# SUPPORTING INFORMATION

Neutral Bis(1,4-diaza-1,3-butadiene)nickel Complexes and the Corresponding Monocations: Molecular and Electronic Structures. A Combined Experimental and Density Functional Theoretical Study

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DFT, BS(2,2), M_s = 0, B3LYP, Spin-unrestricted Kohn-Sham Functional
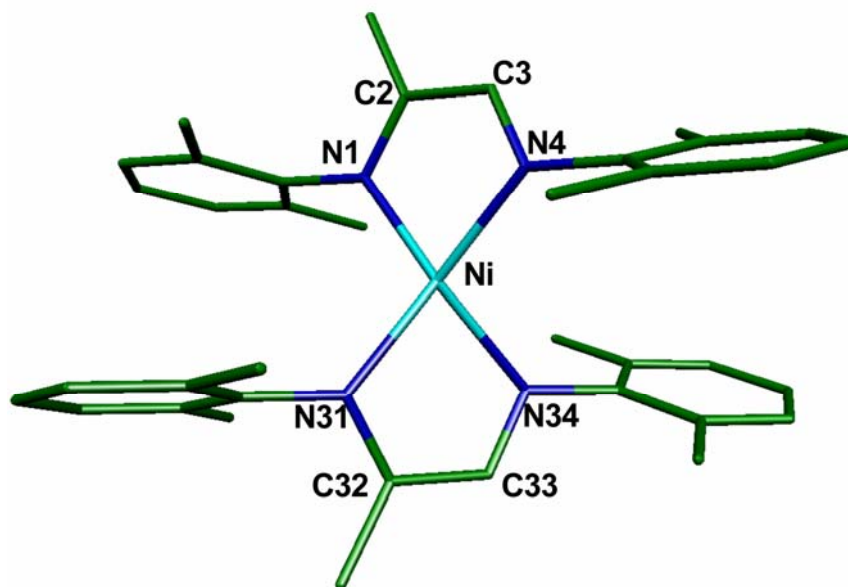
Bond Lengths

	$[Ni^{II}(^1L^{\bullet})_2]$ Expt.	$[Ni^{II}(^1L^{\bullet})_2]$ Calcd.
Ni1-N1	1.9475(14)	2.060
Ni1-N4	1.9206(14)	2.032
Ni1-N31	1.9483(14)	2.046
Ni1-N34	1.9276(14)	2.043
N1-C2	1.337(2)	1.325
C2-C3	1.438(2)	1.420
C3-N4	1.330(2)	1.324
N31-C32	1.338(2)	1.336
C32-C33	1.397(2)	1.420
C33-N34	1.330(2)	1.324
Dihedral angle	**47.9°**	**47°**

Spin Density Map
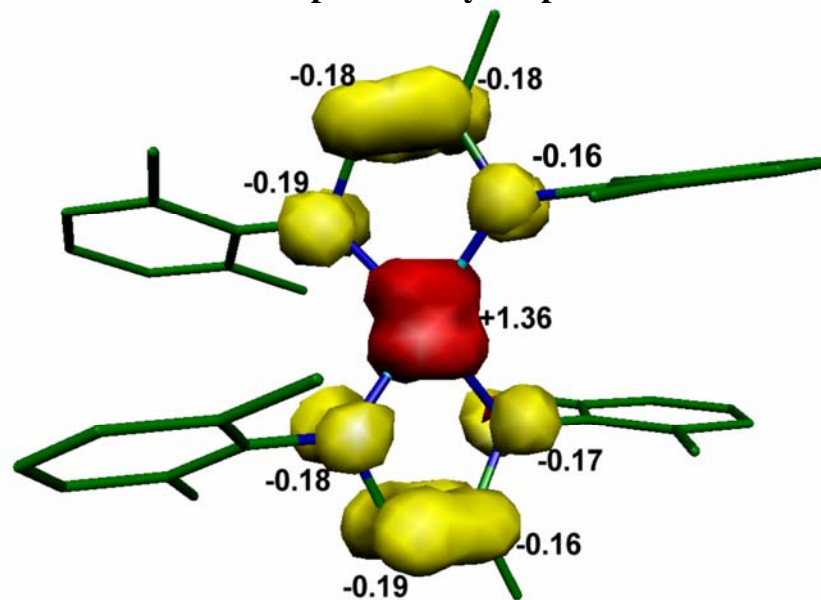
Mulliken Population Analysis

Ni	1.357906
N31	-0.166702
C32	-0.163077
C33	-0.192871
N34	-0.177246
N1	-0.155882
C2	-0.178488
C3	-0.175277
N4	-0.187957

Qualitative MO scheme
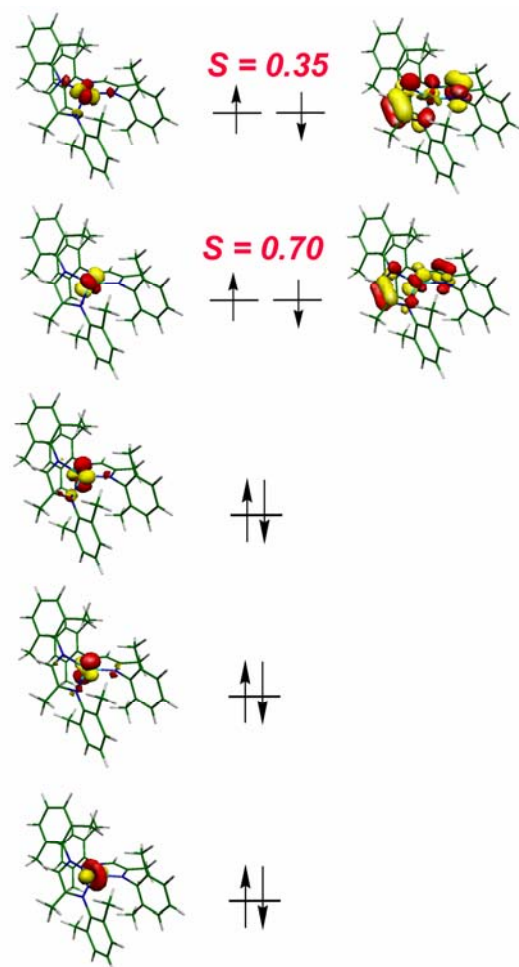
2

DFT, S = 1/2, B3LYP, Spin-unrestricted Kohn-Sham Functional
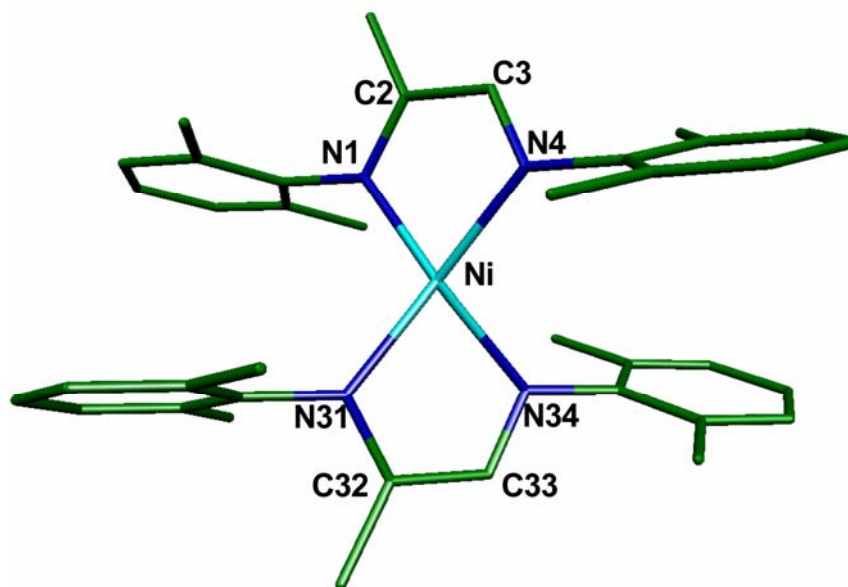
Bond Lengths

	$[Ni^I(^1L^{Ox})_2]^{1+}$ Calcd.
Ni1-N1	2.095
Ni1-N4	2.086
Ni1-N31	2.088
Ni1-N34	2.093
N1-C2	1.297
C2-C3	1.474
C3-N4	1.288
N31-C32	1.297
C32-C33	1.474
C33-N34	1.288
Dihedral angle	**38°**

Spin Density Map
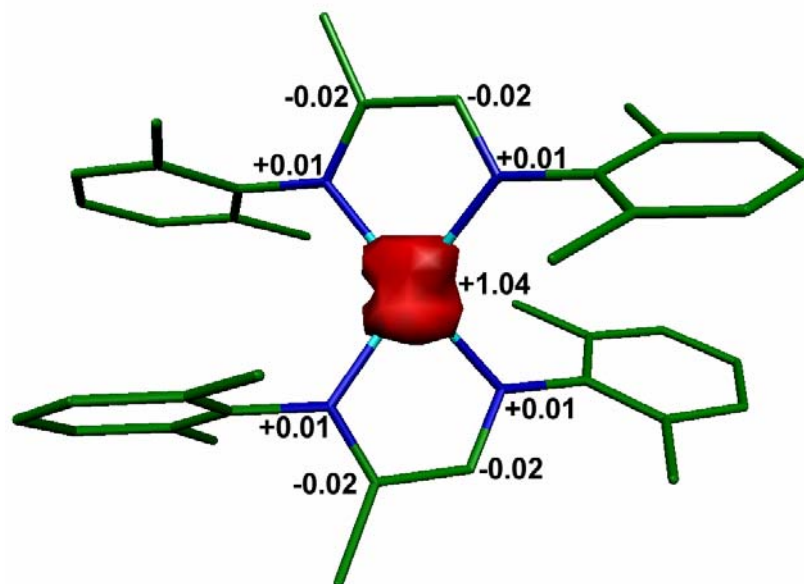
Mulliken Population Analysis

Ni	1.035113
N31	0.013322
C32	-0.020746
C33	-0.023622
N34	0.011501
N1	0.015177
C2	-0.022630
C3	-0.019507
N4	0.010308

Qualitative MO scheme
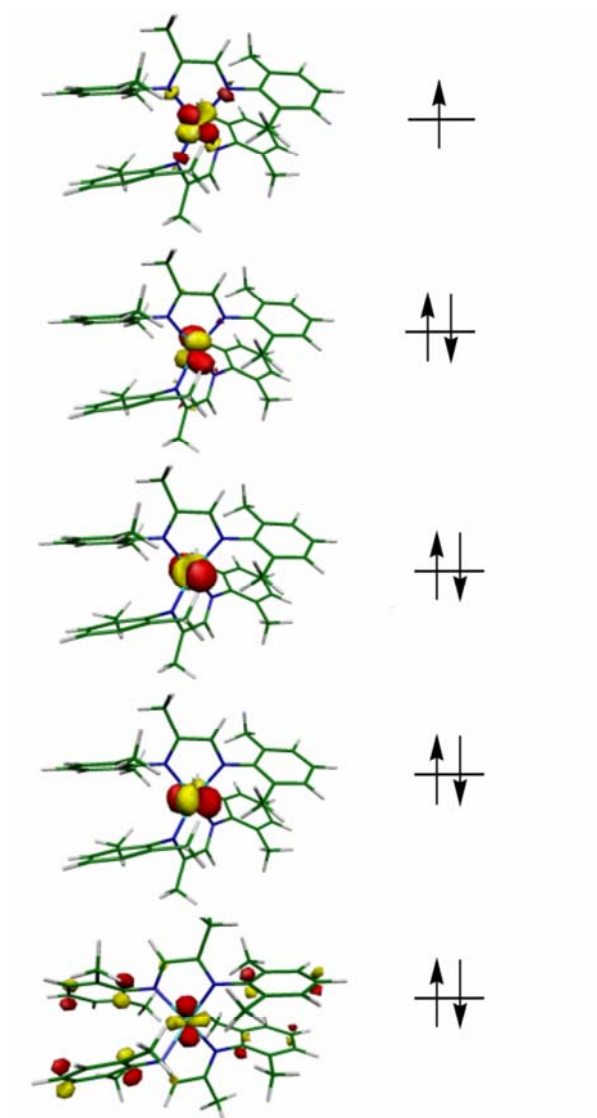
g values (B3LYP)

	g_x	g_y	g_z
Expt.	2.040	2.10	2.26
Calcd.	2.067	2.182	2.271

DFT, BS(2,2), M_s = 0, B3LYP, Spin-unrestricted Kohn-Sham Functional
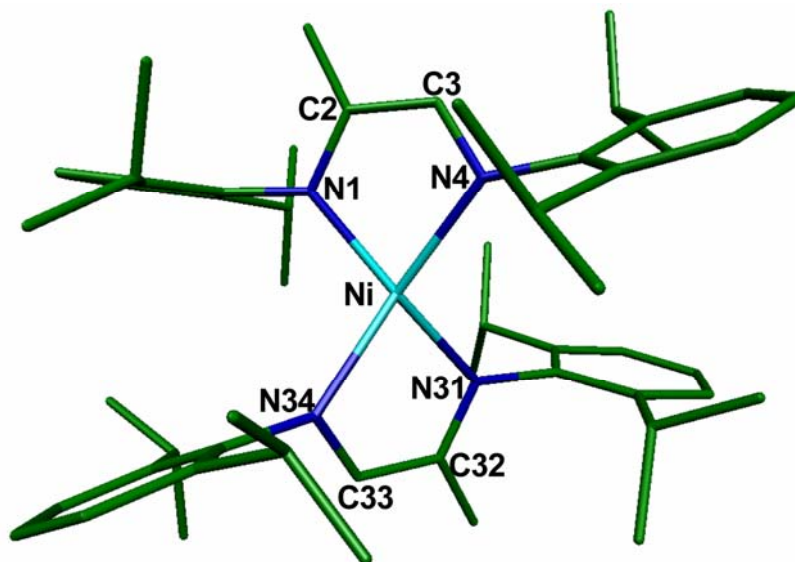
Bond Lengths

|	$[Ni^{II}(^2L^{\bullet})_2]$ Expt.	$[Ni^{II}(^2L^{\bullet})_2]$ Calcd.
Ni1-N1	1.963(2)	2.046
Ni1-N4	1.999(2)	2.140
Ni1-N31	1.967(2)	2.046
Ni1-N34	1.978(2)	2.141
N1-C2	1.327(2)	1.339
C2-C3	1.402(4)	1.419
C3-N4	1.326(2)	1.322
N31-C32	1.340(2)	1.340
C32-C33	1.396(2)	1.418
C33-N34	1.326(3)	1.323
Dihedral angle	**53°**	**52°**

Spin Density Map
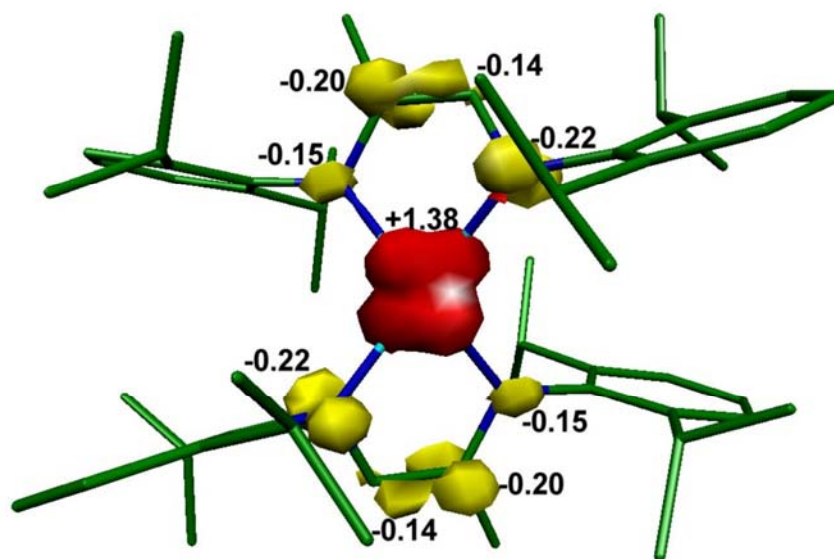
Mulliken Population Analysis

Ni	1.389523
N31	-0.147378
N34	-0.219586
C32	-0.197509
C33	-0.144818
N1	-0.147056
C2	-0.197715
C3	-0.144763
N4	-0.219586

Qualitative MO scheme
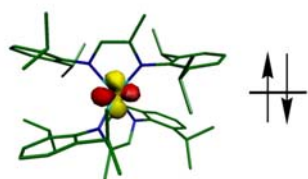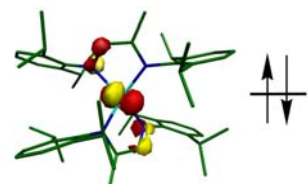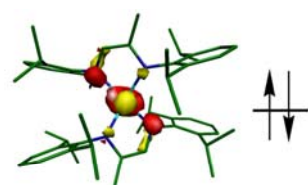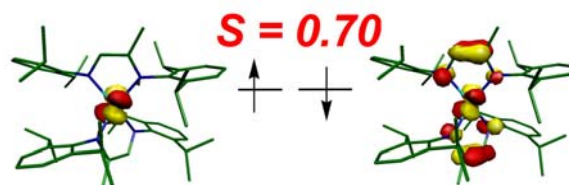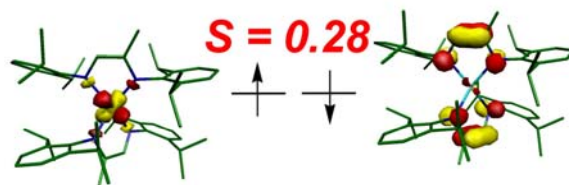
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DFT, S = 1/2, B3LYP, Spin-unrestricted Kohn-Sham Functional
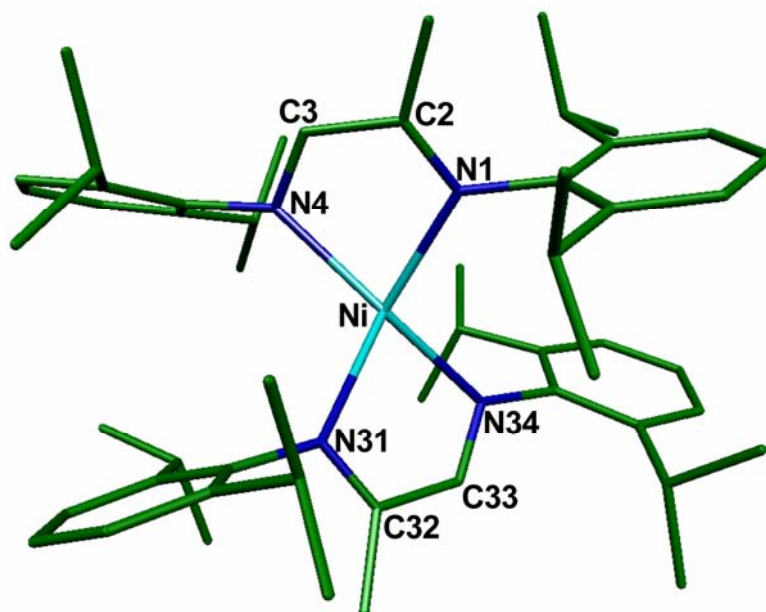
Bond Lengths

	$[\text{Ni}^{I}(^{2}\text{L}^{\text{Ox}})_{2}]^{1+}$ Calcd.
Ni1-N1	2.144
Ni1-N4	2.212
Ni1-N31	2.159
Ni1-N34	2.191
N1-C2	1.292
C2-C3	1.476
C3-N4	1.280
N31-C32	1.294
C32-C33	1.474
C33-N34	1.281
Dihedral angle	**46°**

Spin Density Map
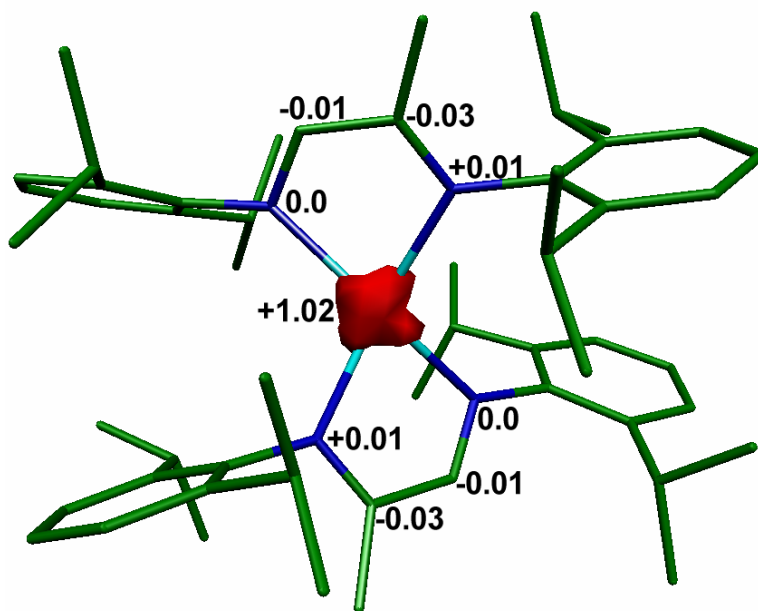
Mulliken Population Analysis

Ni	1.023380
N31	0.014772
N34	0.004864
C32	-0.027899
C33	-0.012482
N1	0.016682
C2	-0.031362
C3	-0.009171
N4	0.000689

Qualitative MO scheme
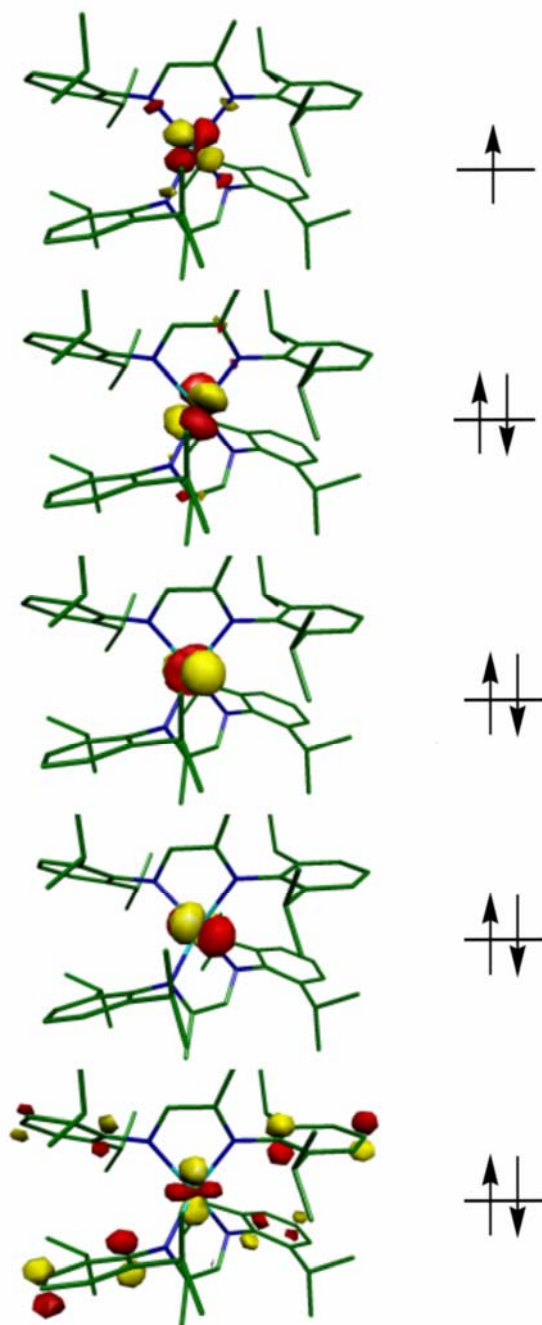
g values (B3LYP)

	g_x	g_y	g_z
Expt.	2.109	2.171	2.258
Calcd	2.095	2.181	2.258

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DFT, S = 1, B3LYP, Spin-unrestricted Kohn-Sham Functional
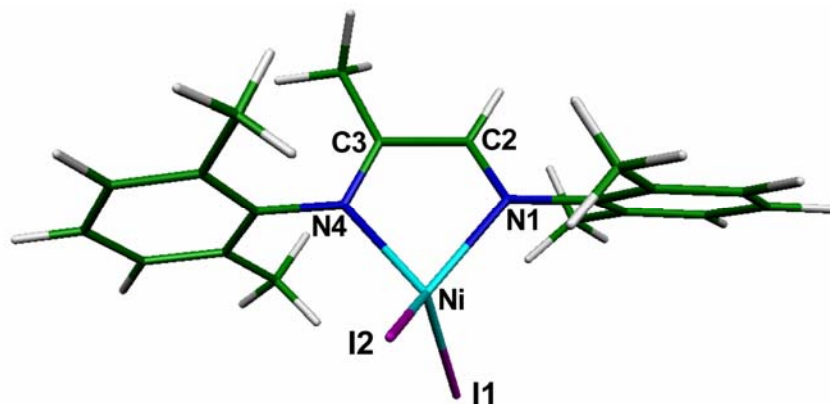
Bond Lengths

	Expt.	Calcd.
Ni1 N1	1.996(16)	2.077
Ni1 N4	2.008(14)	2.080
Ni1 I2	2.471(3)	2.564
Ni1 I1	2.542(3)	2.578
N1 C2	1.28(2)	1.281
C2 C3	1.46(3)	1.470
C3 N4	1.30(2)	1.290

Spin Density Map

+0.06   +0.06

+1.62
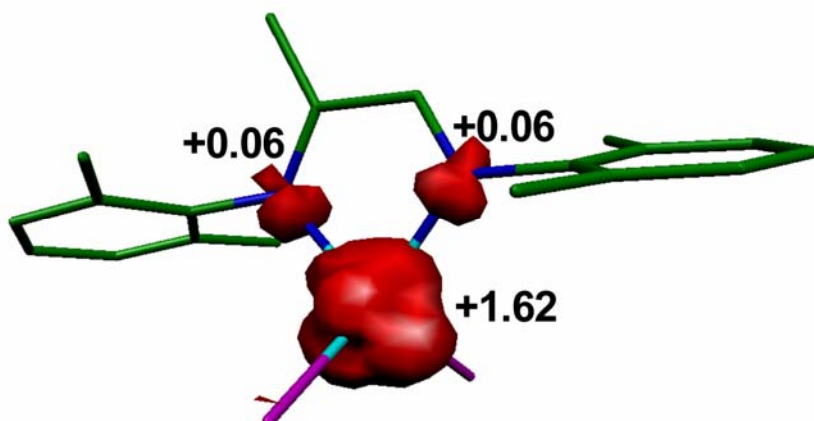
Mulliken Population Analysis

Ni	1.619093
I1	0.130684
I1	0.125165
N4	0.063216
C3	-0.016020
C2	-0.012576
N1	0.056251

Qualitative MO Scheme