An Electron Transfer Series of Octahedral Chromium Complexes containing a Redox Noninnocent α-Diimine Ligand

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Supporting information

Contents:

General. All manipulations of compounds were carried out using standard Schlenk, high vacuum line, and glovebox techniques under an atmosphere of N_2. Solvents were purchased from Fisher Scientific, degassed, and dried by passing through activated alumina. THF-d_8 and C_6D_6 was purchased from Cambridge Isotopes Laboratory and stored under vacuum over Na/K alloy. All other reagents were purchased from Aldrich or Acros and dried using standard procedures when necessary. Room-temperature molar magnetic susceptibilities (χ_m) in the solid state were determined using a Johnson Matthey magnetic susceptibility balance. They were corrected for diamagnetism using Pascal constants and converted into effective magnetic moments (μ_{eff}).

^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker DRX-400 spectrometer and were referenced to the residual protons of the solvent. FTIR spectra were taken on Magna-IR E. S. P. 560 spectrometer. UV/vis spectra were taken using a Thermo UV-1 spectrophotometer. Elemental analyses were performed by Robertson Microlit Laboratories.

Synthesis and characterization of Cr Complexes:

Preparation of [$^{H}L^{Cy}_3$Cr]BArF (2): 0.100 g (0.140 mmol) of **1** was placed in 30mL of Et_2O. To this solution was slowly added a solution of 0.147 g (0.140 mmol) of $[(C_5H_5)_2Fe][BARF]$ in 10 mL of Et_2O. The solution was stirred for three hours, and then the Et_2O was removed. The purple residue was washed with pentane to remove ferrocene. The residue was dissolved in a very small amount of Et_2O (~1mL) and about 15 mL of toluene was added. The solution was cooled to -30ºC overnight to give 0.200 g of **2** (92% yield). ^{1}H NMR (THF-d_8): 7.69 (8H, BARF), 7.49 (4H, BARF), 2.02, 1.29, 0.41ppm. IR (KBr; cm^{-1}): 2937 (s), 2858 (s), 1653 (w), 1610 (w), 1452 (m), 1421 (m), 1396 (m), 1355 (s), 1275 (s), 1233 (m), 1126 (s), 1024 (m), 944 (m), 887 (m), 839 (m), 809 (w), 744 (w), 732 (m), 713 (m), 682 (m), 670 (m), 650 (m). Anal. Calcd. for $C_{74}H_{84}N_6CrBF_{24}$: C, 56.39; H, 5.37; N, 5.33. Found: C, 56.01; H, 4.98; N, 5.69. UV/Vis (Et_2O; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 364 (2700), 515 (8700), 570(2300), 644(2100), 871(800), 1389(7965). μ_{eff} (294 K) = 1.9(1) μ_B. M.p.: 182ºC (dec).

Preparation of [$^{H}L^{Cy}_3$Cr][BArF]$_2$ (3): 0.100 g (0.140 mmol) of **1** was placed in 30mL of Et_2O. To this was slowly added a solution of 0.294 g (0.280 mmol) of $[(C_5H_5)_2Fe][BArF]$ in 10 mL of Et_2O. The solution was stirred three hours and then the Et_2O was removed. The green residue was washed with pentane to remove ferrocene. The residue was dissolved in methylene chloride and cooled to -30ºC overnight to give 0.239 g of **3** (70% yield). ^{1}H NMR (THF-d_8): 11.00, 9.4, 7.69 (8H, BARF), 7.49 (4H, BARF), 2.45, 1.35, 0.34, -4.0, -6.9, -43.7, -74.5 ppm. IR (KBr; cm^{-1}): 2946 (s), 2863 (s), 1677 (w), 1611 (m), 1453 (m), 1404 (m), 1356 (s), 1279 (s), 1129 (s), 1124 (w), 1005 (w), 932 (w), 887 (m), 839 (s), 745 (w), 712 (s), 682 (s), 671 (s), 623 (w). UV/Vis (Et_2O; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 342 (2200), 461 (2040), 619(1013), 923(1671), 1006(1678), 1394 (477). The elemental analysis and magnetism measurement were done using [$^{H}L^{Cy}_3$Cr][BF_4]$_2$, (**3'**). The synthetic procedure was as the same as that for **3**. Anal. Calcd. for $C_{42}H_{72}N_6CrB_2F_8$: C, 56.89; H, 8.18; N, 9.48. Found: C, 56.48; H, 8.62; N, 9.56. μ_{eff} (294 K) = 2.97(1) μ_B. M.p.: 171ºC (dec).

Single crystal X-ray diffraction studies of 2 and 3: Crystals were mounted using viscous oil onto a plastic mesh and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) monochromated with graphite. Unit cell parameters were obtained from 36 data frames, 0.5º ω, from three different sections of the Ewald sphere. The systematic absences in the diffraction data are uniquely consistent with $P2_1/c$ for **2**. No symmetry higher than triclinic was observed for **3**, and refinement in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. The data-sets were treated with multi-scan absorption corrections (SADABS, Madison, WI, 2000). The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F^2 (Sheldrick, G.M. 2008. Acta Cryst. A64, 112-122). One –CF_3 group in **2** was located disordered in two positions with a refined site occupancy of 60/40. Three -CF_3 groups in 3 were similarly disordered and had independently refined site occupancies (50/50, 50/50, 85/15). Another two –CF_3 groups in **3**

were displaying distorted geometry presumably because of unresolved disorder. All disordered $-CF_3$ groups were treated with noncrystallographic symmetry restraints, equal atomic displacement parameters for chemically equivalent parts, and atomic displacement rigid-bond restraints. Global three-dimensional, atomic displacement rigid-bond restraints were applied to **3**. A toluene molecule of solvation was located in the asymmetric unit of **2**. Two severely disordered methylene chloride molecules of solvation per asymmetric unit were treated as diffused contributions in **3** (Squeeze, Platon: Spek, A. L., J. Appl. Cryst., 2003, 36, 7-13). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions with geometrically calculated positions and with U_{iso} equal to 1.2, or 1.5 for methyl, U_{eq} of the attached atom. Atomic scattering factors are contained in the SHELXTL program library (Sheldrick, G., *op. cit*.). The CIFs have been deposited at the Cambridge Structural Database under CCDC 1000091 for **2**, and 10000092 for **3**. The librationally corrected bond lengths (Schomaker, V., Trueblood, K. N., Acta Cryst. B, 1968, 24, 63-76) were calculated using Platon (Spek, A. L., *op. cit*.) from CIFs.

Electrochemistry: Electrochemistry was carried out using methods detailed earlier (Laws, D.R.; Chong, D.; Nash, K.; Rheingold, A.L.; Geiger, W.E. *J. Am. Chem. Soc.* **2008**, *130*, 9859). Potentials are given *vs* the ferrocene/ferrocenium couple. The redox processes for **1** were diffusion-controlled, quasi-Nernstian, reactions as determined by standard mechanistic diagnoses ((a) Bard, A.J.; Faulkner, L.R. *Electrochemical Methods*, John Wiley & Sons, New York, 2001, 2nd Ed. (b) Geiger, W.E. in Kissinger, P.T.; Heineman, W.R. (Eds) *Laboratory Techniques in Electroanalytical Chemistry*, Marcel Dekker, Inc., New York, 1996, 2nd Ed., pp 683-718). $[NBu_4][B(C_6F_5)_4]$ was prepared as described elsewhere (D. Barrière, F.; Geiger, W.E. *J. Am. Chem. Soc.* **2006**, *128*, 3980) Solvents were passed through alumina under nitrogen.

Table S1. Crystallographic data and refinement details for **2** and **3**

	2	**3**
Formula	$C_{88}H_{100}BCrF_{24}N_6$	$C_{108}H_{100}B_2Cl_4CrF_{48}N_6$
Formula Wt.	1760.5	2609.35
Space group	$P2_1/c$	P-1
Color	purple	green
a, Å	22.049(12)	13.962(9)
b, Å	17.219(9)	17.728(11)
c, Å	25.078(13)	26.214(16)
α, deg	90	79.116(10)
β, deg	114.243(9)	77.828(10)
γ, deg	90	70.078(10)
V, Å3	8681(8)	5915(6)
Z	4	2
D(calcd), g•cm-3	1.347	1.417
μ(Mo Kα), mm-1	0.231	0.265
Temp, K	120	200
Tmax/Tmin	1.0000/0.8580	0.7457/0.6697
no. data/params	21671/1093	29142/1498
GOF on F^2	1.001	1.016
R(F), %[a]	6.39	9.36
Rw(F^2), %[a]	13.47	23.79

[a] Quantity minimized: $R_w(F^2) = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o-F_c)$

Librational Corrections for compound 1

Bond		Bond Distance		Components of the Correction			MSDA from U(obs) Vibration Along the Interatomic Bond				Angle with Lib. Axes		
Atom(I)	Atom(J)	Obsd	Calcd	Del(L)	Del(M)	Del(N)	I to J	J to I	Difference	Sqrt(Diff)	L(1)	L(2)	L(3)
Cr	- N(1)	2.0360(16)	2.0377	-0.0009	0.0012	0.0009	0.01877(17)	0.0204(6)	0.0016(6)	0.0400	109.74	71.11	27.90
Cr	- N(2)	2.0401(14)	2.0418	0.0009	0.0015	-0.0002	0.01873(17)	0.0197(6)	0.0010(6)	0.0316	50.49	41.63	78.97
N(1)	- C(1)	1.332(2)	1.3329	0.0004	0.0011	-0.0000	0.0233(6)	0.0247(9)	0.0014(11)	0.0374	59.80	38.55	68.45
N(1)	- C(8)	1.475(2)	1.4762	-0.0010	-0.0002	0.0007	0.0211(6)	0.0217(8)	0.0006(10)	0.0245	138.70	111.98	57.08
N(2)	- C(2)	1.331(2)	1.3317	-0.0005	0.0009	0.0005	0.0236(6)	0.0254(9)	0.0018(11)	0.0424	100.62	61.41	30.89
N(2)	- C(14)	1.476(2)	1.4770	0.0010	0.0001	-0.0007	0.0211(6)	0.0214(8)	0.0003(10)	0.0173	44.54	68.48	126.70
C(1)	- C(2)	1.389(3)	1.3900	0.0010	0.0001	-0.0006	0.0290(9)	0.0295(9)	0.0005(12)	0.0224	39.60	70.63	122.97
C(3)	- C(4)	1.528(3)	1.5291	-0.0010	-0.0003	0.0006	0.0340(9)	0.0344(12)	0.0004(15)	0.0200	140.72	116.29	63.12
C(3)	- C(8)	1.530(2)	1.5313	0.0008	-0.0010	0.0001	0.0272(9)	0.0257(8)	0.0015(12)	0.0387	56.76	132.77	119.23
C(4)	- C(5)	1.523(4)	1.5243	0.0002	-0.0003	0.0013	0.0449(12)	0.0460(10)	0.0011(16)	0.0332	71.29	133.48	49.39
C(5)	- C(6)	1.520(3)	1.5213	0.0009	-0.0010	0.0001	0.0471(10)	0.0486(10)	0.0015(14)	0.0387	54.51	132.61	116.90
C(6)	- C(7)	1.530(3)	1.5316	0.0010	0.0003	-0.0007	0.0284(10)	0.0274(9)	0.0010(13)	0.0316	40.88	64.70	119.75
C(7)	- C(8)	1.532(3)	1.5333	-0.0002	0.0003	-0.0013	0.0275(9)	0.0272(8)	0.0003(12)	0.0173	109.29	46.16	129.88
C(9)	- C(10)	1.533(3)	1.5343	0.0010	0	-0.0008	0.0307(9)	0.0308(10)	0.0001(14)	0.0100	46.97	72.52	131.80
C(9)	- C(14)	1.533(3)	1.5340	-0.0008	-0.0008	-0.0005	0.0255(9)	0.0237(8)	0.0018(12)	0.0424	145.68	108.46	117.79
C(10)	- C(11)	1.518(3)	1.5191	-0.0003	0.0003	-0.0012	0.0411(10)	0.0420(10)	0.0009(14)	0.0300	111.00	43.74	126.22
C(11)	- C(12)	1.523(3)	1.5240	-0.0008	-0.0008	-0.0005	0.0446(10)	0.0448(10)	0.0002(14)	0.0141	147.37	107.06	116.87
C(12)	- C(13)	1.530(3)	1.5310	-0.0010	-0.0000	0.0008	0.0263(10)	0.0264(9)	0.0001(14)	0.0100	132.96	108.39	48.69
C(13)	- C(14)	1.526(3)	1.5272	0.0003	-0.0004	0.0012	0.0251(9)	0.0249(8)	0.0002(12)	0.0141	68.58	136.83	54.67

Sqrt(Sum(DelIJ**2)/Nrb) = 0.0010

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Librational Corrections for compound 2

Bond		Bond Distance		Components of the Correction			MSDA from U(obs) Vibration Along the Interatomic Bond				Angle with Lib. Axes		
Atom(I)	Atom(J)	Obsd	Calcd	Del(L)	Del(M)	Del(N)	I to J	J to I	Difference	Sqrt(Diff)	L(1)	L(2)	L(3)
Cr(1)	- N(1)	2.023(3)	2.0246	-0.0009	-0.0001	-0.0015	0.0198(2)	0.0210(12)	0.0012(12)	0.0346	132.73	127.92	66.28
Cr(1)	- N(2)	2.023(2)	2.0245	0.0010	0.0007	-0.0015	0.0209(2)	0.0233(12)	0.0024(12)	0.0490	70.11	95.40	20.71
Cr(1)	- N(3)	2.017(3)	2.0186	-0.0012	0.0013	0.0003	0.0179(2)	0.0208(12)	0.0029(12)	0.0539	56.14	138.32	111.27
Cr(1)	- N(4)	2.022(3)	2.0230	0.0009	0.0004	0.0013	0.0189(2)	0.0206(12)	0.0017(12)	0.0412	35.56	60.69	108.25
Cr(1)	- N(5)	2.024(3)	2.0256	0.0012	-0.0014	0.0001	0.0180(2)	0.0216(12)	0.0036(12)	0.0600	120.47	32.75	79.15
Cr(1)	- N(6)	2.028(3)	2.0294	-0.0010	-0.0009	0.0013	0.0202(2)	0.0234(12)	0.0032(12)	0.0566	120.60	83.06	148.43
N(1)	- C(1)	1.313(4)	1.3144	0.0005	0.0004	-0.0011	0.0243(12)	0.0277(15)	0.0034(19)	0.0583	80.99	103.68	16.46
N(1)	- C(8)	1.483(4)	1.4844	-0.0010	-0.0005	0.0001	0.0207(12)	0.0198(15)	0.0009(19)	0.0300	146.82	108.99	116.13
N(2)	- C(2)	1.314(4)	1.3156	-0.0004	0.0001	-0.0011	0.0238(12)	0.0271(15)	0.0033(19)	0.0574	122.62	127.37	54.24
N(2)	- C(14)	1.485(4)	1.4864	0.0010	0.0005	0	0.0179(12)	0.0196(15)	0.0017(19)	0.0412	31.80	67.95	68.27

N(3)	- C(15)	1.317(4)	1.3175	0.0004	0.0004	0.0008	0.0205(12)	0.0212(15)	0.0007(19)	0.0265	27.11	73.87	111.11
N(3)	- C(22)	1.483(4)	1.4848	-0.0011	0.0005	-0.0007	0.0209(12)	0.0180(15)	0.0029(19)	0.0539	102.66	167.25	88.01
N(4)	- C(16)	1.317(4)	1.3176	-0.0006	0.0009	0.0004	0.0221(12)	0.0261(15)	0.0040(19)	0.0632	45.03	125.41	113.90
N(4)	- C(28)	1.474(4)	1.4753	0.0011	-0.0006	0.0006	0.0201(12)	0.0198(15)	0.0003(19)	0.0173	82.18	7.86	90.01
N(5)	- C(29)	1.317(4)	1.3177	-0.0004	-0.0007	0.0008	0.0248(12)	0.0269(16)	0.002(2)	0.0447	125.46	71.95	138.83
N(5)	- C(36)	1.475(4)	1.4761	0.0012	-0.0003	-0.0008	0.0234(12)	0.0230(15)	0.0004(19)	0.0200	90.67	59.02	31.02
N(6)	- C(30)	1.315(4)	1.3160	0.0006	-0.0010	0.0003	0.0246(12)	0.0249(15)	0.000(2)	0	125.23	35.28	91.38
N(6)	- C(42)	1.483(4)	1.4844	-0.0012	0.0003	0.0007	0.0248(12)	0.0223(15)	0.0025(19)	0.0500	86.33	124.23	145.51
C(1)	- C(2)	1.407(4)	1.4084	0.0010	0.0004	-0.0000	0.0263(15)	0.0263(15)	0.000(2)	0	35.39	66.30	65.33
C(3)	- C(4)	1.531(5)	1.5322	-0.0010	-0.0006	0.0002	0.0255(16)	0.0283(18)	0.003(2)	0.0548	145.43	104.89	120.39
C(3)	- C(8)	1.526(5)	1.5275	0.0010	-0.0005	0.0009	0.0261(16)	0.0241(15)	0.002(2)	0.0447	74.93	19.95	102.77
C(4)	- C(5)	1.528(5)	1.5291	0.0005	-0.0011	-0.0002	0.0368(18)	0.0341(17)	0.003(2)	0.0548	138.72	51.18	78.16
C(5)	- C(6)	1.517(5)	1.5180	0.0010	-0.0005	0.0009	0.0352(17)	0.0343(17)	0.001(2)	0.0316	75.49	18.26	100.75
C(6)	- C(7)	1.523(4)	1.5242	0.0010	0.0006	-0.0002	0.0252(17)	0.0239(15)	0.001(2)	0.0316	32.98	75.15	61.30
C(7)	- C(8)	1.532(4)	1.5330	-0.0006	0.0011	0.0002	0.0254(15)	0.0233(15)	0.002(2)	0.0447	41.48	128.84	102.24
C(9)	- C(10)	1.523(5)	1.5243	0.0010	0.0005	0.0002	0.0300(17)	0.0301(19)	0.000(3)	0	30.00	64.84	74.72
C(9)	- C(14)	1.527(4)	1.5284	-0.0011	0.0001	0.0011	0.0281(17)	0.0262(15)	0.002(2)	0.0447	86.88	108.77	160.94
C(10)	- C(11)	1.528(5)	1.5292	-0.0005	0.0012	0	0.0474(19)	0.0469(19)	0.001(3)	0.0316	40.91	130.44	95.12
C(11)	- C(12)	1.520(5)	1.5215	-0.0011	0.0002	0.0010	0.0465(19)	0.0471(19)	0.001(3)	0.0316	87.12	111.73	158.05
C(12)	- C(13)	1.524(5)	1.5251	-0.0010	-0.0005	-0.0002	0.0261(19)	0.0253(16)	0.001(2)	0.0316	150.75	113.15	106.86
C(13)	- C(14)	1.531(4)	1.5320	0.0005	-0.0012	-0.0000	0.0250(16)	0.0266(15)	0.002(2)	0.0447	137.97	48.50	84.61
C(15)	- C(16)	1.396(5)	1.3974	0.0011	-0.0005	0.0005	0.0264(15)	0.0274(15)	0.001(2)	0.0316	78.44	11.66	88.39
C(17)	- C(18)	1.523(5)	1.5245	-0.0011	0.0005	-0.0008	0.0298(16)	0.0290(17)	0.001(2)	0.0316	108.34	160.72	84.25
C(17)	- C(22)	1.528(4)	1.5296	0.0011	-0.0005	-0.0008	0.0221(16)	0.0249(15)	0.003(2)	0.0548	106.01	58.47	36.23
C(18)	- C(19)	1.514(5)	1.5150	0.0003	0.0008	-0.0012	0.0600(17)	0.0606(19)	0.001(3)	0.0316	67.38	115.06	34.93
C(19)	- C(20)	1.511(5)	1.5123	0.0011	-0.0005	-0.0008	0.0464(19)	0.0418(18)	0.005(3)	0.0707	104.57	58.66	35.31
C(20)	- C(21)	1.529(5)	1.5309	0.0011	-0.0005	0.0008	0.0245(18)	0.0231(16)	0.001(2)	0.0316	73.88	16.83	94.91
C(21)	- C(22)	1.522(4)	1.5230	-0.0003	-0.0008	0.0012	0.0337(16)	0.0339(15)	0.000(2)	0	111.94	65.61	146.12
C(23)	- C(24)	1.527(5)	1.5283	0.0012	-0.0007	0.0006	0.0287(18)	0.029(2)	0.000(3)	0	86.80	3.54	88.84
C(23)	- C(28)	1.523(4)	1.5244	0.0003	0.0007	-0.0013	0.0316(18)	0.0282(15)	0.003(2)	0.0548	75.24	112.90	27.72
C(24)	- C(25)	1.516(5)	1.5172	0.0010	0.0006	0.0001	0.053(2)	0.048(2)	0.005(3)	0.0707	26.19	71.11	72.52
C(25)	- C(26)	1.516(5)	1.5173	0.0003	0.0007	-0.0013	0.061(2)	0.061(2)	0.000(3)	0	74.61	114.54	29.55
C(26)	- C(27)	1.527(5)	1.5288	-0.0012	0.0007	-0.0005	0.031(2)	0.0276(18)	0.003(3)	0.0548	91.71	176.86	92.86
C(27)	- C(28)	1.533(5)	1.5340	-0.0009	-0.0006	-0.0002	0.0235(18)	0.0244(15)	0.001(2)	0.0316	157.29	107.19	104.36
C(29)	- C(30)	1.396(4)	1.3969	-0.0012	0.0003	0.0007	0.0317(16)	0.0306(15)	0.001(2)	0.0316	90.02	124.57	145.39
C(31)	- C(32)	1.532(5)	1.5330	0.0012	-0.0001	-0.0009	0.0377(18)	0.0362(19)	0.002(3)	0.0447	87.10	64.38	25.85
C(31)	- C(36)	1.531(5)	1.5327	-0.0010	0.0009	-0.0007	0.0254(18)	0.0243(15)	0.001(2)	0.0316	84.58	172.34	84.53
C(32)	- C(33)	1.515(5)	1.5166	-0.0002	-0.0003	-0.0012	0.0593(19)	0.0664(19)	0.007(3)	0.0837	135.42	110.52	52.53
C(33)	- C(34)	1.519(5)	1.5208	-0.0010	0.0008	-0.0007	0.0428(19)	0.0461(18)	0.003(3)	0.0548	86.50	173.73	84.66
C(34)	- C(35)	1.529(5)	1.5308	-0.0012	0.0002	0.0009	0.0245(18)	0.0261(16)	0.002(2)	0.0447	91.22	116.71	153.29
C(35)	- C(36)	1.531(4)	1.5323	0.0002	0.0003	0.0012	0.0338(16)	0.0355(15)	0.002(2)	0.0447	44.84	69.00	127.39
C(37)	- C(38)	1.535(5)	1.5361	-0.0012	0.0005	0.0007	0.0319(16)	0.0313(18)	0.001(2)	0.0316	81.87	127.31	141.48
C(37)	- C(42)	1.529(4)	1.5297	0.0009	0.0007	-0.0002	0.0228(16)	0.0231(15)	0.000(2)	0	30.34	81.97	61.00
C(38)	- C(39)	1.520(5)	1.5212	0.0002	0.0002	0.0013	0.0460(18)	0.0437(19)	0.002(3)	0.0447	47.17	67.44	128.68
C(39)	- C(40)	1.518(5)	1.5189	0.0009	0.0007	-0.0002	0.0369(19)	0.0374(19)	0.001(3)	0.0316	30.20	80.79	61.54
C(40)	- C(41)	1.530(5)	1.5310	0.0012	-0.0004	-0.0007	0.0363(19)	0.0320(18)	0.004(3)	0.0632	97.30	53.93	37.08
C(41)	- C(42)	1.529(4)	1.5303	-0.0002	-0.0002	-0.0013	0.0282(18)	0.0265(15)	0.002(2)	0.0447	133.29	112.41	51.67

Sqrt(Sum(DelIJ**2)/Nrb) = 0.0024

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Librational Corrections for compound 3

Bond		Bond Distance		Components of the Correction			Vibration Along the Interatomic Bond				Angle with Lib. Axes		
Atom(I)	Atom(J)	Obsd	Calcd	Del(L)	Del(M)	Del(N)	I to J	J to I	Difference	Sqrt(Diff)	L(1)	L(2)	L(3)
Cr(1)	- N(1)	2.084(4)	2.0875	-0.0015	-0.0015	0.0028	0.0423(4)	0.047(2)	0.005(2)	0.0707	58.67	116.51	136.75
Cr(1)	- N(2)	2.102(4)	2.1050	0.0017	0.0010	0.0027	0.0316(4)	0.035(2)	0.003(2)	0.0548	71.08	37.91	121.44
Cr(1)	- N(3)	2.058(4)	2.0610	0.0014	-0.0027	0.0003	0.0353(4)	0.043(2)	0.008(2)	0.0894	149.51	97.39	119.39
Cr(1)	- N(4)	2.045(4)	2.0481	-0.0018	-0.0014	-0.0022	0.0325(4)	0.032(2)	0.001(2)	0.0316	107.90	150.71	67.63
Cr(1)	- N(5)	2.042(4)	2.0456	0.0015	0.0018	-0.0025	0.0427(4)	0.045(2)	0.002(2)	0.0447	114.04	56.73	43.10
Cr(1)	- N(6)	2.076(4)	2.0790	-0.0016	0.0027	-0.0011	0.0350(4)	0.045(2)	0.010(2)	0.1000	40.59	87.40	49.55
N(1)	- C(1)	1.298(7)	1.3005	0.0008	0.0004	0.0020	0.036(2)	0.036(3)	0.000(4)	0	64.89	49.78	129.44
N(1)	- C(8)	1.482(7)	1.4842	-0.0017	-0.0015	0	0.046(2)	0.044(3)	0.002(4)	0.0447	84.77	168.37	100.35
N(2)	- C(2)	1.289(6)	1.2913	-0.0007	-0.0007	0.0020	0.044(2)	0.049(3)	0.005(4)	0.0707	55.34	105.58	141.03
N(2)	- C(14)	1.488(7)	1.4898	0.0017	0.0015	-0.0001	0.046(2)	0.040(3)	0.006(4)	0.0775	96.35	13.53	78.20
N(3)	- C(15)	1.322(7)	1.3239	-0.0009	-0.0012	-0.0013	0.037(2)	0.039(3)	0.002(4)	0.0447	117.52	148.57	76.03
N(3)	- C(22)	1.496(7)	1.4982	0.0019	-0.0007	0.0015	0.038(2)	0.037(3)	0.001(3)	0.0316	116.33	53.95	132.51
N(4)	- C(16)	1.297(6)	1.2987	0.0006	-0.0018	-0.0001	0.041(2)	0.043(3)	0.002(4)	0.0447	149.22	109.06	113.19
N(4)	- C(28)	1.517(7)	1.5195	-0.0019	0.0008	-0.0016	0.037(2)	0.036(3)	0.001(4)	0.0316	64.38	123.24	44.28
N(5)	- C(29)	1.307(7)	1.3089	-0.0008	0.0018	-0.0011	0.041(2)	0.044(3)	0.003(4)	0.0548	53.97	84.15	36.68
N(5)	- C(36)	1.488(7)	1.4897	0.0018	-0.0005	-0.0008	0.052(2)	0.052(3)	0.000(4)	0	155.92	66.08	87.76
N(6)	- C(30)	1.285(7)	1.2867	0.0006	0.0013	-0.0018	0.056(2)	0.059(3)	0.003(4)	0.0548	105.53	63.98	30.98
N(6)	- C(42)	1.491(7)	1.4928	-0.0017	0.0004	0.0010	0.054(2)	0.056(3)	0.002(4)	0.0447	23.61	112.82	95.65
C(1)	- C(2)	1.442(8)	1.4444	0.0018	0.0013	-0.0001	0.052(3)	0.047(3)	0.005(4)	0.0707	98.77	13.12	80.27
C(3)	- C(4)	1.538(9)	1.5404	-0.0018	-0.0015	-0.0002	0.058(4)	0.052(4)	0.006(5)	0.0775	88.41	173.19	96.63
C(3)	- C(8)	1.538(8)	1.5396	0.0016	-0.0006	-0.0011	0.053(4)	0.053(3)	0.000(5)	0	161.38	73.00	82.78
C(4)	- C(5)	1.507(7)	1.5091	0.0006	-0.0022	0.0012	0.068(4)	0.069(3)	0.001(5)	0.0316	123.64	105.90	141.79
C(5)	- C(6)	1.498(9)	1.4997	0.0017	-0.0006	-0.0010	0.052(3)	0.062(4)	0.010(5)	0.1000	161.58	72.17	85.66
C(6)	- C(7)	1.541(9)	1.5430	0.0018	0.0015	0.0001	0.048(4)	0.044(3)	0.004(5)	0.0632	93.04	9.28	81.32
C(7)	- C(8)	1.527(7)	1.5295	-0.0006	0.0022	-0.0012	0.052(3)	0.059(3)	0.007(4)	0.0837	56.73	74.41	37.66
C(9)	- C(10)	1.528(9)	1.5299	0.0017	0.0016	-0.0003	0.055(3)	0.058(4)	0.003(5)	0.0548	96.26	16.98	74.36
C(9)	- C(14)	1.539(8)	1.5412	-0.0015	0.0004	-0.0023	0.041(3)	0.046(3)	0.005(4)	0.0707	89.74	126.92	36.96
C(10)	- C(11)	1.521(11)	1.5233	-0.0007	0.0022	-0.0006	0.080(4)	0.080(4)	0.000(5)	0	43.27	74.04	51.11
C(11)	- C(12)	1.507(11)	1.5093	-0.0014	0.0004	-0.0022	0.092(4)	0.094(4)	0.002(6)	0.0447	88.69	125.55	35.61
C(12)	- C(13)	1.548(10)	1.5505	-0.0017	-0.0016	0.0002	0.056(4)	0.050(4)	0.006(6)	0.0775	84.77	164.27	104.81
C(13)	- C(14)	1.535(7)	1.5376	0.0007	-0.0022	0.0006	0.050(4)	0.046(3)	0.004(5)	0.0632	136.29	106.57	129.02
C(15)	- C(16)	1.412(8)	1.4142	-0.0018	0.0007	-0.0014	0.044(3)	0.041(3)	0.003(4)	0.0548	62.98	125.22	47.25
C(17)	- C(18)	1.555(8)	1.5572	0.0020	-0.0006	0.0015	0.049(3)	0.048(3)	0.001(4)	0.0316	113.00	49.34	130.53
C(17)	- C(22)	1.526(7)	1.5285	0.0003	0.0013	-0.0024	0.041(3)	0.044(3)	0.003(4)	0.0548	107.62	76.82	22.30
C(18)	- C(19)	1.518(7)	1.5198	0.0012	-0.0012	-0.0011	0.058(3)	0.056(3)	0.002(5)	0.0447	176.61	90.68	86.83
C(19)	- C(20)	1.534(7)	1.5370	0.0003	0.0013	-0.0025	0.083(3)	0.080(3)	0.003(4)	0.0548	107.59	77.86	21.58
C(20)	- C(21)	1.516(8)	1.5186	-0.0020	0.0006	-0.0015	0.055(3)	0.053(3)	0.002(4)	0.0447	66.25	129.92	49.25

C(21) - C(22)	1.516(7)	1.5178	-0.0012	0.0011	0.0011	0.045(3)	0.044(3)	0.001(4)	0.0316	3.09	89.89	92.94
C(23) - C(24)	1.526(10)	1.5289	-0.0018	0.0010	-0.0016	0.053(4)	0.054(5)	0.001(6)	0.0316	64.16	118.42	40.17
C(23) - C(28)	1.527(8)	1.5298	-0.0005	-0.0011	0.0025	0.071(4)	0.075(3)	0.004(5)	0.0632	64.59	102.23	151.42
C(24) - C(25)	1.541(13)	1.5429	-0.0017	-0.0016	-0.0000	0.121(5)	0.117(5)	0.004(7)	0.0632	87.94	169.11	100.59
C(25) - C(26)	1.526(12)	1.5282	-0.0005	-0.0011	0.0025	0.132(5)	0.130(5)	0.002(7)	0.0447	65.34	102.07	152.14
C(26) - C(27)	1.552(11)	1.5542	0.0018	-0.0010	0.0016	0.061(5)	0.053(4)	0.008(6)	0.0894	117.85	61.32	137.91
C(27) - C(28)	1.516(10)	1.5183	0.0016	0.0016	0.0001	0.070(4)	0.069(3)	0.001(5)	0.0316	89.13	10.57	79.47
C(29) - C(30)	1.429(8)	1.4308	-0.0017	0.0004	0.0008	0.066(3)	0.072(3)	0.006(4)	0.0775	24.95	114.63	93.64
C(31) - C(32)	1.511(9)	1.5135	0.0018	-0.0006	-0.0008	0.075(3)	0.070(4)	0.005(5)	0.0707	158.46	68.41	89.91
C(31) - C(36)	1.531(8)	1.5332	-0.0015	-0.0018	0.0005	0.051(3)	0.054(3)	0.003(4)	0.0548	88.17	157.59	112.30
C(32) - C(33)	1.522(10)	1.5242	-0.0005	-0.0008	-0.0022	0.067(4)	0.061(4)	0.006(5)	0.0775	128.54	125.85	58.78
C(33) - C(34)	1.528(11)	1.5300	-0.0015	-0.0018	0.0004	0.066(4)	0.067(4)	0.001(5)	0.0316	89.10	158.60	111.33
C(34) - C(35)	1.549(8)	1.5511	-0.0018	0.0006	0.0008	0.063(4)	0.062(3)	0.001(5)	0.0316	21.64	111.61	91.10
C(35) - C(36)	1.528(7)	1.5302	0.0006	0.0008	0.0022	0.050(3)	0.047(3)	0.003(4)	0.0548	52.09	53.30	120.98
C(37) - C(38)	1.558(11)	1.5601	-0.0018	0.0002	0.0012	0.092(4)	0.089(5)	0.003(7)	0.0548	28.09	115.43	101.13
C(37) - C(42)	1.529(9)	1.5313	0.0015	-0.0014	0.0018	0.050(4)	0.049(3)	0.001(5)	0.0316	115.62	73.91	149.06
C(38) - C(39)	1.511(10)	1.5131	0.0006	0.0009	0.0021	0.100(5)	0.099(5)	0.001(7)	0.0316	53.41	50.23	119.01
C(39) - C(40)	1.527(11)	1.5292	0.0015	-0.0014	0.0018	0.094(5)	0.099(4)	0.005(6)	0.0707	115.48	71.65	147.75
C(40) - C(41)	1.536(9)	1.5380	0.0018	-0.0003	-0.0011	0.060(4)	0.065(3)	0.005(5)	0.0707	153.44	65.68	79.98
C(41) - C(42)	1.533(8)	1.5357	-0.0007	-0.0009	-0.0021	0.051(3)	0.055(3)	0.004(4)	0.0632	126.20	130.08	60.87

Sqrt(Sum(DelIJ**2)/Nrb) = 0.0041

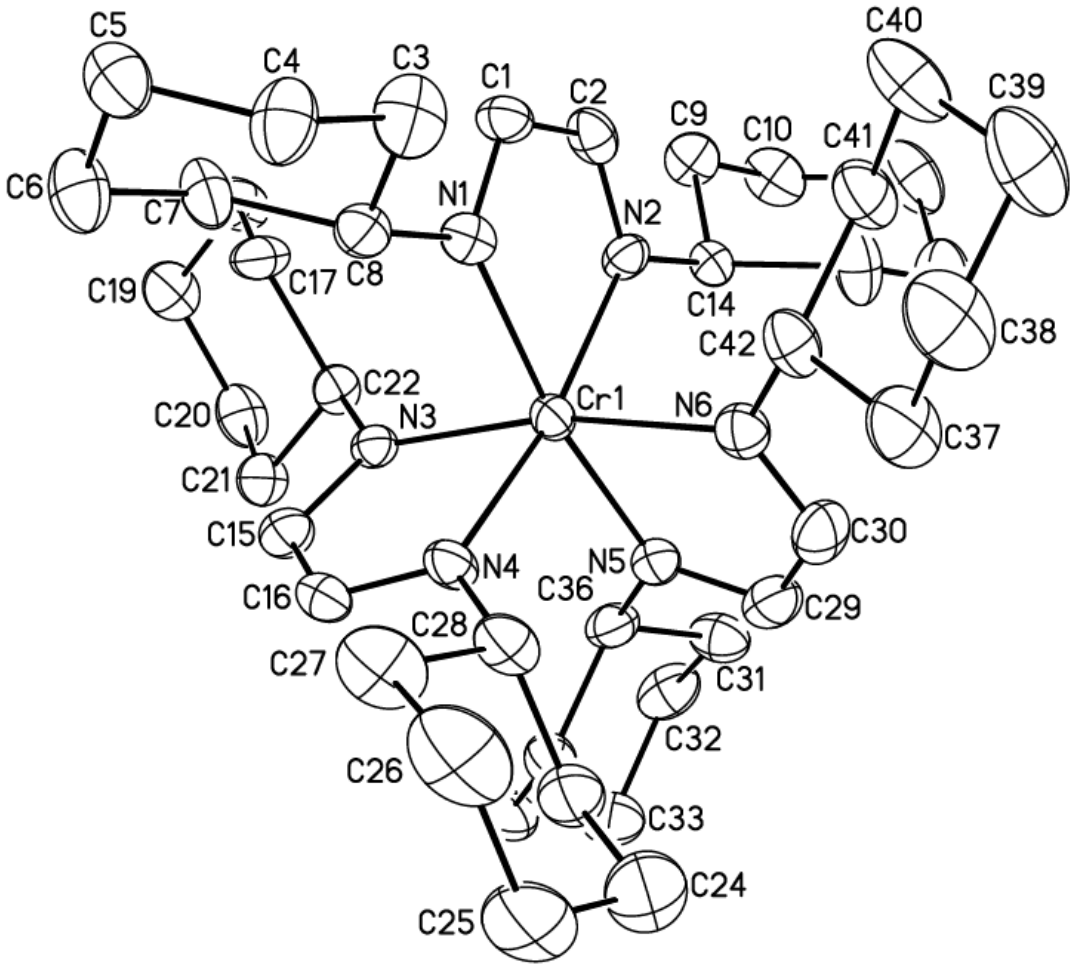
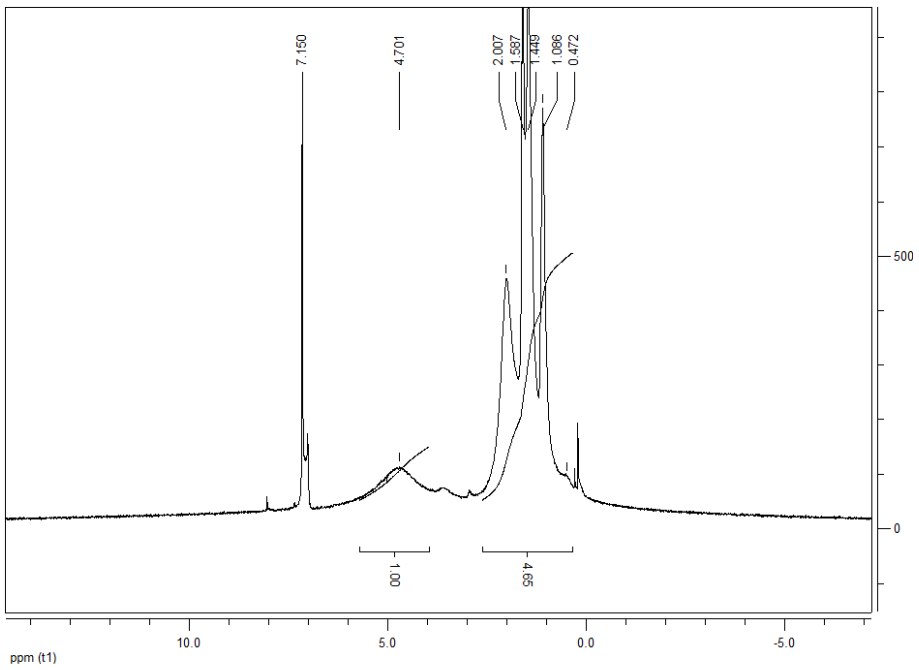


Figure S1 **Molecular structure of $[(^{H}L^{Cy})_3Cr][BARF]_2$ (3) at the 30% probabilit level. The $BARF^-$ counterions, a methylene chloride solvent molecule and all hydrogen atoms have been omitted for clarity.**

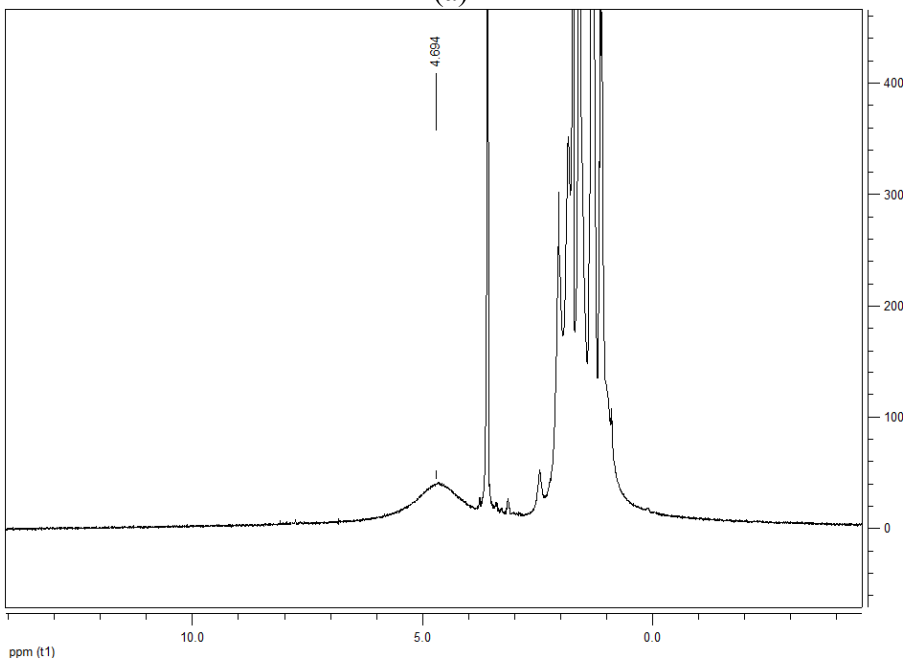
The ^{1}H NMR spectra of complexes **2** and **3** exhibit broad peaks in a large region, indicating that **2** and **3** are paramagnetic. Complex **1** at room temperature exhibited slightly broad peaks in the 0-8 ppm region, suggesting weak paramagnetism at room temperature, which is consistent with its effective magnetic moment of 1.1 μ_B. The ^{1}H NMR spectrum exhibits peaks associated with the cyclohexyl protons within 0.5-2 ppm and one broad peak at 4.7 ppm associated with either the backbone proton and/or the proton at the 1-position of the cyclohexyl groups in a 10: 2 ratio (Figure **S2**); this is inconsistent with the solid state structure. In solution, **1** is expected to exhibit resonances for the cyclohexyl group (10H), the proton at the 1-position of the cyclohexyl group (1H), and the backbone proton (1H) in a 10: 1: 1 intensity ratio. Notably, the variable temperature ^{1}H NMR spectra in toluene-d_8 between -80 ºC and 30 ºC showed a splitting of the broad peak at 4.7 ppm, resulting in 2 resonances (in a 1 : 1 intensity ratio), which resembles a coalescence phenomenon, and all the other peaks remained unchanged at low temperature (Figure **S3**).

To unambiguously assign the peak at 4.7 ppm, the cyclohexyl-substituted diimine with two deuteriums on the backbone, namely $^{D}L^{Cy}$, was synthesized from d_2-glyoxal and cyclohexylamine using the same synthesis route as that was used to obtain $^{H}L^{Cy}$. The complex, namely $(^{D}L^{Cy})_3Cr$, **1**-d_6, was prepared by the same procedure as its unlabeled form. The ^{1}H NMR and ^{2}H NMR spectra of the $^{D}L^{Cy}{}_3Cr$ are shown in Figures **S4** and **S5**. It was confirmed by both NMR spectroscopy and mass spectrometry that the products were primarily the pure labeled complex $^{D}L^{Cy}{}_3Cr$. Interestingly, in its ^{1}H NMR spectrum, the peak at approximately 4.7 ppm in C_6D_6 can still be observed, but the integration now shows a ratio of 1:10 that is consistent with the expected ratio for the cyclohexyl groups. In its ^{2}H NMR spectrum, a broad peak at approximately 4.9 ppm in C_6H_6 can also be observed, suggesting that the protons on the backbone and at the 1-position of the cyclohexyl group are both accidentally equivalent, giving a signal at approximately 4.7 ppm at room temperature.

Variable temperature ^{1}H NMR and ^{2}H NMR spectra of **1**-d_6 are shown in Figures **S6** and **S7**. The ^{1}H spectra, ranging from -80 ºC to 30 ºC, clearly show that the peak for the proton at the 1-position of the cyclohexyl rings at 4.6 ppm at 30 ºC moved upfield as the temperature decreased (4.0 ppm at -80 ºC). The peak became sharper as the temperature decreased, as was observed in the ^{1}H NMR of unlabeled **1**. The ^{2}H spectra, ranging from -70 ºC to 30 ºC, showed that the peak at 4.8 ppm associated with backbone deuterium moved downfield as the temperature decreased (6.3 ppm at -70 ºC). Both the ^{1}H NMR and the ^{2}H NMR spectra for **1**-d_6 exhibit the same temperature-dependent trends and chemical shifts as those for complex **1**. However, we did observe that for unlabeled **1**, the peak at 4.7 ppm splits into two sharper ^{1}H-NMR peaks at low temperatures but that for complex **1**-d_6, the signal associated with the deuterium on the backbone is broader at a lower temperature; this observation remains to be explained satisfactorily.



(a)



(b)

Figure S2 (a) ^{1}H NMR spectrum of complex **1** in C_6D_6 at room temperature. Note: the line broadening was due to small amount of solid in the nmr tube; The solubility of **1** in benzene is scant. (b) ^{1}H NMR spectrum of complex **1** in THF-d_8 at room temperature.

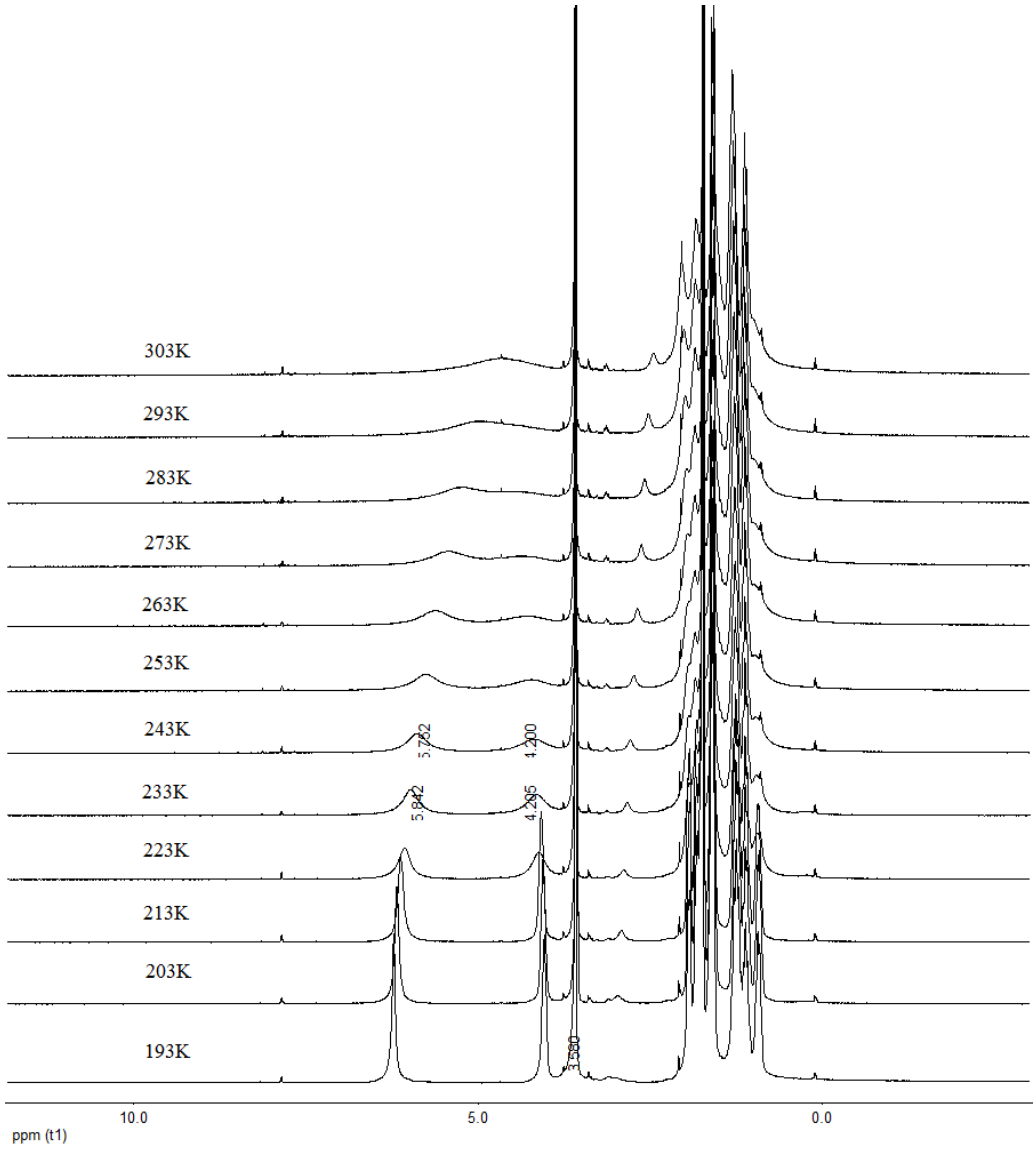
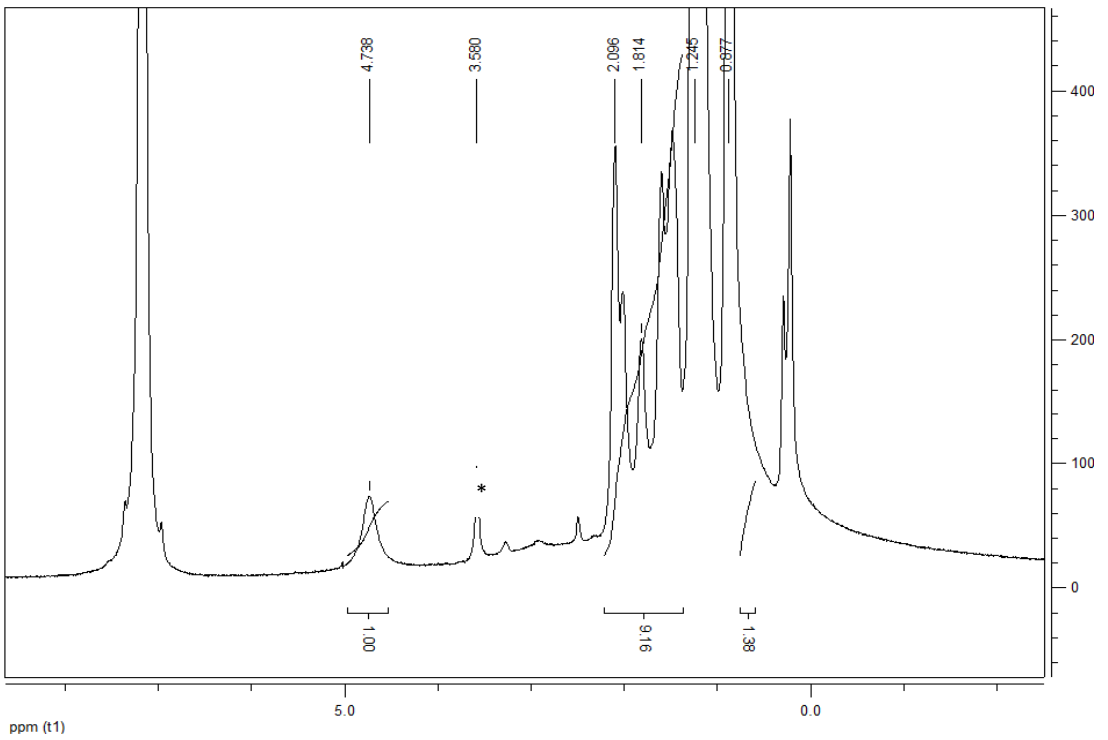
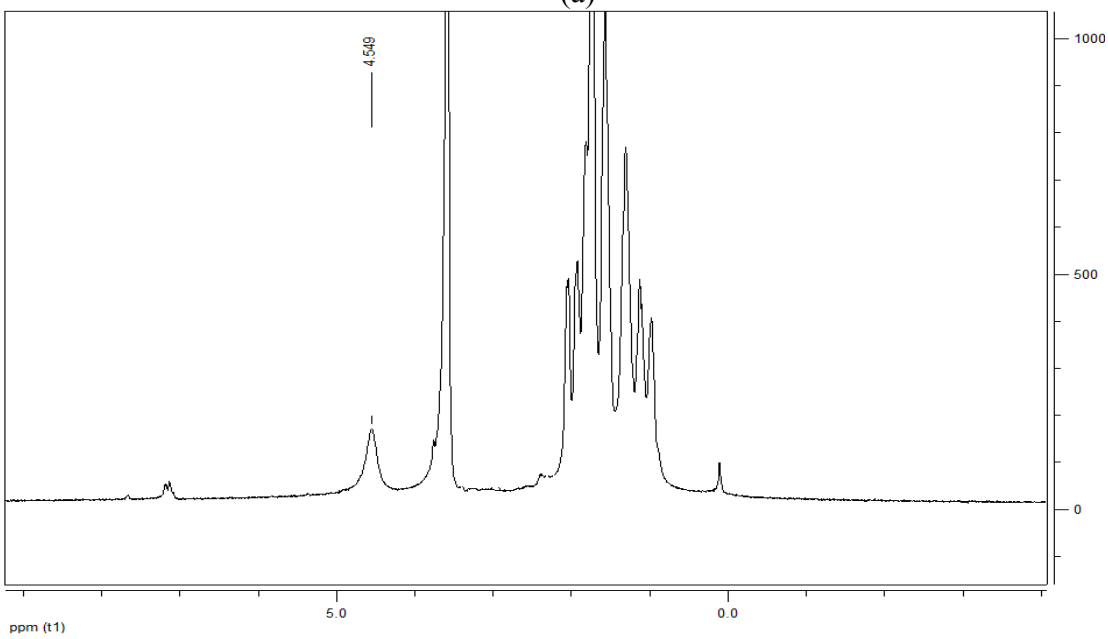


Figure S3 Variable temperature ^{1}H NMR spectra of complex 1 in d_8-THF.

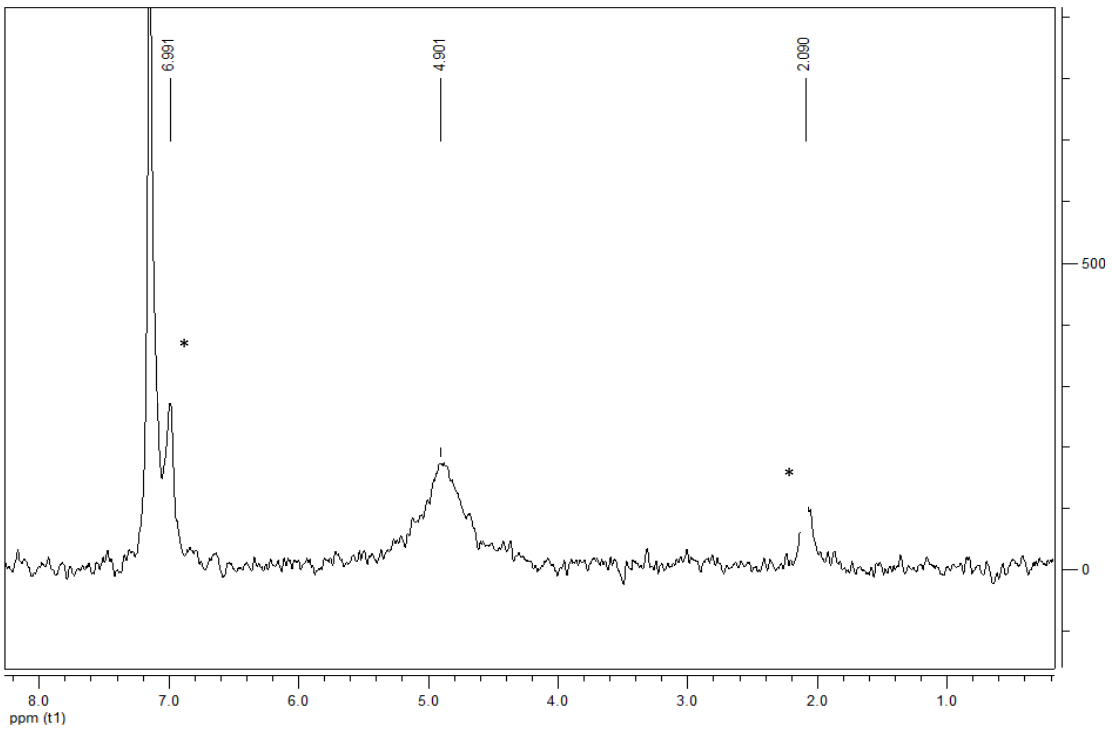


(a)

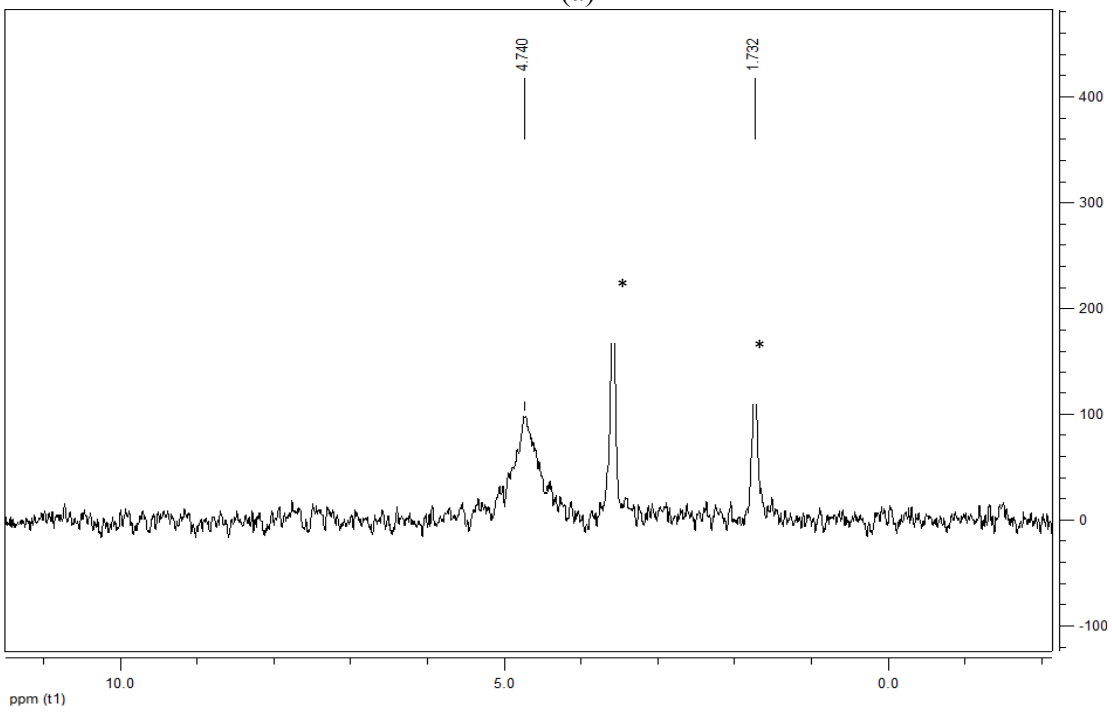


(b)

Figure S4 (a) ^{1}H NMR spectrum of complex 1-d_6 in C_6D_6. * denotes a peak associated with THF solvent residue. (b) ^{1}H NMR spectrum of complex 1- d_6 in THF-d_8.



(a)



(b)

Figure S5 (a) ^{2}H NMR spectrum of complex **1**- d_6 in C_6H_6, * denotes peaks associated with Toluene-d_8 (b) ^{2}H NMR spectrum of complex 1- d_6 in THF. * denotes peaks associated with THF-d_1.

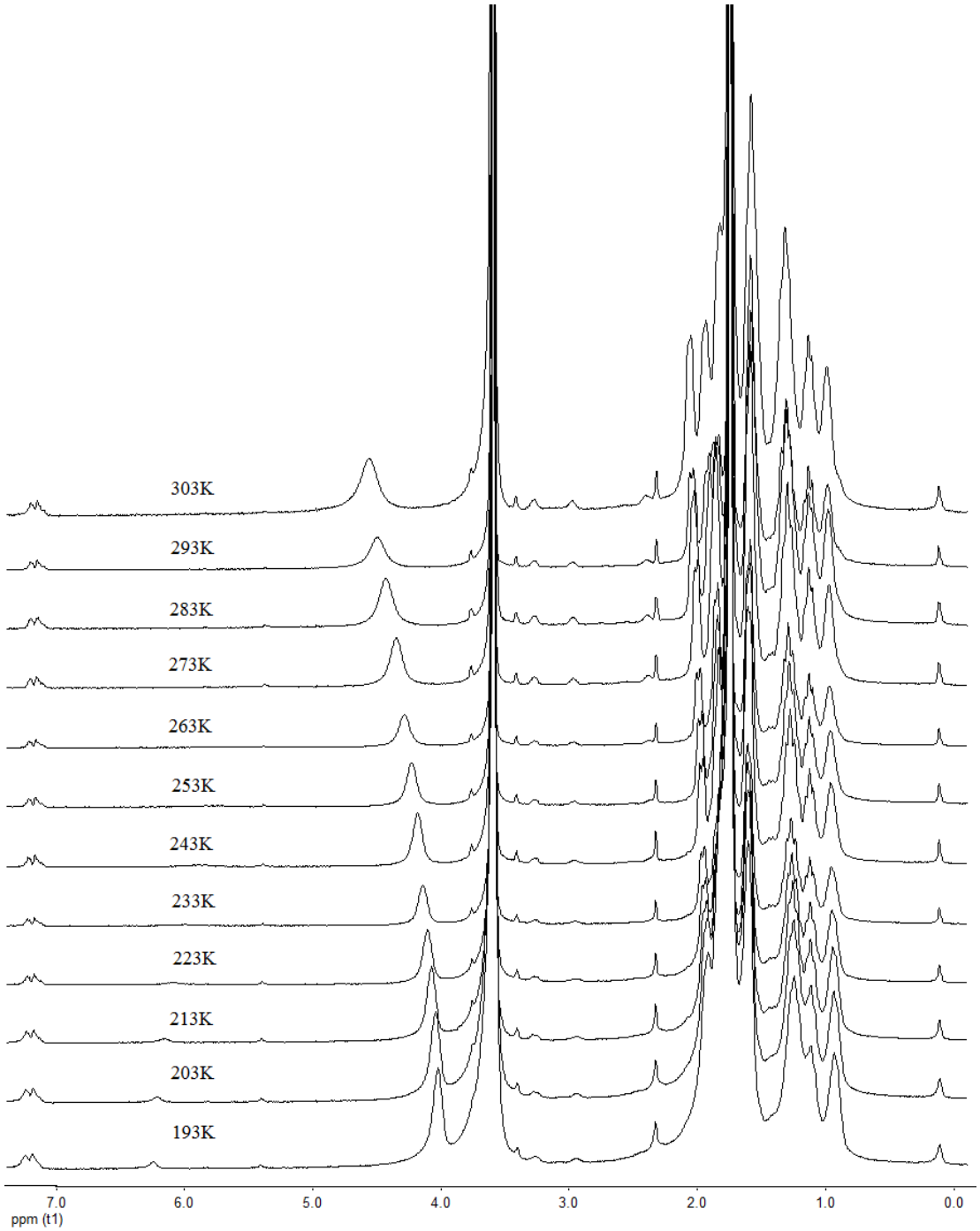


Figure S6 Variable temperature ^{1}H NMR spectra of complex **1**-d_6 in THF-d_8.

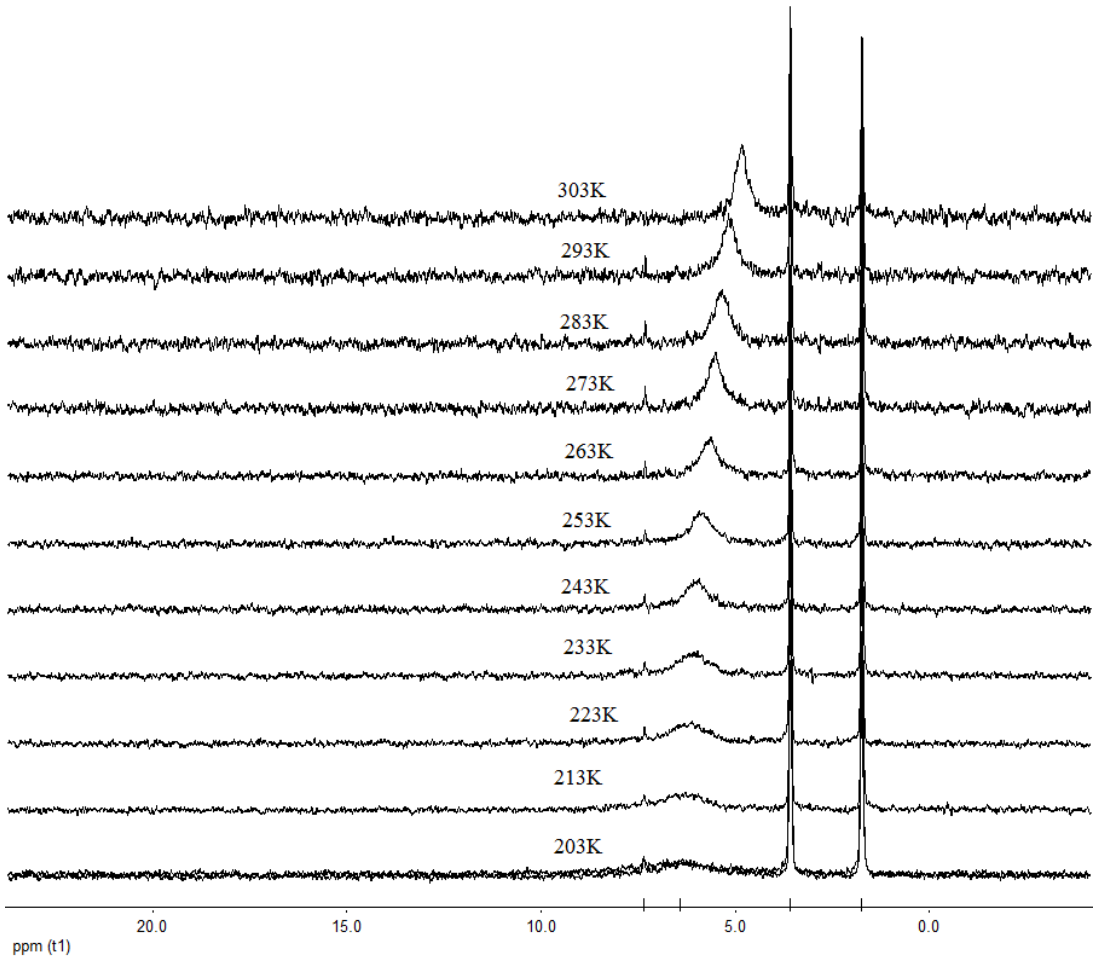


Figure S7 Variable temperature ^{2}H NMR spectra of complex **1**-d_6 in THF.

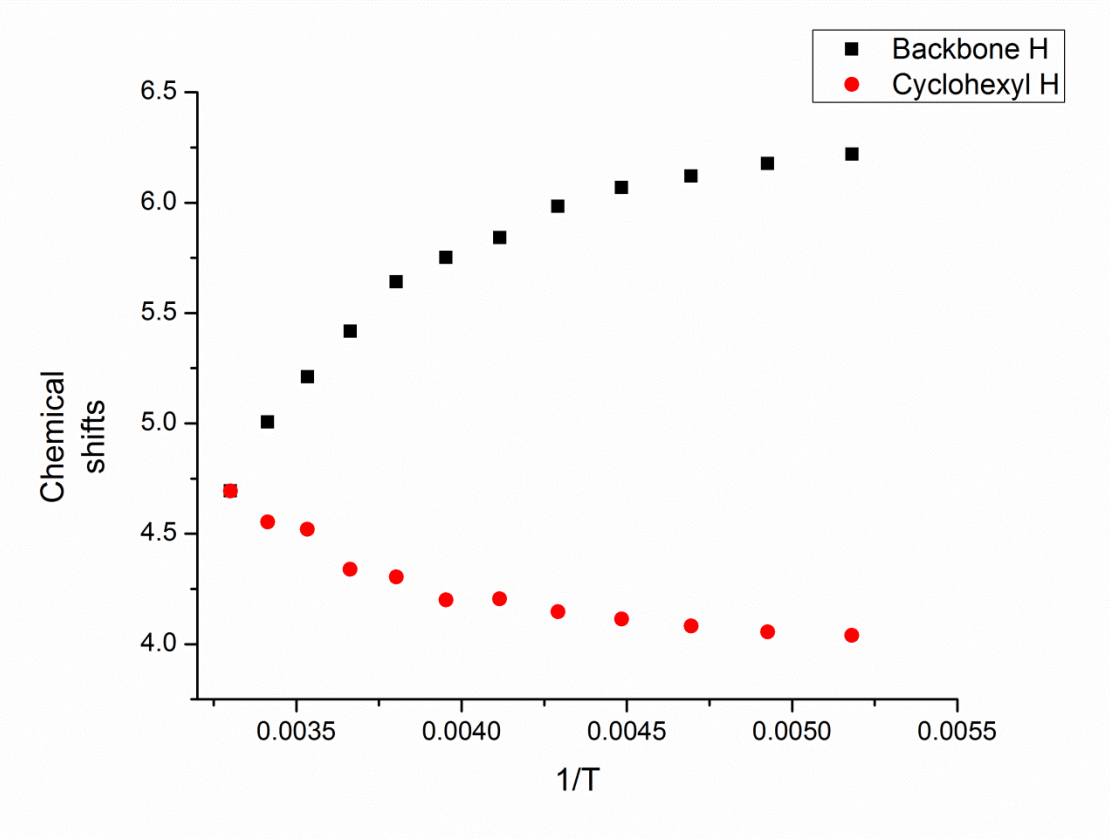


Figure S8 Plots of chemical shifts of 1 versus 1/T.

SQUID measurements of 2 and 3

Field dependent (-3T to 3T) magnetic susceptibility measurements of complex **2** at 300K indicate that there are small amount of ferromagnetic impurity in the solid sample. Presumably it is Cr(0) because the reduction was the first step on the synthesis route. Therefore, the measured magnetic susceptibility $\chi_{meassured}$ is the sum of χ_{sample} for **2** and χ_{ferro} of ferromagnetic impurity. A Honda-Owen correction[20] was performed using field dependent magnetic susceptibility data following the equation (1), (2), and (3). Plots of $\chi_{meassure}$ versus 1/H using the data from -0.1 to -3T for determination of b and the susceptibility of ferromagnetic impurity are shown in Figure **S9** because the data from 0.1 to 3T are noisier. The linear fit gives the b of $2.88*10^{-9}$ and χ_{ferro} of $2.98*10^{-9}$ emu.

$$\chi_{meassured} = a * \frac{1}{H} + b \quad (1)$$

$$\chi_{ferro} = \chi_{measured\ at\ 300K} - b, b\ is\ the\ intercept\ in\ equation\ (1) \quad (2)$$

$$\chi_{sample} = \chi_{measured} - X_{ferro} \quad (3)$$

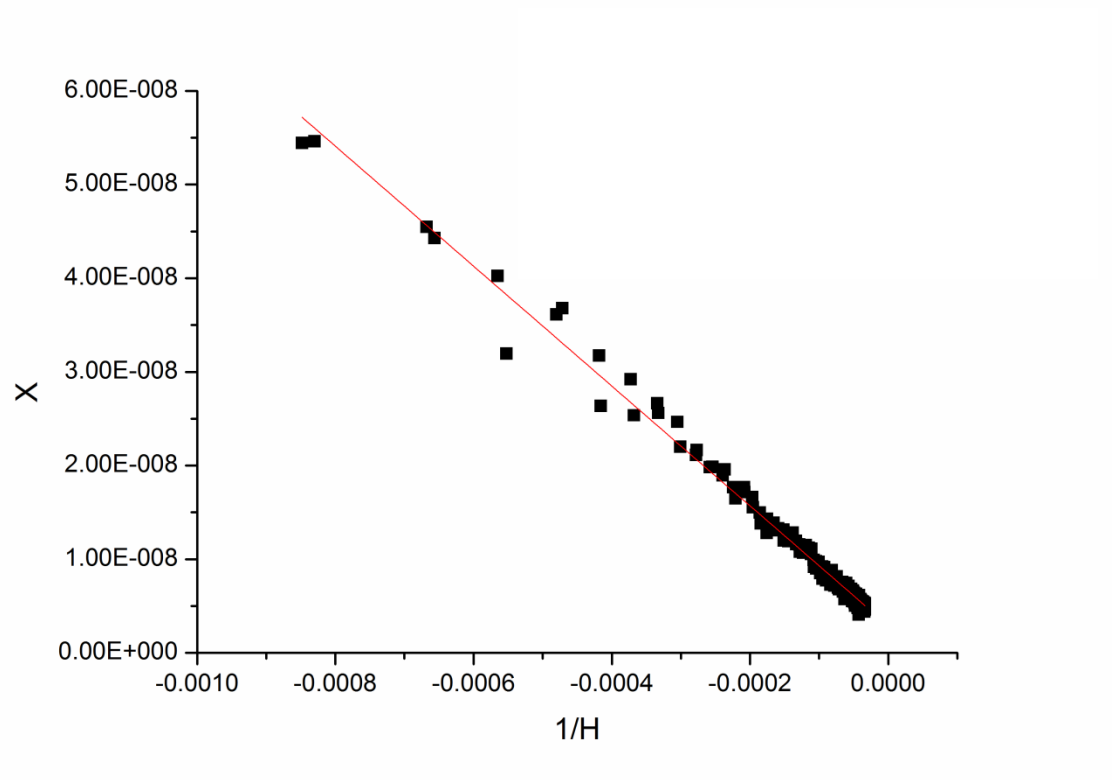


Figure S9 **The Honda-Owens correction for complex 2. The solid line represents a linear fit of measured magnetic susceptibility versus 1/H where H is the magnetic field).**

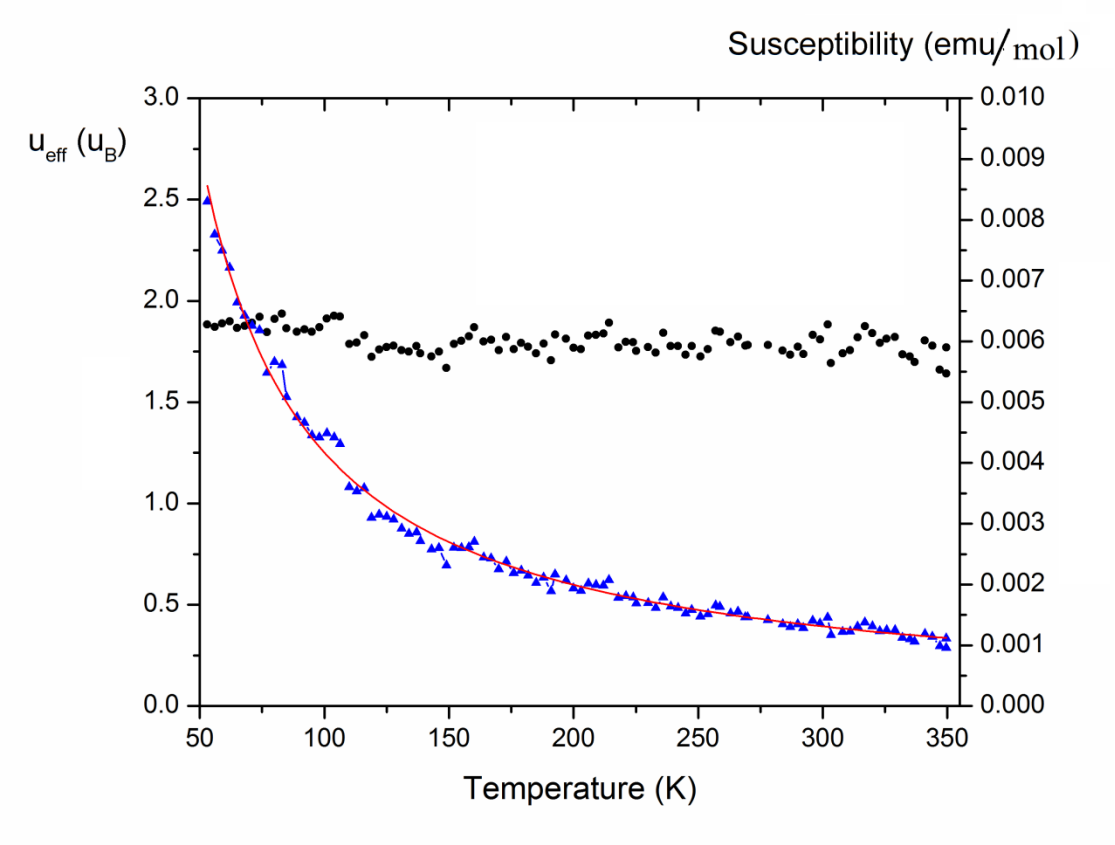


Figure S10 **Temperature dependence of molar magnetic susceptibility (χ_m, triangles) and effective magnetic moment (u_{eff}, circles) for complex 2. The solid line represents a fit of the molar magnetic susceptibility data with the Curie-Weiss law: $\chi_m = C/(T-\Theta)$ where C is the Curie constant, T is the absolute temperature and Θ is the Weiss constant.**

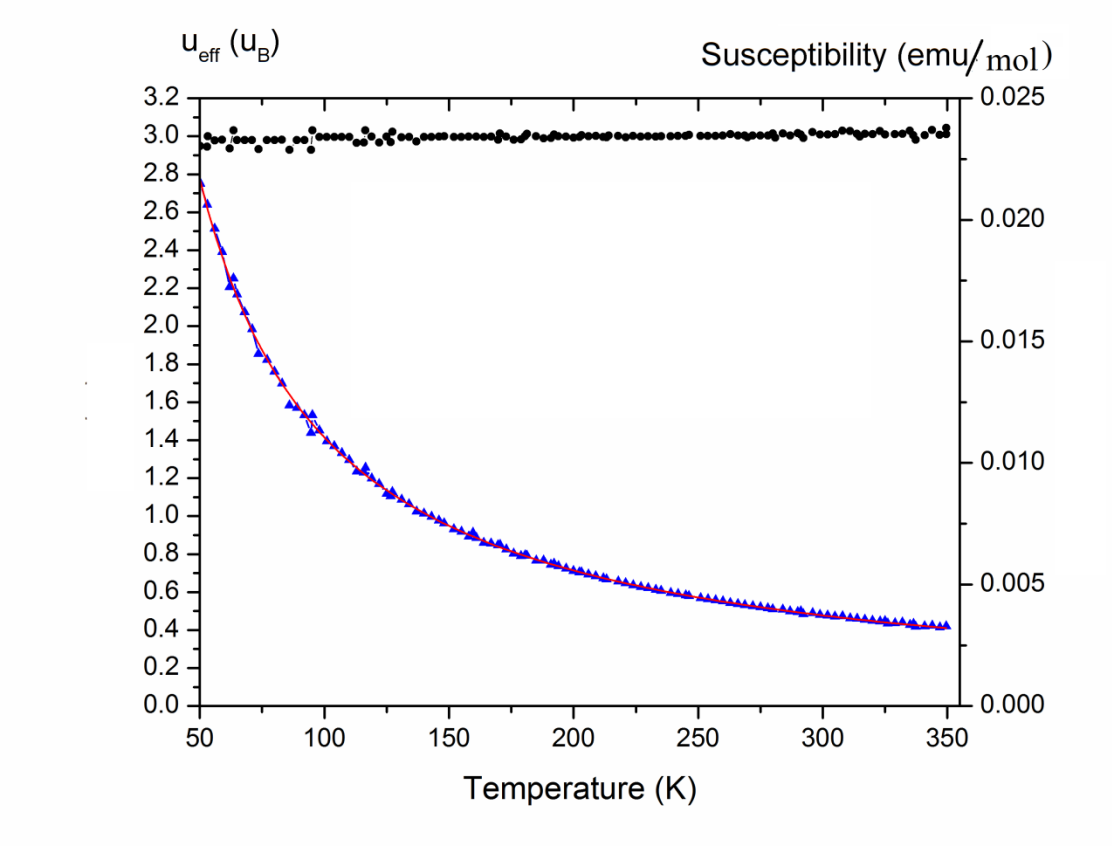


Figure S11 **Temperature dependence of Molar magnetic susceptibility (χ_m, triangles) and effective magnetic moment (u_{eff}, circles) for complex 3'. The solid line represents a fit of the molar magnetic susceptibility data with the Curie-Weiss law: $\chi_m = C/(T-\Theta)$ where C is the Curie constant, T is the absolute temperature and Θ is the Weiss constant.**

The linear simulation of the effective magnetic moment of **2** has a small negative slope due to the Honda-Owen correction. Before the correction, the slope was a small positive value. The magnetic moments suggest that both complexes contain Cr(III), d^3 ions, which are very strongly antiferromagnetically coupled to ligand radicals (two ligand radicals in **2**, one ligand radical in **3'**). Fits of χ_m data with Curie-Weiss Law give Curie constants of 0.3825 emu K/mol for **2** and 1.1260 emu K/mol for **3**. The Weiss constants are 8.297 K for **2** and -1.936 K for **3**

Computational Studies.

Restricted DFT calculations were carried out using Gaussian 09 (Revision D.01).[1] Molecules were built using GaussView, Version 5,[2] and the xyz-coordinates thus generated where copied into the relevant Gaussian input files. For the purposes of the calculations, the cyclohexyl substituents on the diimine employed in the actual experimental work were replaced by hydrogen atoms; the resulting molecules are labeled with a 'prime'.

We have used Becke's hybrid functional B3LYP,[3] using the non-local correlation expression provided by Lee, Yang and Parr,[4] combined with Schäfer's triple zeta basis set TZVP.[5] Structure optimizations to locate stationary points where followed up with frequency calculations to ascertain that the former were minima (as indicated by the absence of imaginary frequencies). Relevant computational output for individual compounds is listed below.

$[(C_2N_2H_4)_3Cr]^+$ ($1'^+$)

SCF Done: E(UB3LYP) = -1608.94228242 A.U. after 11 cycles
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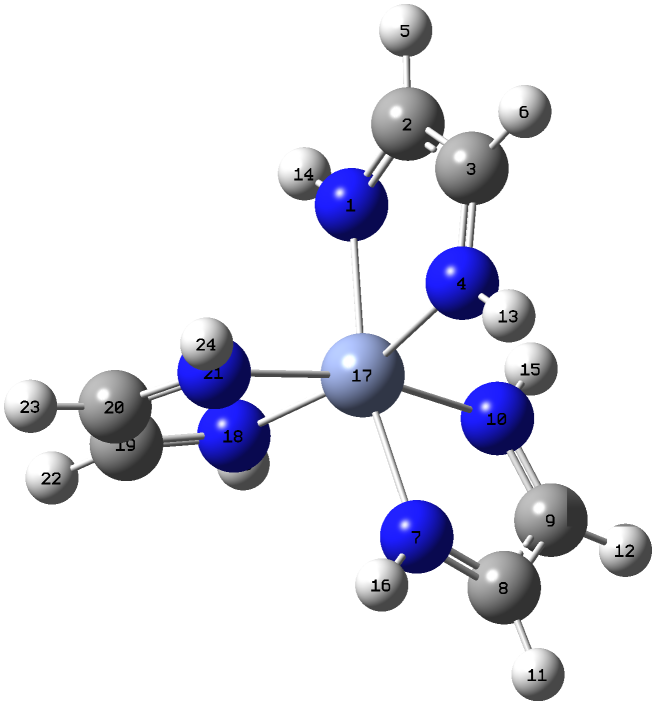
<Sx>= 0.0000 <Sy>= 0.0000 <Sz>= 0.5000 <S**2>= 2.0393 S= 1.0130
<L.S>= 0.000000000000E+00
KE= 1.604662429158D+03 PE=-6.061158070715D+03 EE= 1.706450558159D+03
Annihilation of the first spin contaminant:
S**2 before annihilation 2.0393, after 2.0432



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.308447	-0.188276	0.086361
2	6	0	0.596197	-0.207856	1.366936
3	6	0	1.982405	-0.307009	1.665155
4	7	0	2.765654	-0.405553	0.616399
5	1	0	-0.161488	-0.157241	2.140910
6	1	0	2.359160	-0.296852	2.681838
7	7	0	3.623422	-0.149621	-2.229765
8	6	0	3.981667	1.068463	-2.563196
9	6	0	3.094345	2.090691	-2.129869
10	7	0	2.027441	1.661881	-1.496536
11	1	0	4.880957	1.282694	-3.129821
12	1	0	3.290211	3.142327	-2.307044
13	1	0	3.758258	-0.460355	0.818643
14	1	0	-0.679795	-0.133540	-0.136310
15	1	0	1.395692	2.385088	-1.169429
16	1	0	4.242000	-0.887529	-2.549194
17	24	0	1.869728	-0.349188	-1.212563
18	7	0	0.679651	-0.635229	-2.840685
19	6	0	0.472406	-1.876364	-3.214854
20	6	0	1.093235	-2.857776	-2.395372
21	7	0	1.814684	-2.376151	-1.410081
22	1	0	-0.121365	-2.137370	-4.083761
23	1	0	0.973538	-3.920913	-2.571736
24	1	0	2.249255	-3.069233	-0.810128
25	1	0	0.253508	0.073104	-3.428764

Distance matrix (angstroms):

		1	2	3	4	5
1	N	0.000000				
2	C	1.312652	0.000000			
3	C	2.304088	1.421386	0.000000		
4	N	2.523096	2.304112	1.312661	0.000000	
5	H	2.107836	1.084290	2.201148	3.309676	0.000000
6	H	3.309640	2.201120	1.084294	2.107864	2.581814
7	N	4.044131	4.701462	4.229433	2.983608	5.781731
8	C	4.700223	5.341942	4.875236	3.709614	6.387230
9	C	4.226890	4.873572	4.624670	3.725756	5.821787
10	N	2.980535	3.707270	3.724895	3.046923	4.618618
11	H	5.780608	6.387623	5.824135	4.621563	7.435070
12	H	5.070723	5.655048	5.420944	4.627001	6.525770
13	H	3.537154	3.219163	1.973259	1.014479	4.147852
14	H	1.014495	1.973176	3.219111	3.537185	2.335580

15	H	3.062893	3.714256	3.953035	3.585200	4.454952
16	H	4.786224	5.393506	4.817002	3.526029	6.474651
17	Cr	2.037325	2.880221	2.880232	2.037392	3.925362
18	N	2.984150	4.230092	4.701859	4.044204	5.074670
19	C	3.711407	4.877709	5.343918	4.701146	5.660514
20	C	3.728421	4.628616	4.876978	4.228611	5.426332
21	N	3.048751	3.728008	3.710331	2.982319	4.630157
22	H	4.623162	5.826493	6.389531	5.781486	6.532156
23	H	4.630377	5.426077	5.659448	5.072833	6.136981
24	H	3.587525	3.957232	3.718618	3.065427	4.795832
25	H	3.525258	4.816130	5.392734	4.785743	5.589861

		6	7	8	9	10
6	H	0.000000				
7	N	5.073843	0.000000			
8	C	5.657473	1.312724	0.000000		
9	C	5.421566	2.304104	1.421289	0.000000	
10	N	4.626606	2.523157	2.304107	1.312735	0.000000
11	H	6.529150	2.107847	1.084288	2.201077	3.309676
12	H	6.130559	3.309671	2.201054	1.084294	2.107898
13	H	2.335745	3.067169	3.718069	3.955040	3.586038
14	H	4.147755	4.785446	5.391087	4.813067	3.521772
15	H	4.790964	3.537208	3.219217	1.973458	1.014462
16	H	5.590857	1.014486	1.973290	3.219120	3.537210
17	Cr	3.925385	2.037148	2.879971	2.879956	2.037133
18	N	5.782171	3.045460	3.725973	3.710342	2.983284
19	C	6.389497	3.725714	4.627264	4.877425	4.229648
20	C	5.825716	3.709903	4.877147	5.344367	4.701909
21	N	4.622093	2.983430	4.229758	4.701946	4.044557
22	H	7.437328	4.627297	5.424422	5.659946	5.073994
23	H	6.530988	4.621848	5.826044	6.390027	5.782244
24	H	4.460045	3.525314	4.816122	5.392653	4.785791
25	H	6.473801	3.583787	3.954632	3.718621	3.066684

		11	12	13	14	15
11	H	0.000000				
12	H	2.581796	0.000000			
13	H	4.459713	4.792527	0.000000		
14	H	6.472155	5.586085	4.551379	0.000000	
15	H	4.147948	2.335975	4.198892	3.423225	0.000000
16	H	2.335650	4.147804	3.429112	5.533044	4.551400
17	Cr	3.925101	3.925091	2.775735	2.775769	2.775398
18	N	4.627418	4.622740	4.785298	3.068131	3.525354
19	C	5.424223	5.826783	5.391753	3.720543	4.816242
20	C	5.659483	6.390286	4.814548	3.958341	5.392777
21	N	5.074118	5.782329	3.523487	3.588067	4.785694
22	H	6.134335	6.532288	6.472822	4.462013	5.589939
23	H	6.531225	7.438172	5.587914	4.796770	6.473818

24	H	5.589821	6.473626	3.425818	4.201387	5.532385
25	H	4.792260	4.460936	5.532478	3.428412	3.428476

		16	17	18	19	20
16	H	0.000000				
17	Cr	2.775621	0.000000			
18	N	3.583148	2.036880	0.000000		
19	C	3.953573	2.879920	1.312772	0.000000	
20	C	3.717561	2.880103	2.304142	1.421319	0.000000
21	N	3.066828	2.037308	2.523041	2.304062	1.312726
22	H	4.791237	3.925025	2.107913	1.084292	2.201112
23	H	4.459234	3.925267	3.309747	2.201117	1.084293
24	H	3.428588	2.775723	3.537116	3.219136	1.973346
25	H	4.195775	2.775255	1.014481	1.973347	3.219177

		21	22	23	24	25
21	N	0.000000				
22	H	3.309662	0.000000			
23	H	2.107903	2.581871	0.000000		
24	H	1.014474	4.147876	2.335824	0.000000	
25	H	3.537117	2.335755	4.147904	4.551323	0.000000

Mulliken charges and spin densities with hydrogens summed into heavy atoms:

		1	2
1	N	-0.081997	-0.183757
2	C	0.171897	-0.114778
3	C	0.171509	-0.114733
4	N	-0.081616	-0.183823
7	N	-0.081676	-0.184022
8	C	0.171418	-0.114944
9	C	0.171788	-0.114851
10	N	-0.081612	-0.184171
17	Cr	0.460677	2.793427
18	N	-0.081541	-0.184129
19	C	0.171340	-0.115085
20	C	0.171591	-0.114793
21	N	-0.081777	-0.184341

No imaginary requencies found.

Zero-point correction= 0.199239 (Hartree/Particle)
Thermal correction to Energy= 0.212379
Thermal correction to Enthalpy= 0.213323
Thermal correction to Gibbs Free Energy= 0.159795
Sum of electronic and zero-point Energies= -1608.743044
Sum of electronic and thermal Energies= -1608.729904
Sum of electronic and thermal Enthalpies= -1608.728959
Sum of electronic and thermal Free Energies= -1608.782487

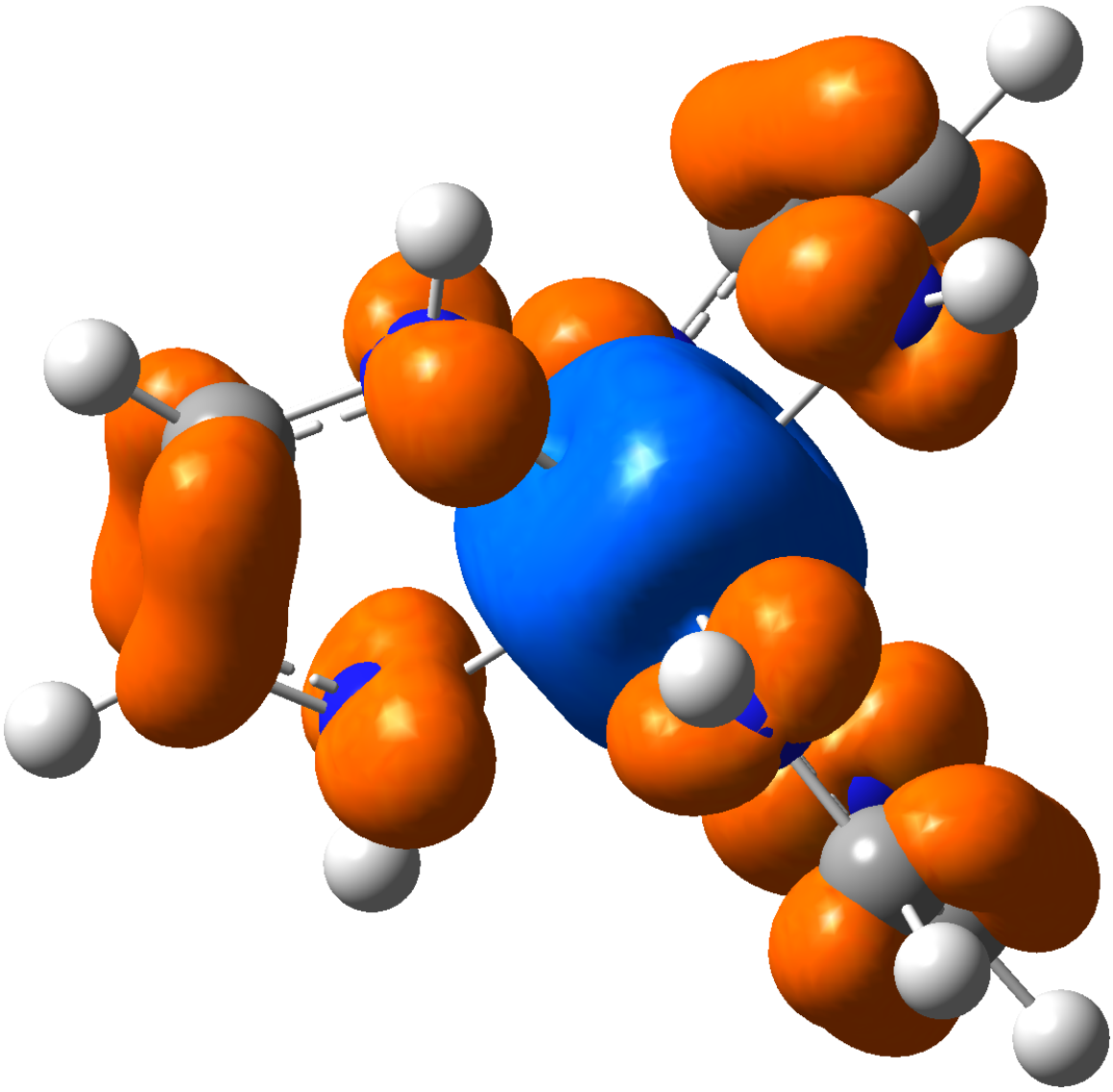
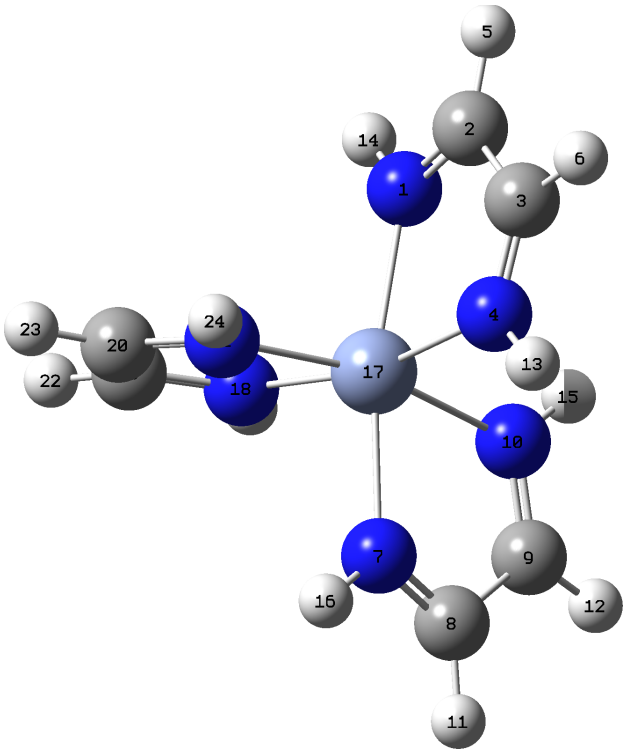


Figure S12. Spin density plot of **1'**$^{+}$. Blue contour is positive (α) spin density on Cr (Mulliken spin density: +2.8) and orange contour is negative (β) spin density on the diimine ligand (Mulliken spin density: -0.6/diimine, total of -1.8.) The spin densities on the individual ligands are identical, and so are the relevant bond distances (see above). This is consistent with delocalization of 2 electrons over 3 diimine ligands.

$[(C_2N_2H_4)_3Cr]2^+$ ($1'^{2+}$)

SCF Done: E(UB3LYP) = -1608.58559770 A.U. after 13 cycles
NFock= 13 Conv=0.74D-08 -V/T= 2.0027
<Sx>= 0.0000 <Sy>= 0.0000 <Sz>= 1.0000 <S**2>= 2.5252 S= 1.1659
<L.S>= 0.000000000000E+00
KE= 1.604311273049D+03 PE=-6.026992094010D+03 EE= 1.680479485365D+03
Annihilation of the first spin contaminant:
S**2 before annihilation 2.5252, after 2.0169



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.275547	-0.236686	0.103170
2	6	0	0.530153	-0.306692	1.360328
3	6	0	1.958656	-0.365616	1.706252
4	7	0	2.771637	-0.352619	0.713277
5	1	0	-0.236511	-0.317509	2.130078
6	1	0	2.280897	-0.403971	2.743935
7	7	0	3.630003	-0.154436	-2.290649
8	6	0	3.971795	1.023372	-2.671157
9	6	0	3.097375	2.110721	-2.202671
10	7	0	2.097509	1.749284	-1.484697

11	1	0	4.841395	1.227647	-3.289724
12	1	0	3.313316	3.146901	-2.451480
13	1	0	3.759136	-0.367017	0.963149
14	1	0	-0.712123	-0.184972	-0.141110
15	1	0	1.513089	2.510602	-1.143015
16	1	0	4.238119	-0.909278	-2.604267
17	24	0	1.876172	-0.337953	-1.204053
18	7	0	0.718058	-0.606193	-2.826532
19	6	0	0.490158	-1.845169	-3.193280
20	6	0	1.104334	-2.829015	-2.364894
21	7	0	1.810335	-2.340353	-1.372786
22	1	0	-0.116050	-2.098768	-4.055636
23	1	0	0.998369	-3.893695	-2.539946
24	1	0	2.257382	-3.033883	-0.778575
25	1	0	0.280463	0.103491	-3.408585

Distance matrix (angstroms):

		1	2	3	4	5
1	N	0.000000				
2	C	1.284590	0.000000			
3	C	2.327950	1.470972	0.000000		
4	N	2.572185	2.333461	1.283397	0.000000	
5	H	2.092151	1.086465	2.236225	3.325285	0.000000
6	H	3.320099	2.233593	1.087242	2.089746	2.592612
7	N	4.121833	4.791856	4.337420	3.130437	5.875317
8	C	4.790290	5.465057	5.014352	3.845533	6.523777
9	C	4.334736	5.012932	4.765355	3.831044	5.981958
10	N	3.128089	3.844192	3.830697	3.115049	4.773456
11	H	5.873922	6.524109	5.984016	4.775474	7.585967
12	H	5.215643	5.848349	5.608887	4.749288	6.752339
13	H	3.590535	3.253878	1.947802	1.018723	4.162856
14	H	1.018744	1.952532	3.252451	3.590914	2.324235
15	H	3.260687	3.894873	4.073019	3.637003	4.666096
16	H	4.846088	5.461698	4.906332	3.669678	6.541142
17	Cr	2.069079	2.896342	2.911606	2.116182	3.947187
18	N	2.985883	4.201762	4.705645	4.100211	5.055939
19	C	3.674215	4.806648	5.324564	4.763826	5.585691
20	C	3.674016	4.535315	4.834505	4.288073	5.320743
21	N	2.993230	3.639307	3.660882	3.037572	4.533380
22	H	4.573441	5.741235	6.364557	5.842115	6.438203
23	H	4.569709	5.319582	5.603543	5.125150	6.010255
24	H	3.539697	3.872441	3.658313	3.111151	4.696643
25	H	3.528195	4.793029	5.403513	4.837740	5.578646

		6	7	8	9	10
6	H	0.000000				
7	N	5.218179	0.000000			

8	C	5.849758	1.284072	0.000000		
9	C	5.608853	2.328598	1.471875	0.000000	
10	N	4.748839	2.573372	2.334005	1.282909	0.000000
11	H	6.754508	2.091835	1.086535	2.236763	3.325528
12	H	6.377062	3.320389	2.234105	1.087292	2.089543
13	H	2.314683	3.263291	3.896997	4.074252	3.637537
14	H	4.162885	4.845152	5.458967	4.902297	3.666143
15	H	4.918602	3.591770	3.254582	1.947496	1.018774
16	H	5.717458	1.018798	1.952061	3.253149	3.592158
17	Cr	3.969228	2.071301	2.897798	2.912830	2.117618
18	N	5.789081	2.995109	3.642311	3.664967	3.041657
19	C	6.366657	3.678579	4.541248	4.840244	4.292193
20	C	5.776268	3.679387	4.812174	5.329121	4.766756
21	N	4.573663	2.988628	4.203846	4.707148	4.101234
22	H	7.406204	4.574769	5.326820	5.610649	5.130017
23	H	6.460840	4.579268	5.747697	6.369662	5.845072
24	H	4.396029	3.530110	4.793996	5.403758	4.837650
25	H	6.489434	3.540582	3.875037	3.663086	3.116350

		11	12	13	14	15
11	H	0.000000				
12	H	2.592530	0.000000			
13	H	4.669171	4.919965	0.000000		
14	H	6.538411	5.713435	4.609195	0.000000	
15	H	4.163166	2.314687	4.214420	3.636138	0.000000
16	H	2.323842	4.163075	3.640045	5.576438	4.610491
17	Cr	3.948882	3.970600	2.871090	2.802235	2.872250
18	N	4.536455	4.578400	4.864878	3.071536	3.630525
19	C	5.327735	5.782841	5.490633	3.676612	4.921658
20	C	5.592624	6.371709	4.917853	3.903292	5.492866
21	N	5.058913	5.790724	3.626082	3.539135	4.865481
22	H	6.018963	6.469228	6.572992	4.397889	5.690672
23	H	6.446639	7.411936	5.686032	4.736541	6.575056
24	H	5.580648	6.489661	3.521511	4.164206	5.606077
25	H	4.698931	4.401885	5.606656	3.427072	3.527939

		16	17	18	19	20
16	H	0.000000				
17	Cr	2.804604	0.000000			
18	N	3.540070	2.011372	0.000000		
19	C	3.907690	2.854779	1.312061	0.000000	
20	C	3.682839	2.854589	2.302880	1.425269	0.000000
21	N	3.075493	2.010574	2.512718	2.302667	1.312062
22	H	4.741323	3.898839	2.105757	1.084185	2.209346
23	H	4.405321	3.898518	3.311853	2.209430	1.084165
24	H	3.430804	2.755793	3.529494	3.219771	1.971776
25	H	4.163613	2.757013	1.016822	1.971701	3.219883

		21	22	23	24	25

21	N	0.000000				
22	H	3.311647	0.000000			
23	H	2.105807	2.600194	0.000000		
24	H	1.016820	4.152921	2.329553	0.000000	
25	H	3.529498	2.329344	4.153001	4.546238	0.000000

Mulliken charges and spin densities with hydrogens summed into heavy atoms:

		1	2
1	N	0.017559	-0.054319
2	C	0.286036	-0.030372
3	C	0.296892	0.035986
4	N	-0.013943	-0.098525
7	N	0.018225	-0.053785
8	C	0.286818	-0.026907
9	C	0.297807	0.037697
10	N	-0.012805	-0.096730
17	Cr	0.411425	2.826634
18	N	-0.039892	-0.145105
19	C	0.245619	-0.124509
20	C	0.245430	-0.126221
21	N	-0.039170	-0.143842

No imaginary requencies found.

Zero-point correction= 0.200397 (Hartree/Particle)
Thermal correction to Energy= 0.213949
Thermal correction to Enthalpy= 0.214893
Thermal correction to Gibbs Free Energy= 0.159620
Sum of electronic and zero-point Energies= -1608.385200
Sum of electronic and thermal Energies= -1608.371649
Sum of electronic and thermal Enthalpies= -1608.370705
Sum of electronic and thermal Free Energies= -1608.425978

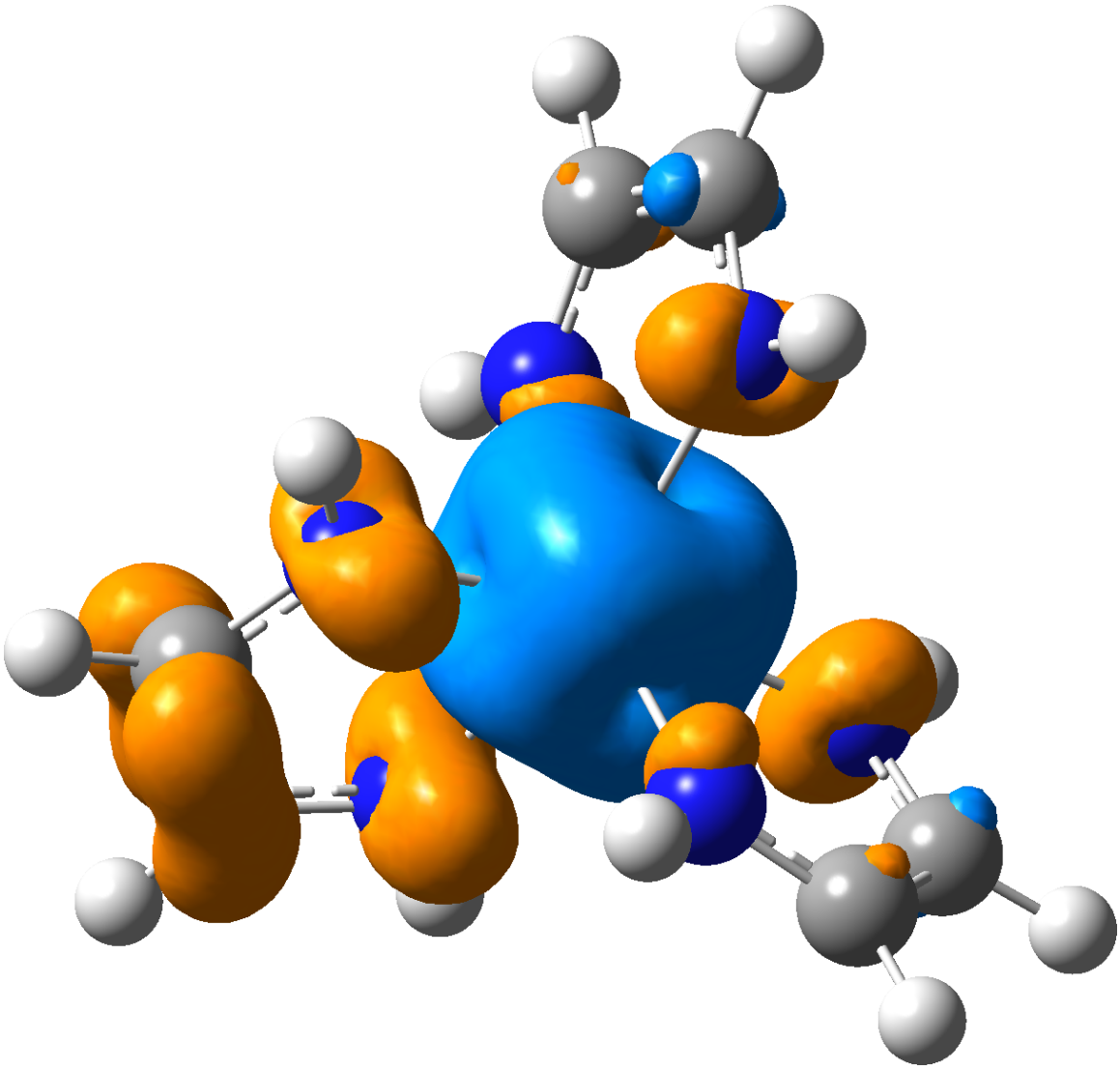


Figure S13. Spin density plot of **1'**$^{2+}$. Blue contour is positive (α) spin density on Cr (Mulliken spin density: +2.8) and orange contour is negative (β) spin density on the diimine ligands (Mulliken spin density: -0.54 for diimine on left, -0.15 for diimine on at right top, and -0.14 for diimine at right bottom, total of -0.83.) Most of the b spin density is concentrated on one of the diimine ligand The bond distance of this diimine are also consistent with a radical anion. Accordingly in **1'**$^{2+}$ the extra electron is largely localized on one diimine ligand, while the other two ligands are neutral.

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