange interactions J_π, J_1, J_2 and the broken symmetry expression used to estimate their magnitude.

$$J = \frac{-(E_{TS} - E_{BSS})}{\langle S^2 \rangle_{TS} - \langle S^2 \rangle_{BSS}}$$

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[11] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[12] (a) L. Noodleman, *J. Chem. Phys*., 1981, **74**, 5737; (b) L. Noodleman and E. R. Davidson, *Chem. Phys*., 1986, **109**, 131. (c) K. Yamaguchi, F. Jensen, A. Dorigo and K. N. Houk, *Chem. Phys. Lett*., 1988, **149**, 537; (d) H. Nagao, M. Nishino, Y. Shigeta, T. Soda, Y. Kitagawa, T. Onishi, Y. Yoshika and K. Yamaguchi, *Coord. Chem. Rev*., 2000, **198**, 265.

Table S2 Calculated Magnetic Exchange Interactions in **1c** at Different Pressures

Pressure	E(Triplet) (H)	$\langle S^2 \rangle$TS	E(BS Singlet) (H)	$\langle S^2 \rangle$BSS	J (cm^{-1})
0.0 GPa					
$J\pi$	-33839.27768420	2.0525	-33839.27773590	1.0476	-11.29
J_1	-33839.28494750	2.0518	-33839.28492670	1.0517	4.56
J_2	-33839.28447850	2.0521	-33839.28446770	1.0519	2.37
0.6 GPa					
$J\pi$	-33839.27005220	2.0518	-33839.27006040	1.0489	-1.79
J_1	-33839.27836430	2.051	-33839.27834230	1.0509	4.83
J_2	-33839.27743220	2.0514	-33839.27742	1.051	1.82
1.6 GPa					
$J\pi$	-33839.16844230	2.0455	-33839.16839850	1.0441	9.60
J_1	-33839.18008870	2.0447	-33839.18006150	1.0447	5.97
J_2	-33839.17898650	2.0452	-33839.17898300	1.0444	0.77
2.4 GPa					
$J\pi$	-33839.16489110	2.046	-33839.16485160	1.0433	8.65
J_1	-33839.17981980	2.0451	-33839.17978540	1.045	7.55
J_2	-33839.17980290	2.0457	-33839.17980210	1.0448	0.18
3.0 GPa					
$J\pi$	-33839.22471760	2.0492	-33839.22469570	1.0443	4.78
J_1	-33839.24283670	2.0481	-33839.24280100	1.0478	7.83
J_2	-33839.24343070	2.0489	-33839.24344030	1.0472	-2.10
3.6 GPa					
$J\pi$	-33839.26114070	2.0531	-33839.26118840	1.0435	-10.37
J_1	-33839.27900310	2.0515	-33839.27899410	1.0482	1.97
J_2	-33839.28518460	2.0528	-33839.28519730	1.0513	-2.78
4.0 GPa					
$J\pi$	-33839.29065020	2.0591	-33839.29081240	1.0409	-34.96
J_1	-33839.31692210	2.0572	-33839.31692610	1.0533	-0.87
J_2	-33839.32349170	2.0586	-33839.32351	1.0566	-4.93

Table S2 (cont'd) Calculated Magnetic Exchange Interactions in **1c** at Different Pressures

Pressure	**E(Triplet) (H)**	**$<S^2>$TS**	**E(BS Singlet) (H)**	**$<S^2>$BSS**	**J (cm^{-1})**
5.0 GPa					
$J\pi$	-33839.29051140	2.0588	-33839.29070910	1.036	-42.42
J_1	-33839.32348860	2.057	-33839.32349380	1.053	-1.14
J_2	-33839.33004080	2.0582	-33839.33008250	1.055	-9.12
5.5 GPa					
$J\pi$	-33839.27703530	2.0556	-33839.27715480	1.0377	-25.77
J_1	-33839.31086910	2.0541	-33839.31084690	1.0524	4.86
J_2	-33839.31373190	2.055	-33839.31376810	1.0517	-7.92
6.7 GPa					
$J\pi$	-33839.22689310	2.051	-33839.22685190	1.0429	8.97
J_1	-33839.25877290	2.0495	-33839.25873230	1.0484	8.90
J_2	-33839.26140110	2.0505	-33839.26142960	1.0474	-6.24
7.1 GPa					
$J\pi$	-33839.14624560	2.0451	-33839.14610290	1.0437	31.28
J_1	-33839.17449470	2.0439	-33839.17444900	1.0438	10.03
J_2	-33839.17158450	2.0446	-33839.17160000	1.0419	-3.39
7.5 GPa					
$J\pi$	-33839.15716250	2.0457	-33839.15700100	1.0447	35.41
J_1	-33839.18439470	2.0442	-33839.18434320	1.0436	11.30
J_2	-33839.18576950	2.0452	-33839.18580180	1.0419	-7.07
8.0 GPa					
$J\pi$	-33839.16194670	2.0461	-33839.16177160	1.045	38.39
J_1	-33839.19340700	2.0447	-33839.19335370	1.0446	11.70
J_2	-33839.19037080	2.0455	-33839.19039240	1.0423	-4.73
8.8 GPa					
$J\pi$	-33839.24395630	2.0518	-33839.24376670	1.0503	41.55
J_1	-33839.27773410	2.0499	-33839.27767340	1.0492	13.31
J_2	-33839.27838160	2.0511	-33839.27842480	1.0466	-9.44