Table 1S. Geometry Comparison: $Ni(TRISOXH_3)Cl_2$ Crystal Structure to results from calculations **E-G**

Feature[a]	Crystal Structure Data[b]	**E** ub3lyp/ 6-31G(d)	**F** ub3lyp/ 6-31G(d) &6-311G	**G** ub3p86/ 6-31G(d)& 6-311+G(d)
Symmetry	N/A	C_1	C_1	C_S
Ni-N1[d]	2.1131(13)	2.1666	2.1525	2.1138
Ni-N(a)	2.0367(14)	2.0194	2.0306	2.0042
Ni-N(b)	2.0485(14)	2.1093	2.1106	2.0741
Ni-N(c)	*2.0957(14)**	2.0195	2.0304	2.0042
Ni-Cl(axial)	2.4003(4)	2.4266	2.4143	2.3928
Ni-Cl(eq)	2.4344(4)	2.4105	2.3973	2.3689
C=N(a)	1.274(2)	1.2808	1.2814	1.2795
C=N(b)	1.273(2)	1.278	1.2786	1.2767
C=N(c)	1.280(2)	1.2808	1.2814	1.2795
N(a)-O	1.3921(18)	1.3756	1.3745	1.3613
N(b)-O	1.3952(17)	1.3706	1.3702	1.3575
N(c)-O	1.4022(17)	1.3756	1.3745	1.3613
H(a)•••Cl(axial) [f]	2.502	2.315	2.6410	2.5491
H(b)•••Cl(axial)	2.353	2.1107	2.1274	2.0843
H(c)•••Cl(axial)	*3.601*	2.315	2.6390	2.5491
∠O-N(a)-Ni	125.99(11)	125.33	126.08	125.44
∠O-N(b)-Ni	125.08(10)	124.98	125.42	125.58
∠O-N(c)-Ni	*129.26(10)*	125.32	126.06	125.44
∠N(a)-Ni-N1	79.65(5)	80.01	80.61	81.44
∠N(b)-Ni-N1	80.54(5)	78.61	79.3	80.11
∠N(c)-Ni-N1	*77.90(5)*	80.01	80.64	81.44
∠Cl(eq)-Ni-N1	94.27(4)	92.47	92.33	92.14
∠Cl(ax)-Ni-Cl(eq)	*96.620(15)*	103.12	102.45	101.89
∠N(a)-Ni-Cl(eq)	*92.27(4)*	99.90	99.42	98.58
∠N(b)-Ni-Cl(eq)	*88.40(4)*	85.79	85.92	85.86
∠N(c)-Ni-Cl(eq)	*110.68(4)*	99.88	99.39	98.58
∠Cl(eq)-Ni-N(a)	90.08(4)	89.43	89.03	89.21
∠N(a)-Ni-N(b)	88.18(6)	89.01	89.59	89.63
∠N(b)-Ni-N(c)	*92.80(6)*	89.02	89.56	89.63
∠N(c)-Ni-Cl(eq)	*86.88(4)*	89.43	89.07	89.21

[a] All bond distances shown in Angstroms, bond angles (∠) in degrees. [b] See reference (10) [c] Theoretical models A-F are listed with theory level and basis sets; for those with 2 sets listed, the 1st set was applied to C,N,H,O,Cl and the 2nd to Ni. [d] Letter designations on atoms have the following meaning: N1 represents the amine, N(a) and N(c) are oxime bound N's trans to each other – equivalent in calculations with C_s symmetry, N(b) is the oxime bound N trans to the equatorial Cl^- (denoted Cl(eq)), Cl(axial) is trans to the amine, and H(a) is the proton on the oxygen of oxime with N(a) and similarly for H(b) and H(c). [e] Absolute deviations of calculated values from experimental data are given in parentheses. [f] ••• indicates hydrogen bonding and/or through space distances. * Italicized experimental values and theoretical deviations indicate those which are perturbed by intermolecular hydrogen bonding.

Table 2S: Complete list of 105 vibrational modes calculated with level **C** (B3LYP/6-31g(d) & 6-311+G(d)).

Mode Number	Mode Letter[a]	Sym	Unscaled Frequency[b]	Scaled Frequency	Mode Number	Mode Letter	Sym	Unscaled Frequency	Scaled Frequency
1		A"	44.2	95.5	54		A'	1068.9	1036.8
2		A'	45.2	96.5	55		A"	1073.8	1041.3
3		A"	47.9	98.9	56	**n**	A"	1116.4	1080.4
4		A'	62.4	112.3	57		A'	1123.9	1087.3
5		A"	63.7	113.4	58	**o**	A'	1137.0	1099.3
6		A"	69.1	118.4	59	**p**	A'	1146.9	1108.5
7		A"	85.6	133.5	60	**q**	A"	1152.5	1113.6
8		A"	93.7	141.0	61	**r**	A"	1253.9	1206.7
9		A'	103.2	149.7	62	**s**	A'	1258.8	1211.2
10		A'	117.8	163.1	63	**t**	A'	1267.0	1218.8
11		A"	131.3	175.6	64		A"	1285.4	1235.7
12		A'	140.6	184.1	65	**u**	A"	1343.3	1288.9
13		A"	158.4	200.4	66	**v**	A'	1347.6	1292.8
14		A'	169.7	210.8	67		A"	1388.4	1330.3
15		A'	197.9	236.7	68		A'	1404.9	1345.4
16		A'	219.2	256.3	69		A'	1433.8	1372.0
17		A'	240.5	275.8	70		A'	1434.3	1372.4
18		A"	243.4	278.5	71		A"	1434.5	1372.7
19		A'	256.5	290.5	72		A'	1437.4	1375.3
20		A"	268.8	301.8	73		A"	1472.4	1407.4
21		A'	274.4	307.0	74		A'	1476.3	1411.1
22		A'	282.5	314.4	75		A"	1485.0	1419.1
23		A"	288.7	320.1	76		A'	1496.2	1429.3
24		A"	299.8	330.3	77		A"	1501.8	1434.5
25		A'	305.0	335.0	78		A'	1506.9	1439.1
26		A"	317.6	346.7	79		A'	1511.5	1443.4
27		A'	329.0	357.1	80		A"	1513.6	1445.3
28	**a**	A'	369.8	394.6	81		A"	1515.7	1447.2
29	**b**	A"	387.1	410.5	82		A'	1517.2	1448.6
30		A'	387.8	411.2	83		A'	1519.1	1450.3
31	**c**	A'	460.5	477.9	84		A'	1540.5	1470.0
32	**d**	A'	486.4	501.8	85	**w**	A"	1764.4	1675.7
33		A"	487.4	502.6	86	**x**	A'	1766.6	1677.7
34	**e**	A'	523.7	535.9	87	**y**	A'	1777.5	1687.7
35	**f**	A"	524.7	536.9	88		A"	3021.5	2830.5
36		A"	559.8	569.1	89		A'	3021.4	2830.3
37		A"	563.2	572.3	90		A'	3028.8	2837.2
38		A'	575.9	583.9	91		A"	3049.3	2856.0
39		A'	678.0	677.7	92		A'	3049.4	2856.1
40		A"	688.0	686.9	93		A"	3058.5	2864.5
41		A'	691.4	690.1	94		A'	3058.5	2864.5
42		A"	755.3	748.7	95		A"	3101.1	2903.6
43	**g**	A"	849.7	835.5	96		A'	3101.5	2904.0
44	**h**	A'	864.7	849.2	97		A"	3101.8	2904.2
45	**I**	A'	884.6	867.5	98		A'	3108.4	2910.2
46	**j**	A'	894.8	876.9	99		A"	3119.0	2920.0
47		A"	922.6	902.4	100		A'	3141.4	2940.6
48		A"	942.3	920.5	101		A"	3178.0	2974.2
49	**k**	A'	962.0	938.6	102		A'	3178.0	2974.2
50		A"	1007.3	980.2	103	**z**	A'	3304.2	3090.1
51		A'	1014.6	986.9	104	**aa**	A"	3566.0	3330.7
52	**l**	A'	1023.9	995.4	105	**bb**	A'	3579.4	3343.0
53	**m**	A"	1053.8	1022.9					

[a]Mode letters are given only for the assigned modes. [b]All frequencies given in units of wavenumbers.

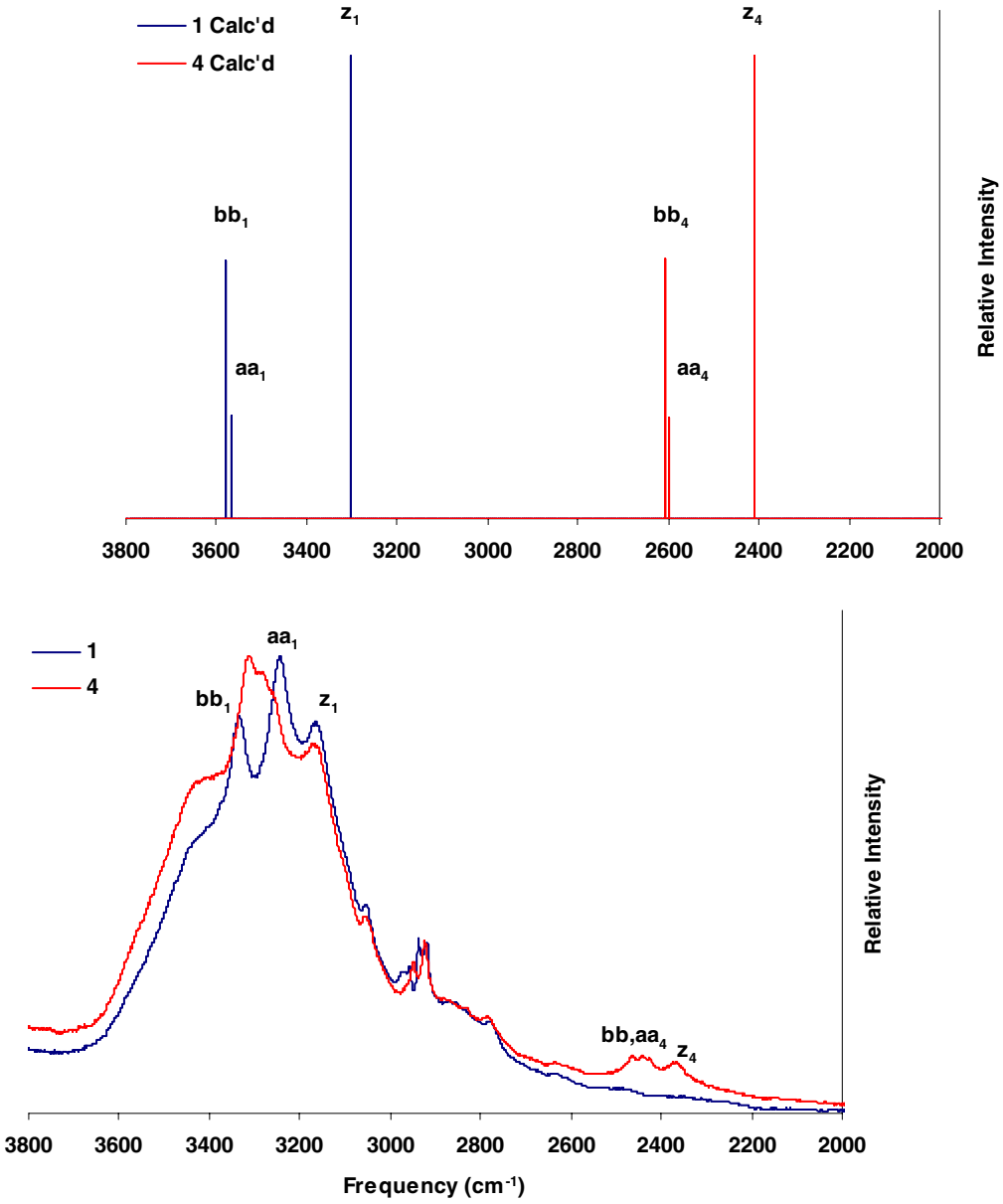

Figure 1S. Infrared Spectra and Theoretical Frequencies for **1** and **4**, 1900-3800 cm^{-1}. A significant portion of **4** remains undeuterated, however the presence of 3 peaks around 2400 cm^{-1} allows vibrational mode assignment.