

**Experimental Charge Density Study on the Ni(II) Coordination Complex
[Ni(H₃L)][NO₃][PF₆] [H₃L = N,N',N''-Tris(2-hydroxy-3-methylbutyl)-1,4,7-triazacyclononane : A Reappraisal.**

L. J. Farrugia,^{*a} C. S. Frampton,^a J. A. K. Howard,^b P. R. Mallinson,^a R. D. Peacock,^a G. T. Smith,^a and B. Stewart.^b

SUPPLEMENTARY MATERIALS

Details of corrections to XD code

A number of major corrections, bug-fixes and improvements have been made since the last official release of XD (Rev 14, 1999)

- The exponents of $3d$ and $4s$ orbitals were interchanged by XDPROP when computing a default single-zeta exponent for the multipoles (option CSZD for DEFV in the SCAT Table). This error could cause severe problems in the topology, but it was quite easily detectable by a simple *check option in the output of XDPROP
- The same occurred for ns and $(n-1)s/p$ for some closed-shell cations.
- The default radial exponent for fourth-row atoms was $n_l = 4$ instead of $n_l = 6$ (in both XDLSM and XDPROP)
- The configuration of the SCAT table was not read by XDPROP and the default configuration (stored in the databank) was always applied.
- When computing the radial function for multipoles with an orbitalic product (option CHFW for DEFV), the normalisation of the spherical harmonics was applied twice in XDPROP. This error gave rise to underestimated deformations around the atom. Because it was mainly adopted for describing $3d$ orbitals of transition metals, its effect was to reduce the polarisation of the inner valence shell, without affecting too seriously the density in the region of the bonding and the overall topology. Again, only the default valence orbitals were used, despite any different request by the user.
- The option GROUP atoms was not applied when computing the electrostatic potential (esp).
- Molecular quadrupole moments had an incorrect unit transformation.
- Molecular dipole and quadrupole calculations did not support the CHFW option for radial functions.
- The anisotropic extinction refinement has been corrected (and a bug concerning interpretation of the wavelength has been removed - see Section 4.6.8 for more details)
- Symmetry operations 6_1 and 6_5 were not properly supported.
- U factors for H atoms were erroneously transformed by XDINI from SHELX input if restraints were present.
- In the presence of atoms in special positions, XDPROP had some problems in correctly reproducing all the atoms requested by users through the APPLY symm option.

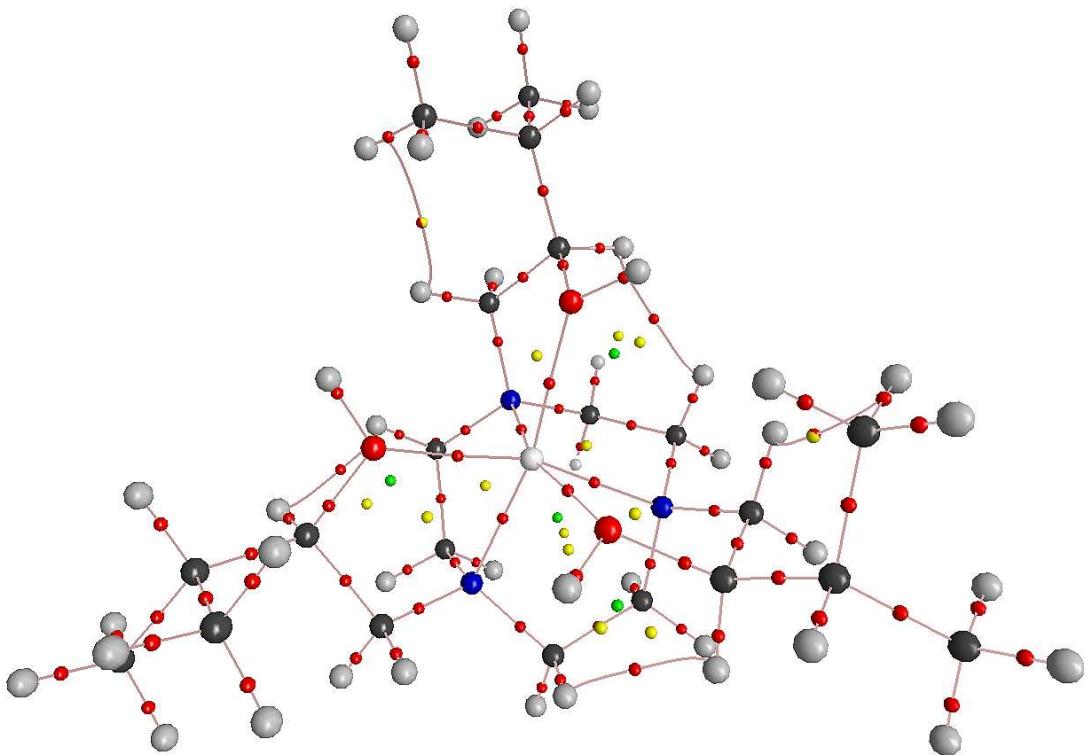


Figure S1 Molecular graph for the cation in **1** from the DFT density, with critical points shown as small spheres. Colour coding for cp's is (3,-1) bcp red, (3,+1) rcp yellow, (3,+3) ccp green.

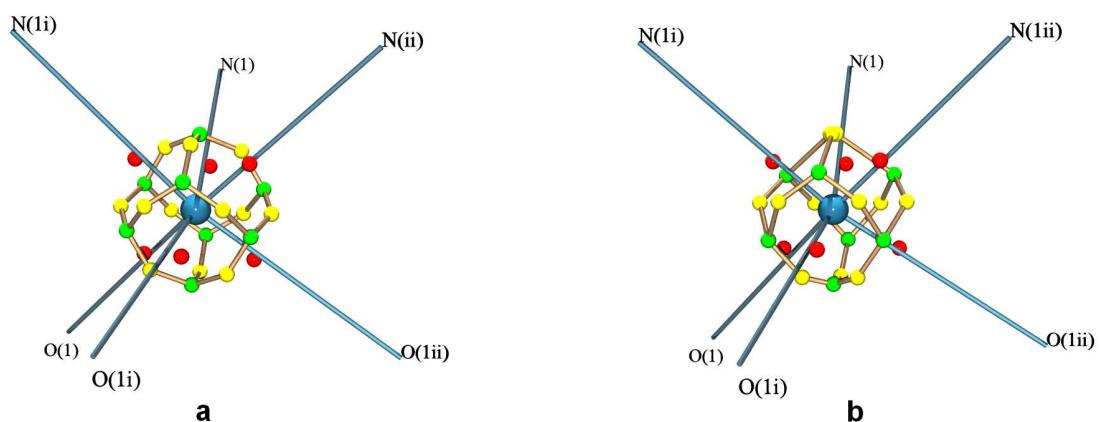


Figure S2 Atomic graph of the Ni atom in **1** from (a) theoretical data (b) experimental data, showing the critical points in $L(\mathbf{r}) \equiv -\nabla^2\rho(\mathbf{r})$ in the VSCC. Color coding for the cp's is (3,-3) green, (3,-1) yellow, (3,+1) red. The blue vectors show the directions of the bonded atoms, not the bond paths.

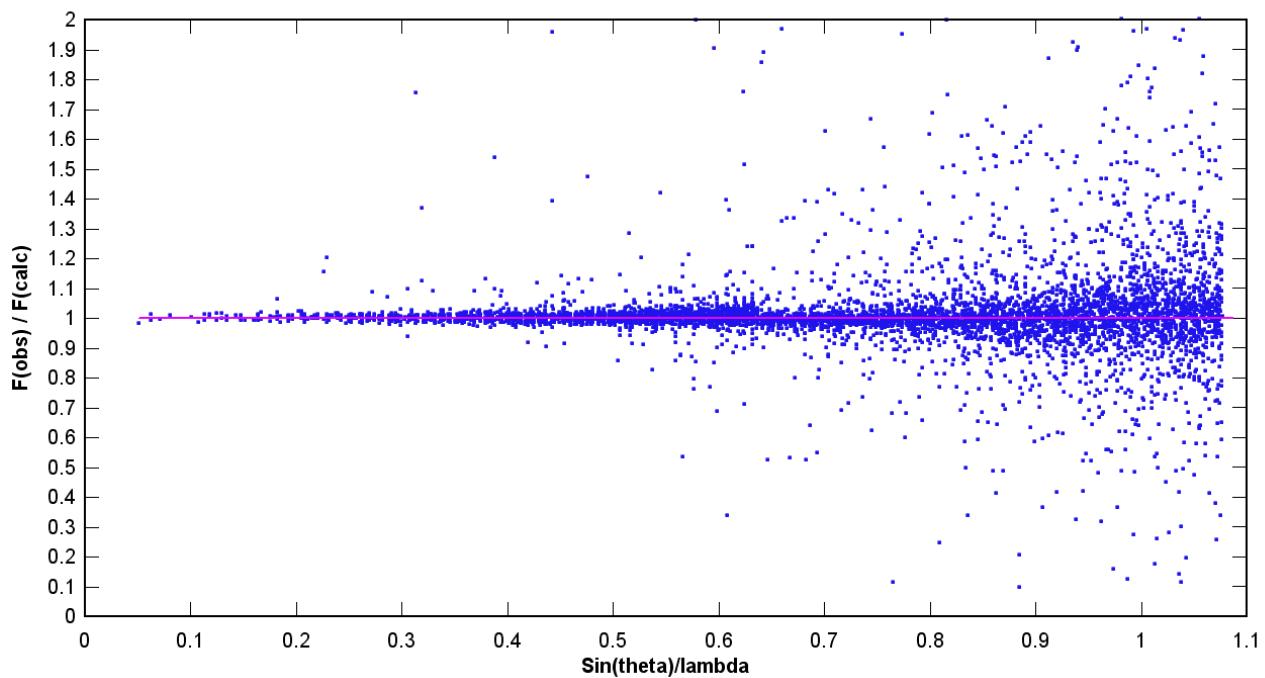


Figure S3. Scatter plot of individual scale factors versus $\sin\theta/\lambda$ from the multipole refinement.

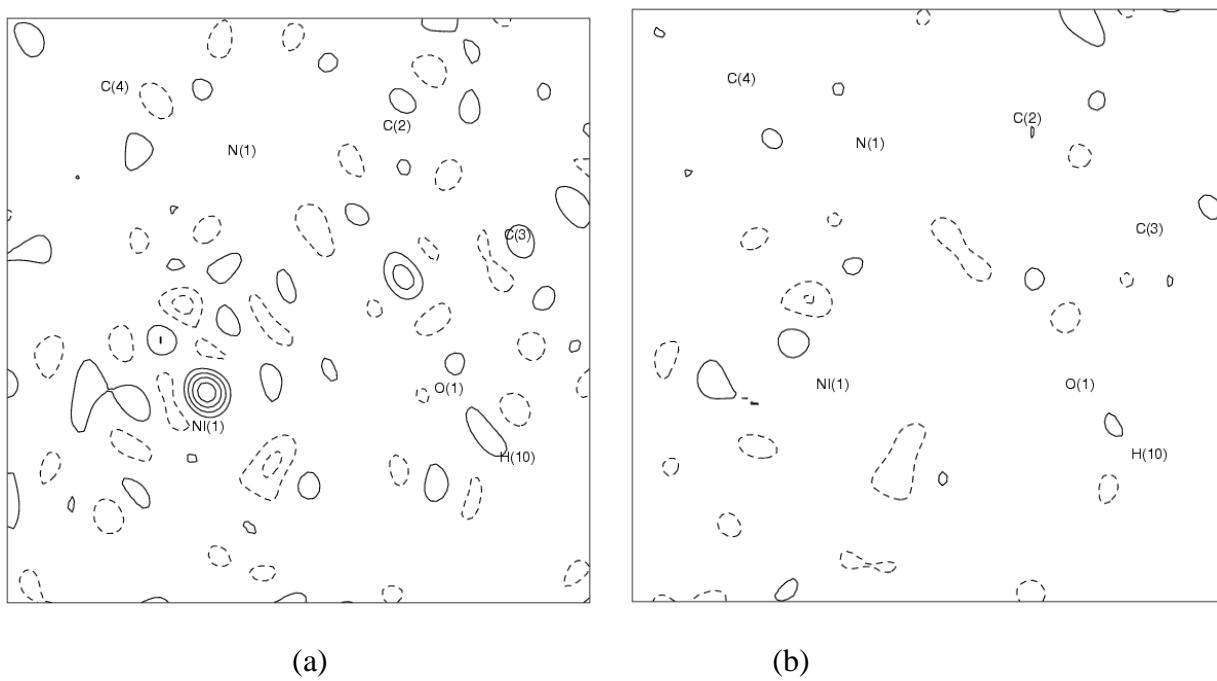


Figure S4. Final residual maps $F_{\text{obs}} - F_{\text{mult}}$ in the $\text{Ni}(1)$ - $\text{N}(1)$ - $\text{O}(1)$ plane, using (a) all data (b) those data with $\sin\theta/\lambda \leq 1.0$. Contours levels are drawn at $\pm 0.1 \text{ e } \text{\AA}^{-3}$.

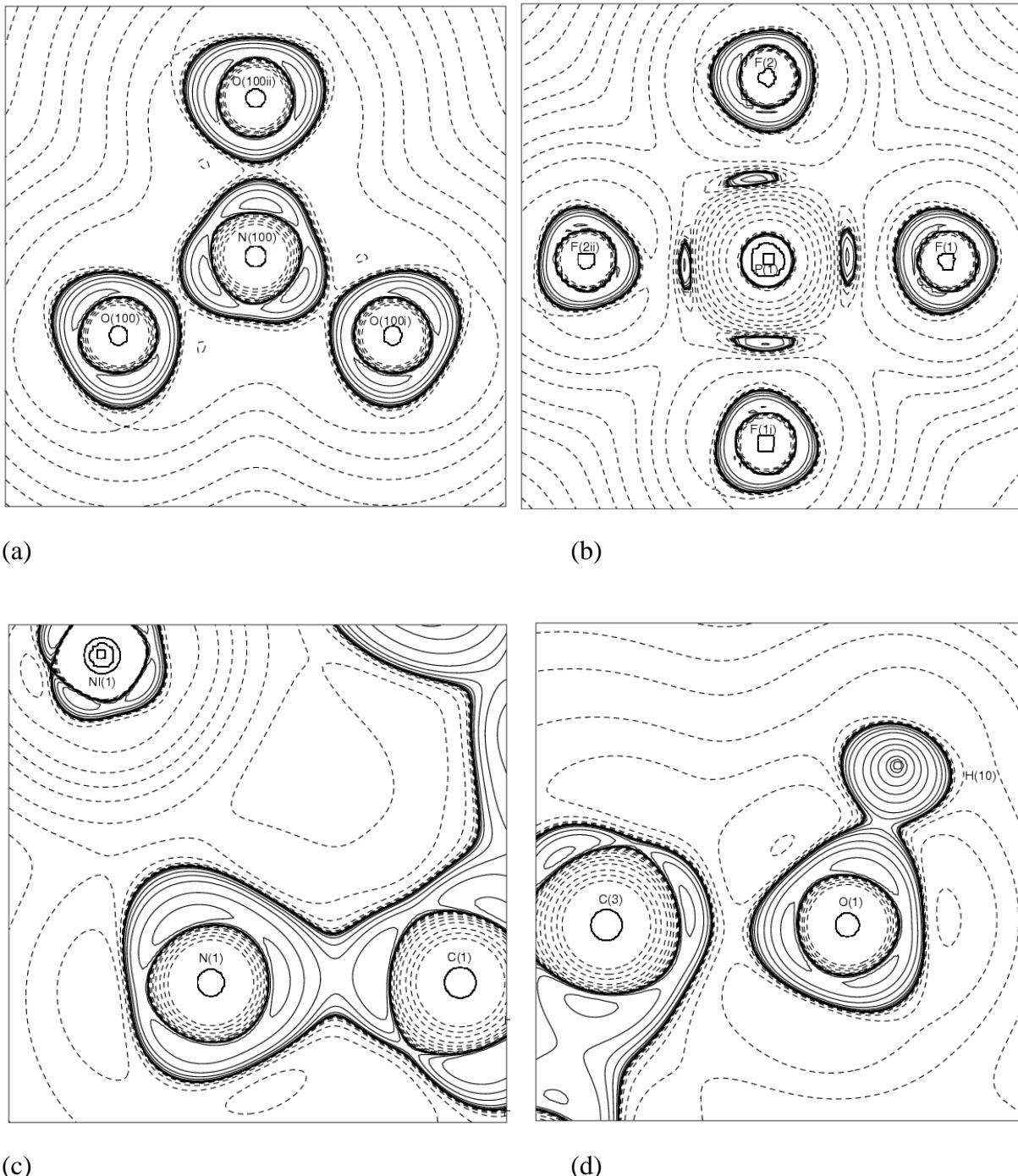


Figure S5. Experimental Laplacian distribution in the planes (a) of the nitrate anion (b) the PF_6^- anion $\text{P}(1)\text{-F}(1)\text{-F}(2)$, (c) $\text{C}(1)\text{-N}(1)\text{-Ni}(1)$ and (d) $\text{C}(3)\text{-O}(1)\text{-H}(10)$. Contours are drawn at -1.0×10^{-3} , $\pm 2.0 \times 10^n$, $\pm 4 \times 10^n$, $\pm 8 \times 10^n$ ($n = -3, -2, -1, 0, +1, +2$) $\text{e} \text{\AA}^{-5}$, with positive contours drawn with a full line and negative contours with a broken line.

Table S1 Fractional atomic coordinates, occupation factors and Uiso or Uequiv

	x/a	y/b	z/c	occ	Uiso
NI(1)	0.69345(1)	0.69345(1)	0.69345(1)	0.3333	0.009
P(1)	0.47892(1)	0.47892(1)	0.47892(1)	0.3333	0.017
F(1)	0.4580(1)	0.5890(1)	0.5038(1)	1.0000	0.025
F(2)	0.4534(1)	0.4996(1)	0.3684(1)	1.0000	0.028
O(1)	0.58562(5)	0.60631(5)	0.74924(5)	1.0000	0.014
O(100)	0.18411(6)	0.06619(6)	0.08485(6)	1.0000	0.020
N(1)	0.65304(4)	0.77733(4)	0.80759(5)	1.0000	0.011
N(100)	0.11162(5)	0.11162(5)	0.11162(5)	0.3333	0.013
C(1)	0.71871(5)	0.75723(5)	0.88902(5)	1.0000	0.013
C(2)	0.55250(5)	0.75265(5)	0.82905(5)	1.0000	0.013
C(3)	0.53937(5)	0.64485(5)	0.83321(5)	1.0000	0.012
C(4)	0.66283(5)	0.87696(5)	0.77258(5)	1.0000	0.013
C(5)	0.43404(5)	0.61416(6)	0.83787(6)	1.0000	0.015
C(6)	0.37601(6)	0.64558(7)	0.75103(6)	1.0000	0.022
C(7)	0.38804(6)	0.64875(7)	0.93077(6)	1.0000	0.022
H(1A)	0.67784	0.75478	0.95461	1.0000	0.030
H(1B)	0.76990	0.81483	0.89530	1.0000	0.022
H(2A)	0.50627	0.78210	0.77452	1.0000	0.027
H(2B)	0.53221	0.78371	0.89688	1.0000	0.024
H(3)	0.57562	0.61785	0.89593	1.0000	0.023
H(4A)	0.66059	0.92580	0.83247	1.0000	0.019
H(4B)	0.60381	0.89405	0.72566	1.0000	0.015
H(5)	0.43274	0.53687	0.83939	1.0000	0.026
H(6A)	0.30501	0.61524	0.75493	1.0000	0.047
H(6B)	0.41082	0.62082	0.68659	1.0000	0.053
H(6C)	0.37111	0.72273	0.74952	1.0000	0.037
H(7A)	0.38488	0.72600	0.93070	1.0000	0.040
H(7B)	0.43060	0.62496	0.99077	1.0000	0.043
H(7C)	0.31657	0.61986	0.93668	1.0000	0.045
H(10)	0.58838	0.53540	0.75699	1.0000	0.013

Table S2 Anisotropic Thermal Paprameters Uij

	U11	U22	U33	U12	U13	U23
NI(1)	0.00909(2)	0.00909(2)	0.00909(2)	-0.00027(5)	-0.00027(5)	-0.00027(5)
P(1)	0.01702(6)	0.01702(6)	0.01702(6)	0.00449(7)	0.00449(7)	0.00449(7)
F(1)	0.0276(5)	0.0183(4)	0.0288(5)	0.0074(4)	0.0037(5)	0.0027(4)
F(2)	0.0321(6)	0.0323(6)	0.0190(5)	0.0049(5)	-0.0003(5)	0.0059(5)
O(1)	0.0150(3)	0.0101(2)	0.0181(3)	-0.0014(2)	0.0045(2)	-0.0025(2)
O(100)	0.0214(4)	0.0227(3)	0.0170(3)	0.0076(3)	0.0043(3)	0.0011(3)
N(1)	0.0117(2)	0.0100(2)	0.0113(2)	-0.0005(2)	0.0000(2)	-0.0005(2)
N(100)	0.0134(2)	0.0134(2)	0.0134(2)	-0.0002(2)	-0.0002(2)	-0.0002(2)
C(1)	0.0158(3)	0.0133(3)	0.0109(2)	0.0007(2)	-0.0006(2)	-0.0022(2)
C(2)	0.0124(3)	0.0107(3)	0.0157(3)	0.0001(2)	0.0024(2)	-0.0004(2)
C(3)	0.0117(3)	0.0114(3)	0.0143(3)	-0.0002(2)	0.0012(2)	0.0008(2)
C(4)	0.0144(3)	0.0097(2)	0.0148(3)	0.0003(2)	0.0014(2)	-0.0010(2)
C(5)	0.0128(3)	0.0135(3)	0.0182(3)	-0.0009(2)	0.0020(2)	0.0008(2)
C(6)	0.0165(3)	0.0290(4)	0.0195(3)	-0.0034(3)	-0.0034(3)	0.0009(3)
C(7)	0.0173(3)	0.0299(4)	0.0175(3)	0.0004(3)	0.0056(3)	0.0022(3)

Table S3 Bond lengths (Angstroms)

N1(1) - O(1)	2.0935(7)
N1(1) - N(1)	2.0633(7)
P(1) - F(1)	1.6077(12)
P(1) - F(2)	1.6147(13)
O(1) - C(3)	1.4472(9)
O(1) - H(3)	2.0659(8)
O(1) - H(10)	1.0000(7)
O(100)- N(100)	1.2557(8)
O(100)- H(10)	1.9012(9)
N(1) - C(1)	1.4922(9)
N(1) - C(2)	1.4810(9)
N(1) - C(4)	1.4856(9)
C(1) - C(4)	1.5319(9)
C(1) - H(1A)	1.0830(7)
C(1) - H(1B)	1.0830(7)
C(2) - C(3)	1.5223(9)
C(2) - H(2A)	1.0830(7)
C(2) - H(2B)	1.0830(7)
C(3) - C(5)	1.5382(10)
C(3) - H(3)	1.0830(7)
C(3) - H(10)	1.9904(7)
C(4) - H(4A)	1.0830(7)
C(4) - H(4B)	1.0830(8)
C(5) - C(6)	1.5278(11)
C(5) - C(7)	1.5308(11)
C(5) - H(5)	1.0830(8)
C(6) - H(6A)	1.0830(8)
C(6) - H(6B)	1.0830(9)
C(6) - H(6C)	1.0830(10)
C(7) - H(7A)	1.0830(10)
C(7) - H(7B)	1.0830(9)
C(7) - H(7C)	1.0830(9)

Table S4 Bond Angles (deg)

O(1) - NI(1) - O(1)	93.80(3)	C(3) - C(5) - C(6)	113.33(7)
O(1) - NI(1) - N(1)	81.07(3)	C(3) - C(5) - C(7)	110.57(7)
O(1) - NI(1) - N(1)	100.75(3)	C(3) - C(5) - H(5)	107.24(6)
O(1) - NI(1) - N(1)	164.83(3)	C(6) - C(5) - C(7)	111.20(7)
O(1) - NI(1) - O(1)	93.80(3)	C(6) - C(5) - H(5)	107.14(7)
O(1) - NI(1) - N(1)	164.83(3)	C(7) - C(5) - H(5)	107.02(7)
N(1) - NI(1) - N(1)	85.85(3)	C(5) - C(6) - H(6A)	109.59(7)
F(1) - P(1) - F(1)	90.37(7)	C(5) - C(6) - H(6B)	109.38(7)
F(1) - P(1) - F(2)	89.75(7)	C(5) - C(6) - H(6C)	109.68(7)
F(1) - P(1) - F(2)	89.94(7)	H(6A) - C(6) - H(6B)	109.26(8)
F(1) - P(1) - F(2)	179.67(8)	H(6A) - C(6) - H(6C)	109.54(8)
F(1) - P(1) - F(2)	89.75(7)	H(6B) - C(6) - H(6C)	109.38(8)
F(1) - P(1) - F(2)	89.94(7)	C(5) - C(7) - H(7A)	109.44(7)
F(2) - P(1) - F(2)	89.94(8)	C(5) - C(7) - H(7B)	109.31(7)
NI(1) - O(1) - C(3)	114.14(5)	C(5) - C(7) - H(7C)	109.62(8)
NI(1) - O(1) - H(3)	112.00(3)	H(7A) - C(7) - H(7B)	109.31(8)
NI(1) - O(1) - H(10)	126.29(6)	H(7A) - C(7) - H(7C)	109.62(8)
C(3) - O(1) - H(3)	29.79(3)	H(7B) - C(7) - H(7C)	109.53(7)
C(3) - O(1) - H(10)	107.43(6)	C(1) - H(1A) - H(1B)	36.13(4)
H(3) - O(1) - H(10)	88.41(5)	C(1) - H(1B) - H(1A)	36.13(4)
N(100) - O(100) - H(10)	122.18(6)	C(2) - H(2A) - H(2B)	36.01(4)
NI(1) - N(1) - C(1)	108.41(4)	C(2) - H(2B) - H(2A)	36.01(4)
NI(1) - N(1) - C(2)	106.58(5)	O(1) - H(3) - C(3)	41.60(4)
NI(1) - N(1) - C(1)	108.41(4)	C(4) - H(4A) - H(4B)	36.02(4)
NI(1) - N(1) - C(2)	106.58(5)	C(4) - H(4B) - H(4A)	36.02(4)
NI(1) - N(1) - C(4)	104.71(5)	C(6) - H(6A) - H(6B)	35.37(5)
NI(1) - N(1) - C(2)	106.58(5)	C(6) - H(6A) - H(6C)	35.23(5)
C(1) - N(1) - C(2)	112.77(6)	C(6) - H(6B) - H(6A)	35.37(4)
C(1) - N(1) - C(4)	111.88(6)	C(6) - H(6B) - H(6C)	35.31(5)
C(2) - N(1) - C(4)	111.96(6)	C(6) - H(6C) - H(6A)	35.23(4)
O(100) - N(100) - O(100)	119.9997(4)	C(6) - H(6C) - H(6B)	35.31(5)
O(100) - N(100) - O(100)	119.9997(4)	C(7) - H(7A) - H(7B)	35.34(5)
O(100) - N(100) - O(100)	119.9997(4)	C(7) - H(7A) - H(7C)	35.19(4)
N(1) - C(1) - C(4)	112.47(6)	C(7) - H(7B) - H(7A)	35.35(5)
N(1) - C(1) - H(1A)	109.18(6)	C(7) - H(7B) - H(7C)	35.23(5)
N(1) - C(1) - H(1B)	109.25(6)	C(7) - H(7C) - H(7A)	35.19(5)
C(4) - C(1) - H(1A)	109.06(6)	C(7) - H(7C) - H(7B)	35.23(5)
C(4) - C(1) - H(1B)	109.02(6)	O(1) - H(10) - O(100)	157.06(5)
H(1A) - C(1) - H(1B)	107.75(6)	O(1) - H(10) - C(3)	43.93(4)
N(1) - C(2) - C(3)	110.75(6)	O(100) - H(10) - C(3)	113.16(4)
N(1) - C(2) - H(2A)	109.67(6)		
N(1) - C(2) - H(2B)	109.50(6)		
C(3) - C(2) - H(2A)	109.42(6)		
C(3) - C(2) - H(2B)	109.47(6)		
H(2A) - C(2) - H(2B)	107.99(6)		
O(1) - C(3) - C(2)	106.55(6)		
O(1) - C(3) - C(5)	111.08(6)		
O(1) - C(3) - H(3)	108.61(6)		
O(1) - C(3) - H(10)	28.64(3)		
C(2) - C(3) - C(5)	113.25(6)		
C(2) - C(3) - H(3)	108.71(6)		
C(2) - C(3) - H(10)	134.58(5)		
C(5) - C(3) - H(3)	108.53(6)		
C(5) - C(3) - H(10)	97.95(5)		
H(3) - C(3) - H(10)	90.25(4)		
N(1) - C(4) - C(1)	110.23(6)		
N(1) - C(4) - H(4A)	109.58(6)		
N(1) - C(4) - H(4B)	109.73(6)		

Table S5. Monopole Populations, Radial Parameters and Net Atomic Charges.

Atom	Pval	Kappa	P00	Kappa'	Net charge
NI(1)	8.417(37)	0.982	0.000	0.889	-0.416
P(1)	4.164(98)	0.980	0.000	1.000	+0.836
F(1)	7.306(16)	0.981	0.000	0.921	-0.306
F(2)	7.306(16)	0.981	0.000	0.921	-0.306
O(1)	6.499(27)	0.977	0.000	0.795	-0.499
O(100)	6.326(21)	0.977	0.000	0.795	-0.326
N(1)	5.288(30)	0.983	0.000	0.786	-0.288
N(100)	5.022(63)	0.983	0.000	0.786	-0.021
C(1)	4.168(50)	1.004	0.000	0.868	-0.167
C(2)	4.045(48)	1.004	0.000	0.868	-0.045
C(3)	3.965(46)	1.004	0.000	0.868	+0.035
C(4)	4.203(49)	1.004	0.000	0.868	-0.203
C(5)	4.003(45)	1.004	0.000	0.868	-0.002
C(6)	4.072(57)	1.004	0.000	0.868	-0.071
C(7)	4.085(54)	1.004	0.000	0.868	-0.084
H(1A)	0.821(20)	1.200	0.000	1.200	+0.178
H(1B)	0.821(20)	1.200	0.000	1.200	+0.178
H(2A)	0.882(21)	1.200	0.000	1.200	+0.118
H(2B)	0.882(21)	1.200	0.000	1.200	+0.118
H(3)	0.961(30)	1.200	0.000	1.200	+0.039
H(4A)	0.772(19)	1.200	0.000	1.200	+0.228
H(4B)	0.772(19)	1.200	0.000	1.200	+0.228
H(5)	0.852(31)	1.200	0.000	1.200	+0.148
H(6A)	0.930(21)	1.200	0.000	1.200	+0.069
H(6B)	0.930(21)	1.200	0.000	1.200	+0.069
H(6C)	0.930(21)	1.200	0.000	1.200	+0.069
H(7A)	0.914(19)	1.200	0.000	1.200	+0.085
H(7B)	0.914(19)	1.200	0.000	1.200	+0.085
H(7C)	0.914(19)	1.200	0.000	1.200	+0.085
H(10)	0.570(25)	1.200	0.000	1.200	+0.429

Table S6. Dipole Population Parameters.

Atom	D11+	D11-	D10	Kappa'
N(1)	0.000	0.000	-0.043(21)	0.889
P(1)	0.000	0.000	-0.148(38)	1.000
F(1)	0.033(26)	0.001(25)	0.152(25)	0.921
F(2)	-0.081(29)	-0.169(28)	0.028(26)	0.921
O(1)	-0.061(19)	0.004(20)	-0.002(22)	0.795
O(100)	-0.046(27)	0.023(22)	-0.036(23)	0.795
N(1)	0.106(21)	-0.036(24)	-0.018(23)	0.786
N(100)	0.000	0.000	-0.088(40)	0.786
C(1)	0.053(27)	0.029(25)	-0.095(26)	0.868
C(2)	0.022(23)	-0.016(28)	-0.093(25)	0.868
C(3)	0.059(27)	0.012(25)	0.048(25)	0.868
C(4)	0.107(27)	0.016(23)	-0.122(26)	0.868
C(5)	0.028(29)	-0.015(30)	0.016(26)	0.868
C(6)	-0.018(24)	-0.021(25)	-0.004(31)	0.868
C(7)	-0.027(25)	-0.023(26)	-0.043(30)	0.868
H(1A)	0.000	0.000	0.100(19)	1.200
H(1B)	0.000	0.000	0.132(18)	1.200
H(2A)	0.000	0.000	0.156(19)	1.200
H(2B)	0.000	0.000	0.109(19)	1.200
H(3)	0.000	0.000	0.135(21)	1.200
H(4A)	0.000	0.000	0.107(20)	1.200
H(4B)	0.000	0.000	0.090(16)	1.200
H(5)	0.000	0.000	0.088(22)	1.200
H(6A)	0.000	0.000	0.216(24)	1.200
H(6B)	0.000	0.000	0.235(24)	1.200
H(6C)	0.000	0.000	0.140(25)	1.200
H(7A)	0.000	0.000	0.099(25)	1.200
H(7B)	0.000	0.000	0.161(21)	1.200
H(7C)	0.000	0.000	0.141(23)	1.200
H(10)	0.000	0.000	0.102(20)	1.200

Table S7. Quadrupole Population Parameters.

Atom	Q20	Q21+	Q21-	Q22+	Q22-	Kappa '
NI(1)	-0.008(38)	0.000	0.000	0.000	0.000	0.889
P(1)	0.005(40)	0.000	0.000	0.000	0.000	1.000
F(1)	-0.019(41)	-0.004(0)	0.004(0)	-0.022(0)	-0.007(0)	0.921
F(2)	-0.035(43)	0.022(0)	-0.010(0)	-0.041(0)	-0.028(0)	0.921
O(1)	0.038(0)	-0.009(0)	-0.013(0)	0.062(0)	-0.021(0)	0.795
O(100)	-0.144(0)	0.012(0)	0.016(38)	0.057(0)	-0.018(0)	0.795
N(1)	-0.017(0)	-0.009(0)	-0.011(40)	0.091(0)	0.004(0)	0.786
N(100)	-0.175(0)	0.000	0.000	0.000	0.000	0.786
C(1)	-0.119(0)	0.013(0)	0.010(43)	0.025(41)	-0.020(0)	0.868
C(2)	-0.074(0)	-0.040(0)	-0.013(0)	0.007(0)	0.018(0)	0.868
C(3)	0.093(0)	-0.059(0)	-0.018(0)	-0.066(0)	-0.074(38)	0.868
C(4)	-0.037(0)	-0.016(0)	-0.094(0)	0.003(0)	-0.047(40)	0.868
C(5)	-0.044(0)	0.013(36)	-0.016(0)	0.051(0)	-0.052(41)	0.868
C(6)	0.070(0)	-0.002(41)	0.005(0)	0.012(0)	-0.010(43)	0.868
C(7)	0.078(0)	-0.008(0)	-0.045(0)	-0.018(0)	-0.009(0)	0.868

Table S8. Octupole Population Parameters.

Atom	O30	O31+	O31-	O32+	O32-	O33+	O33-	Kappa'
NI(1)	-0.228(35)	0.000	0.000	0.000	0.000	0.176(26)	-0.098(21)	0.889
P(1)	-0.248(41)	0.000	0.000	0.000	0.000	0.089(36)	0.026(34)	1.000
F(1)	0.006(17)	0.038(15)	0.025(16)	-0.074(16)	0.106(18)	-0.010(15)	-0.012(15)	0.921
F(2)	0.060(17)	0.054(16)	0.030(16)	-0.035(16)	-0.109(18)	0.029(16)	0.081(16)	0.921
O(1)	0.146(17)	-0.027(15)	-0.035(15)	0.091(17)	0.061(15)	0.012(16)	-0.052(15)	0.795
O(100)	0.042(20)	0.008(22)	0.028(20)	-0.078(17)	-0.007(15)	0.018(16)	0.047(17)	0.795
N(1)	0.243(20)	-0.033(20)	-0.017(22)	0.137(21)	0.062(20)	0.157(18)	0.009(20)	0.786
N(100)	-0.026(42)	0.000	0.000	0.000	0.000	-0.097(65)	-0.307(43)	0.786
C(1)	0.288(24)	-0.049(23)	-0.092(24)	-0.045(21)	-0.062(21)	0.213(22)	-0.165(21)	0.868
C(2)	0.294(25)	0.063(22)	0.007(23)	0.075(22)	0.089(22)	-0.092(21)	-0.230(23)	0.868
C(3)	0.304(25)	-0.032(25)	0.047(25)	0.078(24)	0.034(26)	0.007(23)	-0.180(23)	0.868
C(4)	0.149(23)	-0.016(22)	0.273(22)	0.031(23)	-0.066(22)	-0.113(22)	-0.236(22)	0.868
C(5)	0.264(26)	-0.103(25)	0.042(27)	-0.008(25)	-0.062(26)	-0.004(24)	-0.200(24)	0.868
C(6)	0.346(27)	0.013(24)	-0.044(23)	-0.013(22)	0.038(22)	0.057(21)	0.140(24)	0.868
C(7)	0.253(27)	0.009(24)	-0.039(23)	0.076(22)	-0.003(23)	0.075(21)	0.189(26)	0.868

Table S9. Hexadecapole Population Parameters.

Atom	H40	H41+	H41-	H42+	H42-	H43+	H43-	H44+	H44-	Kappa'
NI(1)	0.104(32)	0.000	0.000	0.000	0.000	-0.488(29)	0.201(32)	0.000	0.000	0.889
P(1)	-0.203(43)	0.000	0.000	0.000	0.000	-0.056(41)	-0.291(43)	0.000	0.000	1.000