

Two-Coordinate, Non-Linear Vanadium(II) and Chromium(II) Complexes of the Silylamide Ligand –N(SiMePh₂)₂: Characterization and Confirmation of Orbitally Quenched Magnetic Moments in Complexes with Sub-d⁵ Electron Configurations

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1 Materials and Methods

Computational details

The geometries used in the calculations were extracted from the crystal structure. The positions of the hydrogen atoms were optimized using density functional theory (DFT) while the positions of heavier atoms were kept frozen to their crystal-structure coordinates. The DFT calculations were carried out using the *ADF* 2019 quantum chemistry software.^{1–3} The pure generalized gradient approximation PBE was used as the exchange-correlation functional.^{4,5} Dispersion effects were treated using Grimme’s empirical DFT-D3 correction⁶ with the Becke–Johnson damping function.⁷ Scalar relativistic effects were treated using the zeroth-order regular approximation (ZORA) as implemented in ADF.^{8–10} Slater-type valence triple- ζ -quality basis sets designed for ZORA calculations with two sets of polarization functions (TZ2P) with a small frozen core were used for all atoms.¹¹ The geometry convergence tolerances were increased to 10^{-4} , 10^{-4} , 10^{-3} and 10^{-1} atomic units for energy, gradient, maximum bond distances and maximum angle, respectively. Numerical quality in *ADF* was set to “Good”.

The electronic structure was then modeled using state-averaged complete active space self-consistent field (SA-CASSCF) calculations.^{12–15} The active space consisted of the metal 3d electrons and the five 3d orbitals. All electronic states constructed within this space were treated in a single state-averaged calculation with equal weights for each multiplicity and each state within each multiplicity. This amounted to 10 quartets and 40 doublets for **1**, and 5 quintets, 45 triplets and 50 singlets for **2**. Electron correlation effects outside the active space were treated to second order using the *N*-electron valence state perturbation theory (NEVPT2) in its strongly contracted formulation.^{16–18} Test calculations were carried out using the quasi-degenerate formulation of the strongly contracted NEVPT2 method,^{19,20} but no visible improvement in the results were observed. Spin-orbit coupling (SOC) was then included using the quasi-degenerate perturbation theory (QDPT) where the SOC operator is constructed in the basis of the SA-CASSCF eigenstates and diagonalized to yield the spin-orbit coupled states and eigenvalues.^{21,22} The SOC operator was constructed using the spin-orbit mean-field (SOMF) operator.^{23–25} The **g** and **D** tensors were extracted from the calculated states using the effective Hamiltonian approach²⁶ and the powder magnetic susceptibility was calculated as $\chi = M/B$, where M is the powder magnetization and B is the magnitude of the magnetic field. The SA-CASSCF calculations were carried out using the *Orca* quantum chemistry code version 4.2.1.^{27,28} Scalar relativistic effects were included using the standard second-order Douglas–Kroll–Heß (DKH) transformation.^{29,30} DKH-def2 basis sets were used in all SA-

CASSCF calculations.^{31,32} Valence triple- ζ -quality basis set with two sets of polarization functions (DKH-def2-TZVPP) were used for the metal ions, polarized valence double- ζ -quality basis set (DKH-def2-SVP) was used for the hydrogen atoms and a polarized valence triple- ζ -quality basis set (DKH-def2-TZVP) was used for the remaining atoms. The resolution of identity approximation was used in the integral transformation. The auxiliary basis sets were generated using the “AutoAux” feature in *Orca*.³³

2 Crystallography

Table S1 Crystallographic data for **1** and **2**.

	1	2
Empirical formula	C ₅₂ H ₅₂ VN ₂ Si ₄	C ₅₂ H ₅₂ CrN ₂ Si ₄
M _r	868.26	869.32
T (K)	104(6)	106(2)
λ (Å)	1.54178	1.54184
Crystal size (mm)	0.0672 × 0.0541 × 0.0427	0.173 × 0.134 × 0.077
Crystal system	Monoclinic	Triclinic
Space group	P 21/c	P-1
a (Å)	15.9682(2)	10.5048(3)
b (Å)	10.47580(10)	13.8527(4)
c (Å)	27.5259(4)	17.4785(5)
α (°)	90	79.991(2)
β (°)	101.215(2)	74.668(3)
γ (°)	90	68.527(3)
V (Å ³)	4516.60(10)	2274.27(13)
Z	4	2
ρ _{calc.} (g cm ⁻³)	1.277	1.269
μ (mm ⁻¹)	3.138	3.362
F(000)	1828	916
2θ _{max} (°)	148.46	148.43
Reflections collected / unique	31266 / 9034	15792 / 8961
R _{int}	0.0328	0.0238
Reflexions observed [$>2\sigma(I)$]	8205	8570
Parameters / restraints	536 / 0	563 / 0
Goodness-of-fit on F ²	1.117	1.047
R ₁ [$\geq 2\sigma(I)$]	0.0356	0.0349
wR ₂ (all data)	0.1075	0.0964
Residuals (e Å ⁻³)	0.450 / -0.388	0.646 / -0.623

3 Characterization data of complex 1

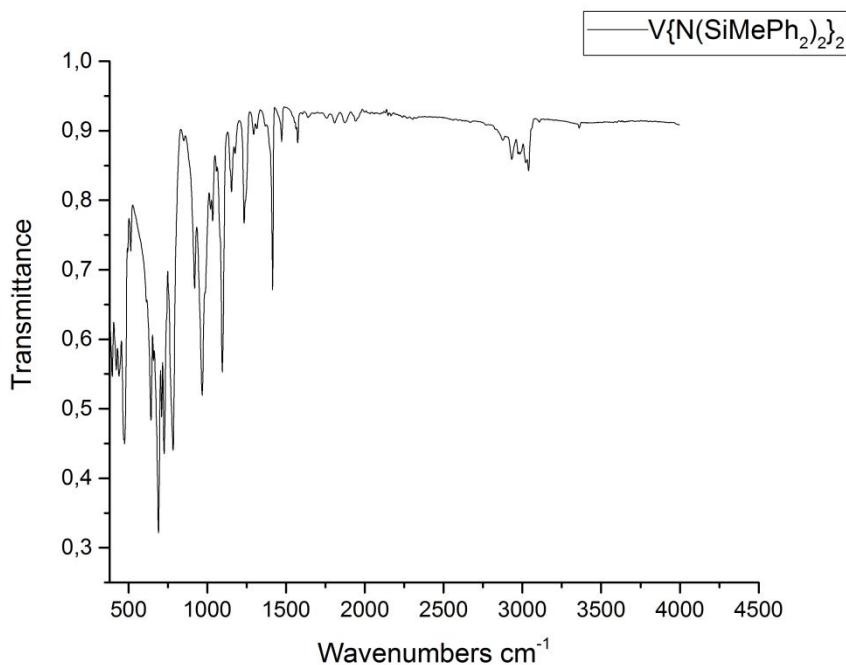


Figure S1. IR spectrum of **1**.

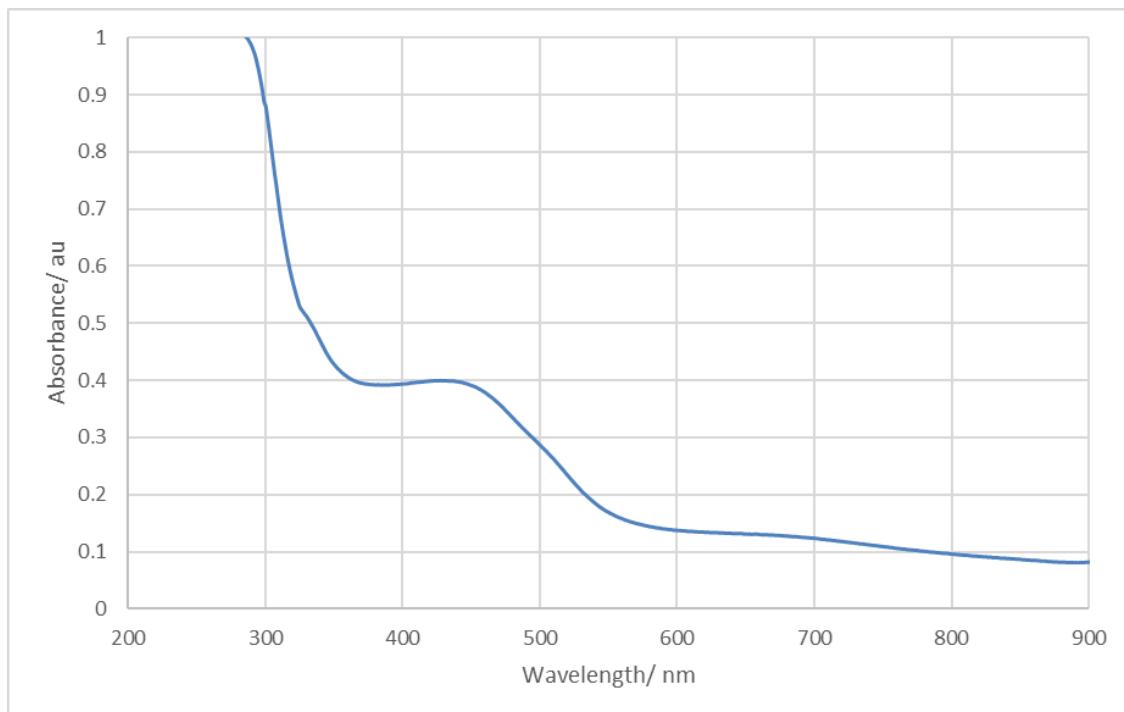


Figure S2. Room Temperature UV-VIS spectrum of **1** (hexanes, 50 μM).

4 Characterization data of complex 2

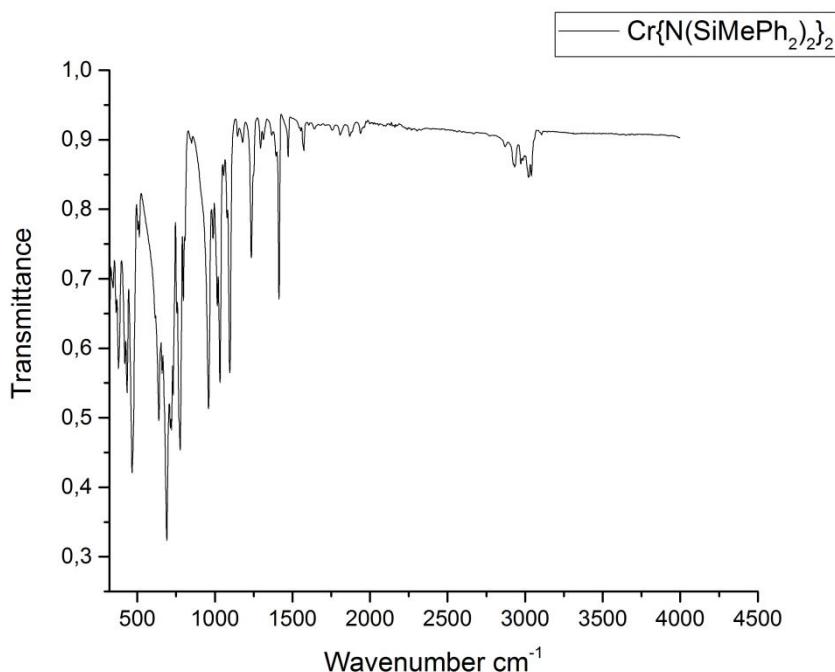


Figure S3. IR spectrum of **2**.

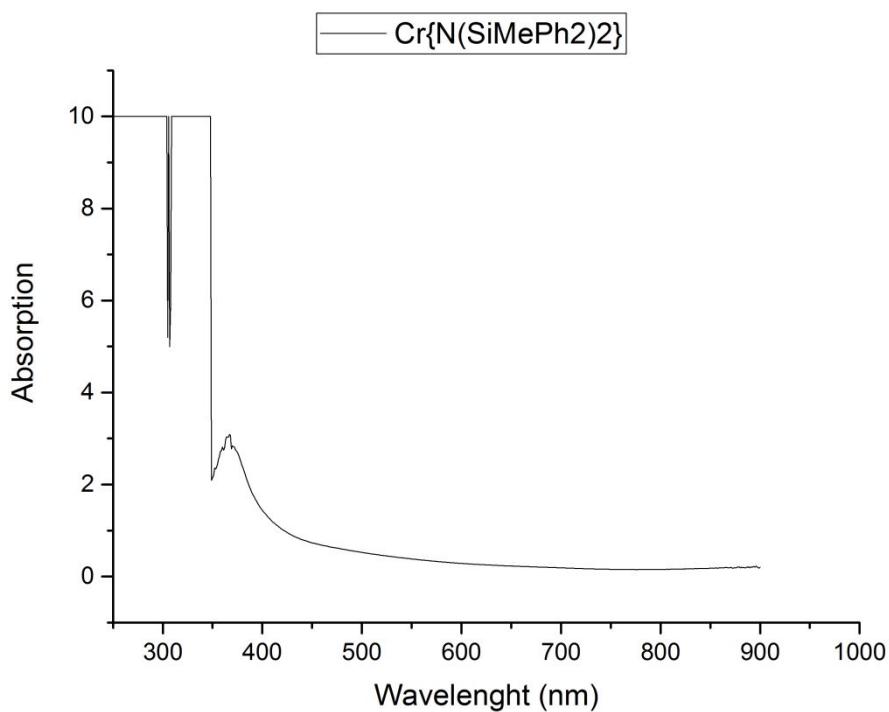


Figure S4. Room temperature UV-VIS spectrum of complex **2**.

5 Computational data

Table S2. Calculated scalar relativistic energies of the eigenstates of **1**.

SA-CASSCF		NEVPT2	
2S + 1	E / cm ⁻¹	2S + 1	E / cm ⁻¹
4	4843.6	4	4316.8
4	6390.7	4	5861.1
2	6779.8	4	6270.5
4	7503.4	4	6877.5
4	8098.7	2	10994.6
2	9334.5	4	11282.0
2	11193.6	4	11956.5
4	11727.3	2	12450.4
2	11909.1	2	13905.4
2	12203.3	2	14645.2
4	12811.0	2	15509.5
2	14203.4	2	16332.8
2	14404.3	2	17553.8
2	15551.8	2	17855.2
2	16417.7	2	18354.0
2	17194.8	4	18826.1
2	17355.4	2	18982.6
4	17478.2	2	19507.8
2	17618.9	2	20109.9
2	19157.4	4	20347.5
2	19685.7	2	21104.1
4	19928.0	2	21648.5
2	19971.8	2	21859.2
2	20850.7	2	22490.8
2	21148.6	2	23669.6
2	21897.4	2	24393.5
2	22027.9	2	25345.8
2	23022.0	2	25625.4
2	23025.2	2	26173.0
2	24222.9	2	26591.8
2	24695.4	4	26978.9
4	25463.4	2	27738.7

2	25993.3	2	28214.8
2	27118.4	2	29569.7
2	27492.7	2	29841.9
2	29936.9	2	31236.0
2	30135.4	2	31622.8
2	30828.5	2	35924.6
2	31777.3	2	36419.2
2	32761.2	2	37793.3
2	34181.1	2	38541.5
2	34215.9	2	38653.9
2	34386.8	2	39041.9
2	35749.2	2	40181.1
2	40417.7	2	49750.2
2	42320.9	2	50784.5
2	47741.5	2	57015.2
2	51334.4	2	60055.4
2	52873.7	2	60904.9

Table S3. Calculated scalar relativistic energies of the eigenstates of **2**.

SA-CASSCF		NEVPT2	
2S + 1	E / cm ⁻¹	2S + 1	E / cm ⁻¹
5	4614.8	5	3294.4
5	8412.0	5	7905.9
5	10818.6	5	10119.1
5	11871.5	5	10959.1
3	15046.8	3	17991.8
3	16149.1	3	18813.6
3	16489.7	3	19026.5
3	16903.8	3	19561.0
3	17827.2	3	20627.8
3	18060.5	3	21230.8
3	18783.6	3	21515.8
3	19534.3	3	21962.5
3	20270.8	3	22446.2
3	20413.5	3	22680.9
3	20588.2	3	23078.9
3	20665.5	3	23474.2

3	21900.2	3	24203.1
3	22016.1	3	24535.3
3	22069.9	3	24703.8
1	22377.7	3	25896.1
1	22443.0	1	26030.6
3	23377.7	1	26070.9
1	23958.8	3	26248.8
1	24031.3	3	26827.0
3	24056.1	3	27303.6
1	24163.0	3	27584.2
3	24200.3	1	27623.6
3	24398.5	1	27710.9
3	24683.6	3	27815.8
1	25055.7	1	28632.9
3	25217.9	3	28716.3
3	26110.0	3	29094.3
1	26687.0	3	29429.6
3	26869.6	1	29443.9
3	27119.9	3	30018.2
1	27143.9	1	30282.3
1	27232.9	1	30422.5
3	27619.4	3	30566.1
1	28282.4	1	31024.3
1	28414.0	3	31385.7
3	28419.2	3	31772.1
3	28743.2	1	31942.2
1	28798.3	1	32354.4
3	29221.1	3	32708.8
1	29426.8	1	32920.6
3	30478.3	3	32923.7
3	30491.9	1	33072.1
1	30516.5	1	34133.8
1	30532.9	1	34474.8
3	30567.9	1	34740.5
1	30872.0	1	35239.8
3	31479.2	3	35357.5
1	31773.8	1	35692.5
1	31823.6	1	35810.3

1	31972.8	3	36139.2
3	32182.2	1	36182.2
1	32332.8	3	36652.5
3	32834.2	1	36932.3
1	33264.6	1	37338.9
3	33855.3	3	37416.1
1	33922.0	3	38574.2
1	35036.5	1	39646.4
1	35803.7	1	40167.2
1	35867.0	1	40431.3
1	36045.5	1	41120.9
1	36191.7	1	41725.4
1	36901.1	1	42008.0
1	37682.1	1	42746.5
1	38644.4	1	44193.4
1	39760.2	1	45984.2
3	40002.4	3	48304.4
3	41493.6	1	48505.0
1	41553.3	3	49602.4
3	42798.1	1	49885.4
1	43628.8	1	50387.2
1	43937.1	3	51167.8
1	43987.7	1	51208.9
3	45554.1	3	53764.9
3	46626.9	3	55003.1
3	48514.1	3	56447.1
1	49094.1	1	58235.6
1	49416.2	1	58471.7
3	50981.1	3	58816.2
3	50985.1	3	59437.5
1	51212.2	1	60327.4
1	51560.4	1	60585.6
3	52782.8	3	61515.0
1	52832.2	1	62201.1
1	53521.1	1	62469.4
1	55014.5	1	63903.3
1	56083.6	3	64282.4
1	56358.8	1	64385.9

3	56579.6	1	64850.0
1	61409.2	1	75053.4
1	63347.6	1	77691.9
1	67708.7	1	81437.5
1	69081.6	1	83927.1
1	70463.7	1	84803.7
1	87113.8	1	105215.9

Table S4. Calculated energies (in cm⁻¹) of the spin-orbit coupled eigenstates of **1** and **2**.

	1		2
0	0.00	0	0.00
1	0.00	1	0.05
2	7.22	2	7.60
3	7.22	3	8.64
4	4831.87	4	10.85
5	4831.87	5	4616.90
6	4848.78	6	4617.10
7	4848.78	7	4626.14
8	6373.58	8	4629.00
9	6373.58	9	4631.25
10	6396.76	10	8415.45
11	6396.76	11	8416.87
12	6797.26	12	8418.49
13	6797.26	13	8424.09
14	7515.03	14	8424.19
15	7515.03	15	10785.18
16	7535.96	16	10785.31
17	7535.96	17	10819.46
18	8100.52	18	10823.66
19	8100.52	19	10834.10
20	8110.78	20	11884.76
21	8110.78	21	11892.99
22	9350.80	22	11894.25
23	9350.80	23	11919.04
24	11188.67	24	11919.06
25	11188.67	25	15036.54
26	11695.97	26	15053.18

27	11695.97	27	15054.03
28	11729.24	28	16147.92
29	11729.24	29	16149.51
30	11931.90	30	16156.47
31	11931.90	31	16484.37
32	12231.28	32	16491.96
33	12231.28	33	16500.13
34	12824.30	34	16906.38
35	12824.30	35	16910.39
36	12846.05	36	16919.32
37	12846.05	37	17803.51
38	14212.43	38	17811.47
39	14212.43	39	17832.92
40	14422.96	40	18068.99
41	14422.96	41	18073.39
42	15573.92	42	18085.09
43	15573.92	43	18771.18
44	16436.48	44	18788.43
45	16436.48	45	18802.80
46	17158.17	46	19532.54
47	17158.17	47	19537.91
48	17363.79	48	19550.24
49	17363.79	49	20247.10
50	17476.63	50	20261.97
51	17476.63	51	20271.64
52	17521.32	52	20355.54
53	17521.32	53	20380.64
54	17652.13	54	20410.58
55	17652.13	55	20585.53
56	19162.12	56	20592.01
57	19162.12	57	20629.51
58	19690.02	58	20690.26
59	19690.02	59	20730.07
60	19877.86	60	20757.91
61	19877.86	61	21834.94
62	19947.40	62	21847.53
63	19947.40	63	21905.40

64	20053.20	64	22024.56
65	20053.20	65	22067.61
66	20870.07	66	22069.03
67	20870.07	67	22099.16
68	21164.41	68	22110.56
69	21164.41	69	22117.23
70	21915.54	70	22438.29
71	21915.54	71	22495.94
72	22048.34	72	23354.24
73	22048.34	73	23363.76
74	22995.83	74	23393.76
75	22995.83	75	23909.20
76	23084.20	76	23979.14
77	23084.20	77	24027.51
78	24236.84	78	24089.48
79	24236.84	79	24108.07
80	24694.77	80	24131.08
81	24694.77	81	24220.37
82	25460.35	82	24260.51
83	25460.35	83	24279.71
84	25496.08	84	24433.84
85	25496.08	85	24451.71
86	26027.00	86	24464.02
87	26027.00	87	24668.76
88	27135.40	88	24689.24
89	27135.40	89	24705.91
90	27511.07	90	25110.99
91	27511.07	91	25244.74
92	29945.17	92	25251.16
93	29945.17	93	25285.67
94	30162.33	94	26126.94
95	30162.33	95	26130.05
96	30840.34	96	26145.51
97	30840.34	97	26690.85
98	31791.37	98	26866.72
99	31791.37	99	26873.92
100	32774.86	100	26894.10

101	32774.86	101	27079.25
102	34184.61	102	27130.34
103	34184.61	103	27146.01
104	34232.50	104	27209.34
105	34232.50	105	27312.85
106	34412.83	106	27641.44
107	34412.83	107	27669.40
108	35764.78	108	27694.07
109	35764.78	109	28314.97
110	40435.33	110	28383.05
111	40435.33	111	28415.00
112	42338.80	112	28441.63
113	42338.80	113	28468.69
114	47757.66	114	28750.65
115	47757.66	115	28765.46
116	51345.55	116	28773.78
117	51345.55	117	28860.58
118	52895.10	118	29237.59
119	52895.10	119	29255.50
		120	29259.39
		121	29478.09
		122	30330.01
		123	30357.60
		124	30440.82
		125	30480.26
		126	30510.99
		127	30553.67
		128	30601.20
		129	30605.27
		130	30634.32
		131	30679.77
		132	30715.41
		133	30911.12
		134	31487.27
		135	31498.62
		136	31501.54
		137	31824.55

138	31856.88
139	32004.79
140	32184.96
141	32202.18
142	32215.97
143	32392.04
144	32845.02
145	32851.82
146	32853.22
147	33306.44
148	33845.43
149	33872.77
150	33878.16
151	33980.25
152	35082.76
153	35837.43
154	35909.00
155	36084.68
156	36226.80
157	36924.08
158	37711.23
159	38657.25
160	39757.60
161	40037.00
162	40044.75
163	40060.95
164	41513.72
165	41525.39
166	41530.95
167	41570.22
168	42817.30
169	42823.76
170	42841.33
171	43638.73
172	43943.10
173	43998.28
174	45583.32

175	45585.96
176	45591.20
177	46647.54
178	46651.63
179	46654.09
180	48527.18
181	48542.29
182	48545.60
183	49119.70
184	49443.67
185	50946.93
186	50954.74
187	51007.58
188	51009.18
189	51037.81
190	51044.11
191	51267.09
192	51602.89
193	52743.92
194	52801.45
195	52809.52
196	52914.84
197	53561.49
198	55042.24
199	56080.57
200	56376.33
201	56609.67
202	56629.50
203	56638.82
204	61435.08
205	63372.58
206	67732.00
207	69104.83
208	70486.49
209	87138.37

Table S5. Ab initio ligand field parameters (in cm⁻¹) calculated for of **1** and **2**.

	1	2
	0.0	0.0
	2952.4	795.1
Orbital energies	3300.5	2694.1
	9272.6	5899.7
	11714.8	9152.7
<i>A</i>	133038.2	150332.5
<i>B</i>	660.1	732.8
<i>C</i>	2355.8	2892.0
ζ	152.5	219.8

Cartesian coordinates used in the calculations**1**

V	3.710473	0.002027	4.479564
Si	0.419845	-1.162419	4.366128
Si	2.795542	-2.535308	5.372885
Si	4.151697	2.424705	3.046145
Si	5.302333	0.164809	1.464808
N	2.120532	-1.099625	4.689197
N	4.458707	0.735165	2.835527
C	-0.582591	-0.770596	5.833326
H	-0.356923	0.119003	6.335170
H	-0.530911	-1.444643	6.628189
H	-1.621466	-0.668750	5.750848
C	-0.176570	-0.094507	2.978594
C	0.617005	0.130359	1.884269
H	1.606824	-0.112669	1.984131
C	0.312698	0.984621	0.871398
H	1.071574	1.348154	0.258637
C	-0.856649	1.669233	0.894371
H	-0.945412	2.537658	0.321965
C	-1.690150	1.478263	1.949017
H	-2.427597	2.206921	2.086875
C	-1.354241	0.616872	2.955251
H	-1.893102	0.746961	3.823675
C	-0.009085	-2.879434	3.777946
C	-0.011424	-3.151112	2.425006
H	0.015980	-2.341946	1.780187
C	-0.507964	-4.298563	1.878074
H	-0.808491	-4.315455	0.870615
C	-1.024350	-5.263833	2.685105
H	-1.679167	-5.963369	2.266534
C	-1.083446	-5.030466	4.024400
H	-1.760753	-5.617382	4.571853

C	-0.597196	-3.862704	4.543714
H	-0.966450	-3.621045	5.479979
C	2.813803	-4.041235	4.403232
H	3.028521	-3.967114	3.396382
H	1.927538	-4.572801	4.387347
H	3.483764	-4.780197	4.697399
C	2.078254	-3.033989	7.012469
C	1.698516	-2.101806	7.944357
H	1.825953	-1.111352	7.689556
C	1.553314	-2.370253	9.273377
H	1.566102	-1.585527	9.959654
C	1.795603	-3.618623	9.752486
H	2.035106	-3.746904	10.764928
C	2.160782	-4.585791	8.870175
H	2.622683	-5.435344	9.279711
C	2.285901	-4.290977	7.541059
H	2.849912	-4.972604	7.010461
C	4.597545	-2.082540	5.551171
C	4.978183	-1.017347	6.340961
H	4.240140	-0.420366	6.721946
C	6.253384	-0.535514	6.458625
H	6.429254	0.406994	6.865490
C	7.245890	-1.117274	5.755218
H	8.126877	-0.584482	5.600963
C	6.935274	-2.152948	4.924563
H	7.641128	-2.373816	4.185680
C	5.654816	-2.604071	4.824208
H	5.466530	-3.161929	3.982068
C	3.198264	3.336790	1.799873
H	3.585820	3.450552	0.836384
H	2.963332	4.335113	2.015950
H	2.250100	2.971633	1.576251
C	5.628376	3.497784	3.441539
C	6.691174	2.963607	4.130616
H	6.669170	1.946718	4.280797
C	7.917361	3.549490	4.237817
H	8.755528	2.963414	4.462076
C	8.142505	4.756939	3.657427
H	9.127533	5.054772	3.471480
C	7.129294	5.343233	2.965025
H	7.410481	6.103119	2.290763
C	5.910779	4.723860	2.871941
H	5.317822	5.086392	2.109460
C	3.144645	2.186005	4.566086
C	3.774647	1.938525	5.791833
H	4.760264	2.274012	5.855883
C	3.059882	2.004713	6.977417
H	3.551337	2.284439	7.856382
C	1.718349	2.164048	6.964413
H	1.225314	2.502498	7.820086
C	1.068833	2.302219	5.769020
H	0.114637	2.723647	5.780649
C	1.777842	2.317521	4.614114
H	1.295386	2.672918	3.777983
C	7.071010	0.158776	1.769203
H	7.684530	-0.317737	1.082339

H	7.348734	-0.321114	2.647036
H	7.546302	1.066194	1.874038
C	4.992054	1.378055	0.074291
C	5.805355	2.445153	-0.243765
H	6.751358	2.507271	0.145170
C	5.584871	3.298862	-1.288633
H	6.339617	3.926737	-1.659321
C	4.508440	3.127362	-2.096704
H	4.500854	3.573038	-3.040665
C	3.687428	2.077197	-1.847825
H	3.061627	1.772366	-2.625640
C	3.935866	1.253201	-0.792678
H	3.471716	0.344296	-0.825788
C	4.986772	-1.613339	1.055150
C	3.873089	-2.315843	1.413194
H	3.131432	-1.796078	1.877405
C	3.531558	-3.534684	0.912320
H	2.544087	-3.852352	0.960569
C	4.332478	-4.152463	0.013998
H	3.931431	-4.891481	-0.604413
C	5.477345	-3.522581	-0.349079
H	5.920636	-3.846013	-1.235969
C	5.783309	-2.300721	0.170073
H	6.498382	-1.785077	-0.348342

2

Cr	8.167258	9.975245	3.848392
C	5.991411	7.498539	6.361559
H	5.781966	8.516114	6.518726
H	6.588757	7.311512	7.196446
H	5.090134	7.082533	6.683924
Si	6.694940	7.105927	4.733648
N	8.053091	8.118243	4.499236
N	6.883350	11.385194	4.073372
C	5.389586	7.489592	3.485351
Si	9.527191	7.612236	3.852717
Si	6.330677	12.070102	2.621571
C	4.268990	8.244602	3.740545
H	3.992780	8.425310	4.716496
Si	6.718960	12.123187	5.599563
C	3.291980	8.476198	2.817684
H	2.356292	8.837563	3.109612
C	3.371122	7.926690	1.579365
H	2.510465	7.848479	0.998360

C	7.196597	10.981180	1.392200
C	4.424197	7.118599	1.304419
H	4.337732	6.471764	0.492129
C	5.395119	6.923958	2.235628
H	6.009380	6.117777	2.073372
C	7.104289	5.264086	4.588646
C	8.017676	14.322495	2.665475
H	8.746728	13.614497	2.761195
C	6.213684	4.267285	4.225821
H	5.211667	4.491957	4.131801
C	10.311176	9.183905	3.275788
C	7.638906	2.483515	4.850589
H	7.725439	1.497687	5.195916
C	8.534640	3.415057	5.271783
H	9.286623	3.082697	5.923942
C	9.298093	13.040233	6.355069
H	8.964270	13.986684	6.131817
C	8.253840	4.747292	5.151483
H	8.802707	5.346303	5.785838
C	4.348561	10.667202	6.028690
H	4.070760	11.007440	5.100338
C	9.516873	6.524382	2.429144
H	8.930095	6.799085	1.619509
H	9.220976	5.545454	2.570840
H	10.438035	6.391239	1.967128
C	8.396188	12.007912	6.332619
C	10.837805	7.096423	5.016389
C	10.856846	7.569864	6.298281
H	10.006988	8.033853	6.641567
C	11.820354	6.191051	4.719334
H	11.710901	5.604567	3.882601
C	12.731592	5.759827	5.634101
H	13.224720	4.851109	5.488755
C	5.899774	14.852634	1.982457
H	5.009524	14.593065	1.542294
C	11.760228	7.165495	7.226730
H	11.539158	7.291377	8.235103
C	10.559073	9.531970	1.972417

H	10.018187	9.065003	1.237830
C	5.520151	11.119284	6.585827
C	11.604634	11.543647	2.589297
H	11.785333	12.529499	2.336774
C	10.745126	10.097645	4.206997
H	10.432698	9.985996	5.174524
C	11.370084	11.260003	3.888310
H	11.412900	12.028627	4.583391
C	6.216336	13.890170	5.564869
H	6.864907	14.567123	5.087954
H	6.073233	14.406630	6.469396
H	5.320295	14.148667	5.080964
C	4.529812	12.034102	2.418647
H	4.111760	12.347055	1.513982
H	3.962451	12.610546	3.085396
H	4.067298	11.112710	2.531602
C	9.988266	10.792315	7.662252
H	10.111726	10.065320	8.396244
C	6.881172	9.634799	1.318484
H	6.048420	9.290761	1.824571
C	7.321648	8.812123	0.318694
H	6.834253	7.905815	0.124548
C	8.441686	15.590329	2.427698
H	9.457319	15.781985	2.303397
C	8.454047	10.614687	-0.630925
H	8.784433	11.041781	-1.521360
C	8.004468	11.416700	0.374899
H	8.027095	12.426655	0.192173
C	3.358417	10.048755	6.730358
H	2.400997	9.932730	6.326408
C	6.741531	13.873650	2.458339
C	6.450056	2.921832	4.356719
H	5.666292	2.213109	4.344471
C	8.802944	10.884157	7.003717
H	8.084463	10.196155	7.257213
C	7.568040	16.520498	1.971806
H	7.938555	17.380682	1.518263
C	8.121379	9.299521	-0.666655

H	8.191235	8.785080	-1.574664
C	10.851479	11.837444	7.655666
H	11.581982	11.887487	8.393453
C	4.609537	10.322930	8.673277
H	4.557394	10.453580	9.706147
C	10.496144	12.970544	6.998921
H	11.005996	13.845545	7.249267
C	5.580730	10.941234	7.945983
H	6.219298	11.538510	8.487761
C	6.286981	16.140319	1.739852
H	5.720154	16.773011	1.125460
C	3.495853	9.847068	8.063124
H	2.650945	9.640279	8.634588
C	11.197358	10.676974	1.627788
H	11.076261	11.056047	0.669297
C	12.710881	6.256443	6.896102
H	13.171094	5.715854	7.654027

References

- (1) ADF2019. SCM, Theoretical Chemistry, Vrije Universiteit Amsterdam, The Netherlands 2019.
- (2) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. Chemistry with ADF. *J. Comput. Chem.* **2001**, *22*, 931–967.
- (3) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. Towards an Order-N DFT Method. *Theor. Chem. Acc.* **1998**, *99*, 391–403.
- (4) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (5) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)]. *Phys. Rev. Lett.* **1997**, *78*, 1396.
- (6) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
- (7) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- (8) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. Relativistic Regular Two-component Hamiltonians. *J. Chem. Phys.* **1993**, *99*, 4597–4610.
- (9) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. Relativistic Total Energy Using Regular Approximations. *J. Chem. Phys.* **1994**, *101*, 9783–9792.
- (10) van Lenthe, E.; van Leeuwen, R.; Baerends, E. J.; Snijders, J. G. Relativistic Regular Two-Component Hamiltonians. *Int. J. Quantum Chem.* **1996**, *57*, 281–293.
- (11) Van Lenthe, E.; Baerends, E. J. Optimized Slater-Type Basis Sets for the Elements 1–118. *J. Comput. Chem.* **2003**, *24*, 1142–1156.
- (12) Roos, B. O. The Complete Active Space Self-Consistent Field Method and Its Applications in Electronic Structure Calculations. *Advances in Chemical Physics*. January 1, 1987, pp 399–445.
- (13) Siegbahn, P.; Heiberg, A.; Roos, B.; Levy, B. A Comparison of the Super-CI and the Newton-Raphson Scheme in the Complete Active Space SCF Method. *Phys. Scr.* **1980**, *21*, 323–327.
- (14) Roos, B. O.; Taylor, P. R.; Sigbahn, P. E. M. A Complete Active Space SCF Method (CASSCF) Using a Density Matrix Formulated Super-CI Approach. *Chem. Phys.* **1980**, *48*, 157–173.
- (15) Siegbahn, P. E. M.; Almlöf, J.; Heiberg, A.; Roos, B. O. The Complete Active Space

- SCF (CASSCF) Method in a Newton–Raphson Formulation with Application to the HNO Molecule. *J. Chem. Phys.* **1981**, *74*, 2384–2396.
- (16) Angeli, C.; Cimiraglia, R.; Evangelisti, S.; Leininger, T.; Malrieu, J.-P. Introduction of N-Electron Valence States for Multireference Perturbation Theory. *J. Chem. Phys.* **2001**, *114*, 10252–10264.
- (17) Angeli, C.; Cimiraglia, R.; Malrieu, J.-P. N-Electron Valence State Perturbation Theory: A Fast Implementation of the Strongly Contracted Variant. *Chem. Phys. Lett.* **2001**, *350*, 297–305.
- (18) Angeli, C.; Cimiraglia, R.; Malrieu, J.-P. N-Electron Valence State Perturbation Theory: A Spinless Formulation and an Efficient Implementation of the Strongly Contracted and of the Partially Contracted Variants. *J. Chem. Phys.* **2002**, *117*, 9138–9153.
- (19) Lang, L.; Sivalingam, K.; Neese, F. The Combination of Multipartitioning of the Hamiltonian with Canonical Van Vleck Perturbation Theory Leads to a Hermitian Variant of Quasidegenerate N-Electron Valence Perturbation Theory. *J. Chem. Phys.* **2020**, *152*, 14109.
- (20) Angeli, C.; Borini, S.; Cestari, M.; Cimiraglia, R. A Quasidegenerate Formulation of the Second Order N-Electron Valence State Perturbation Theory Approach. *J. Chem. Phys.* **2004**, *121*, 4043–4049.
- (21) Neese, F.; Petrenko, T.; Ganyushin, D.; Olbrich, G. Advanced Aspects of Ab Initio Theoretical Optical Spectroscopy of Transition Metal Complexes: Multiplets, Spin-Orbit Coupling and Resonance Raman Intensities. *Coord. Chem. Rev.* **2007**, *251*, 288–327.
- (22) Atanasov, M.; Aravena, D.; Suturina, E.; Bill, E.; Maganas, D.; Neese, F. First Principles Approach to the Electronic Structure, Magnetic Anisotropy and Spin Relaxation in Mononuclear 3d-Transition Metal Single Molecule Magnets. *Coord. Chem. Rev.* **2015**, *289–290*, 177–214.
- (23) Neese, F. Efficient and Accurate Approximations to the Molecular Spin-Orbit Coupling Operator and Their Use in Molecular g-Tensor Calculations. *J. Chem. Phys.* **2005**, *122*, 34107.
- (24) Berning, A.; Schweizer, M.; Werner, H.-J.; Knowles, P. J.; Palmieri, P. Spin-Orbit Matrix Elements for Internally Contracted Multireference Configuration Interaction Wavefunctions. *Mol. Phys.* **2000**, *98*, 1823–1833.
- (25) Heß, B. A.; Marian, C. M.; Wahlgren, U.; Gropen, O. A Mean-Field Spin-Orbit Method Applicable to Correlated Wavefunctions. *Chem. Phys. Lett.* **1996**, *251*, 365–371.
- (26) Maurice, R.; Bastardis, R.; Graaf, C. de; Suaud, N.; Mallah, T.; Guihéry, N. Universal Theoretical Approach to Extract Anisotropic Spin Hamiltonians. *J. Chem. Theory Comput.* **2009**, *5*, 2977–2984.
- (27) Neese, F. Software Update: The ORCA Program System, Version 4.0. *WIREs Comput.*

Mol. Sci. **2018**, *8*, e1327.

- (28) Neese, F.; Wennmohs, F.; Becker, U.; Ripplinger, C. The ORCA Quantum Chemistry Program Package. *J. Chem. Phys.* **2020**, *152*, 224108.
- (29) Douglas, M.; Kroll, N. M. Quantum Electrodynamical Corrections to the Fine Structure of Helium. *Ann. Phys.* **1974**, *82*, 89–155.
- (30) Hess, B. A. Relativistic Electronic-Structure Calculations Employing a Two-Component No-Pair Formalism with External-Field Projection Operators. *Phys. Rev. A* **1986**, *33*, 3742–3748.
- (31) Pantazis, D. A.; Chen, X.-Y.; Landis, C. R.; Neese, F. All-Electron Scalar Relativistic Basis Sets for Third-Row Transition Metal Atoms. *J. Chem. Theory Comput.* **2008**, *4*, 908–919.
- (32) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- (33) Stoychev, G. L.; Auer, A. A.; Neese, F. Automatic Generation of Auxiliary Basis Sets. *J. Chem. Theory Comput.* **2017**, *13*, 554–562.