Supporting Information

Electronically Unsaturated Three-Coordinate Chloride and Methyl Complexes of Iron, Cobalt, and Nickel

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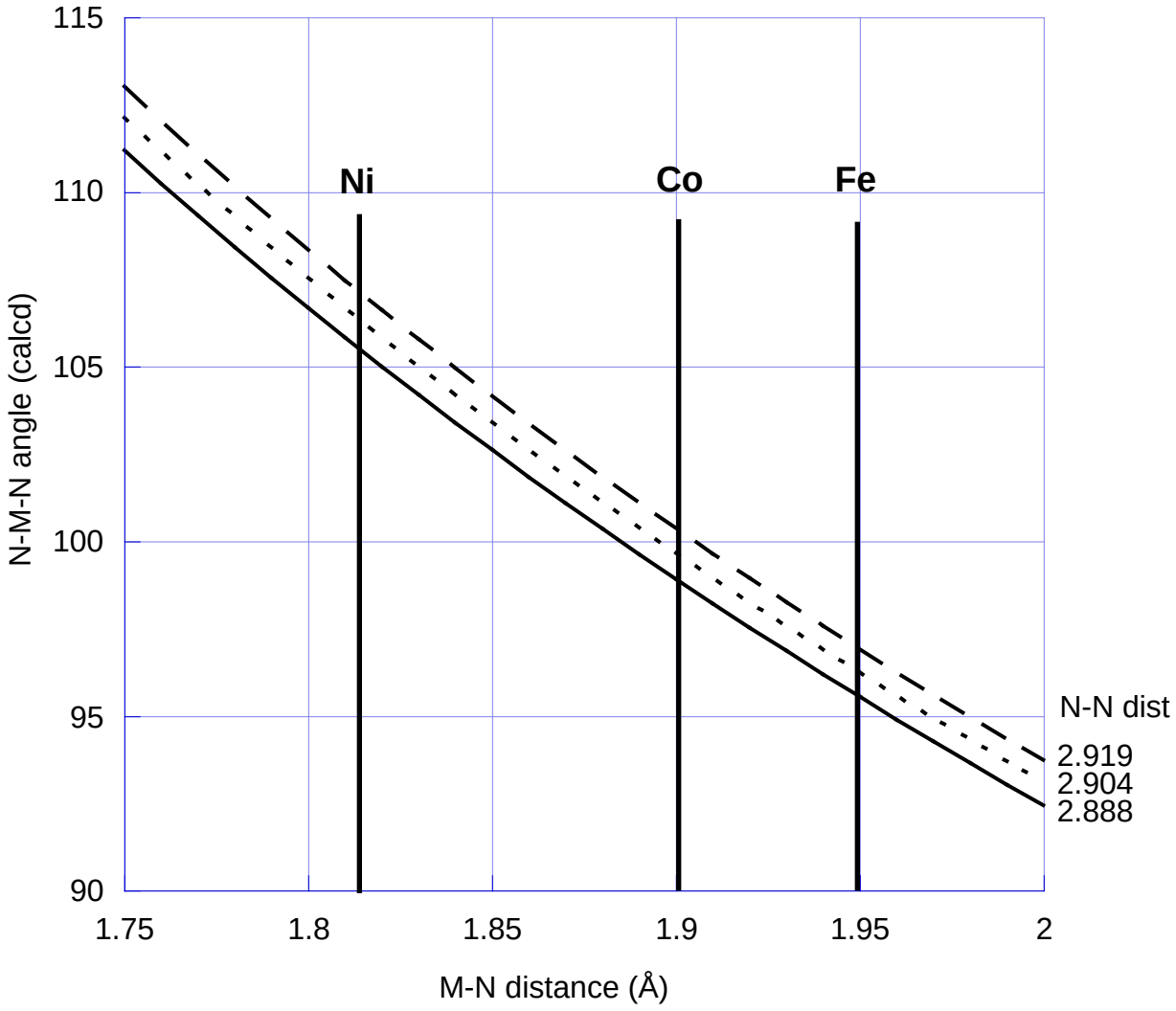
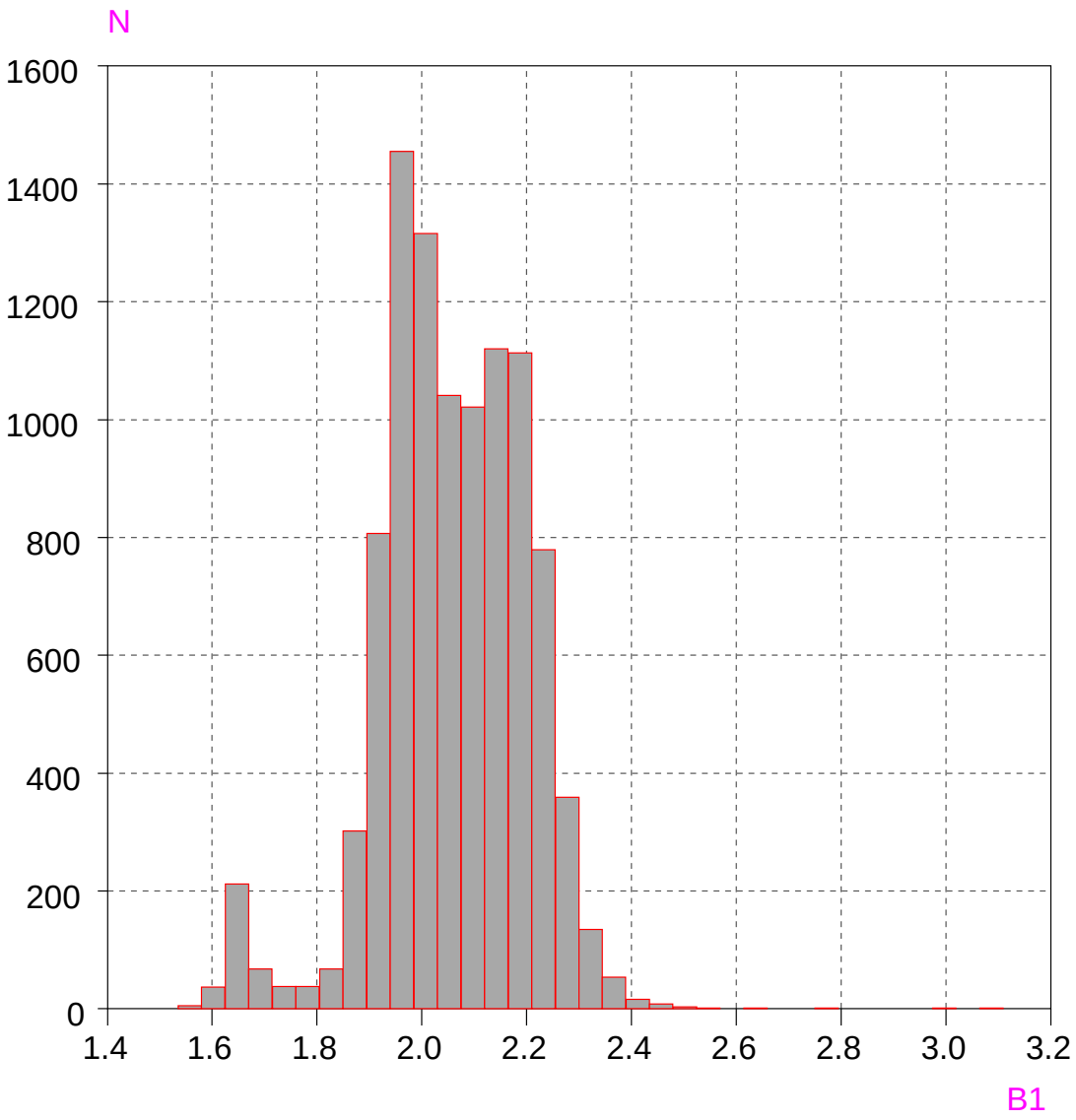
Figure S-1. Calculated N-M-N bond angles for given N-N distance and M-N distance for a rigid diketiminate with coordinated metal. The vertical bars indicate the observed M-N distances in the LMCl complexes.



B1 Figure S-2. Iron-nitrogen bond lengths (Angstrom) in CSD Oct 2001. Histogram from VISTA v2.1.

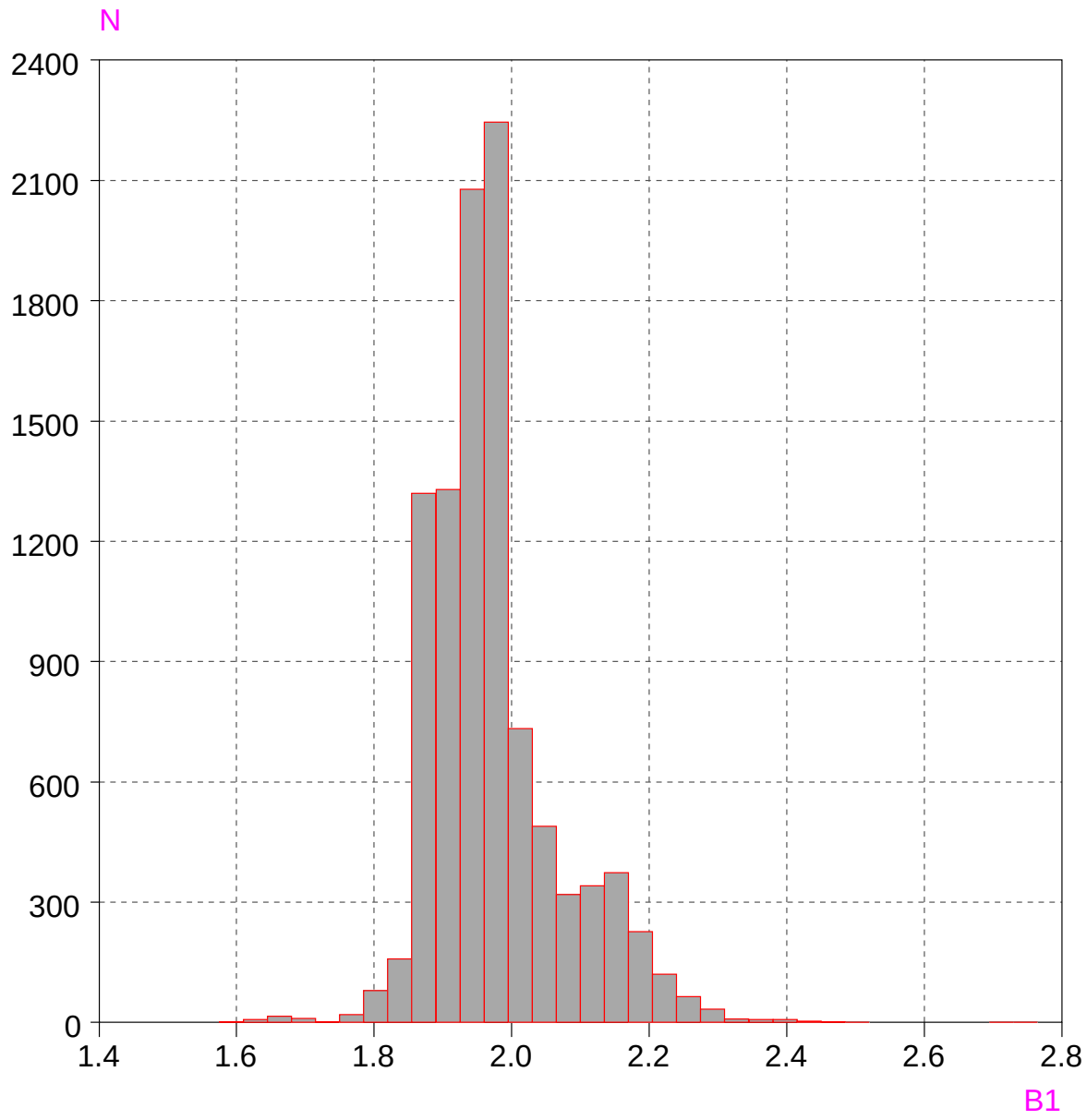


Plot Data
File=fen
Test=2
Tot.Obs.=10000
Obs.=10000
Supp.=0

X-axis
Min.=1.548
Max.=3.108
Range=1.560
Mean=2.059
Mean SE=0.001
Sample SD=0.140

Histogram
Median=2.059
Skew=-0.416
Quantile=10.000
LQ=1.909
HQ=2.227
Bin Width=0.045
Max. Bin =1455.000

B1 Figure S-3. Cobalt-nitrogen bond lengths (Angstrom) in CSD Oct 2001. Histogram from VISTA v2.1.

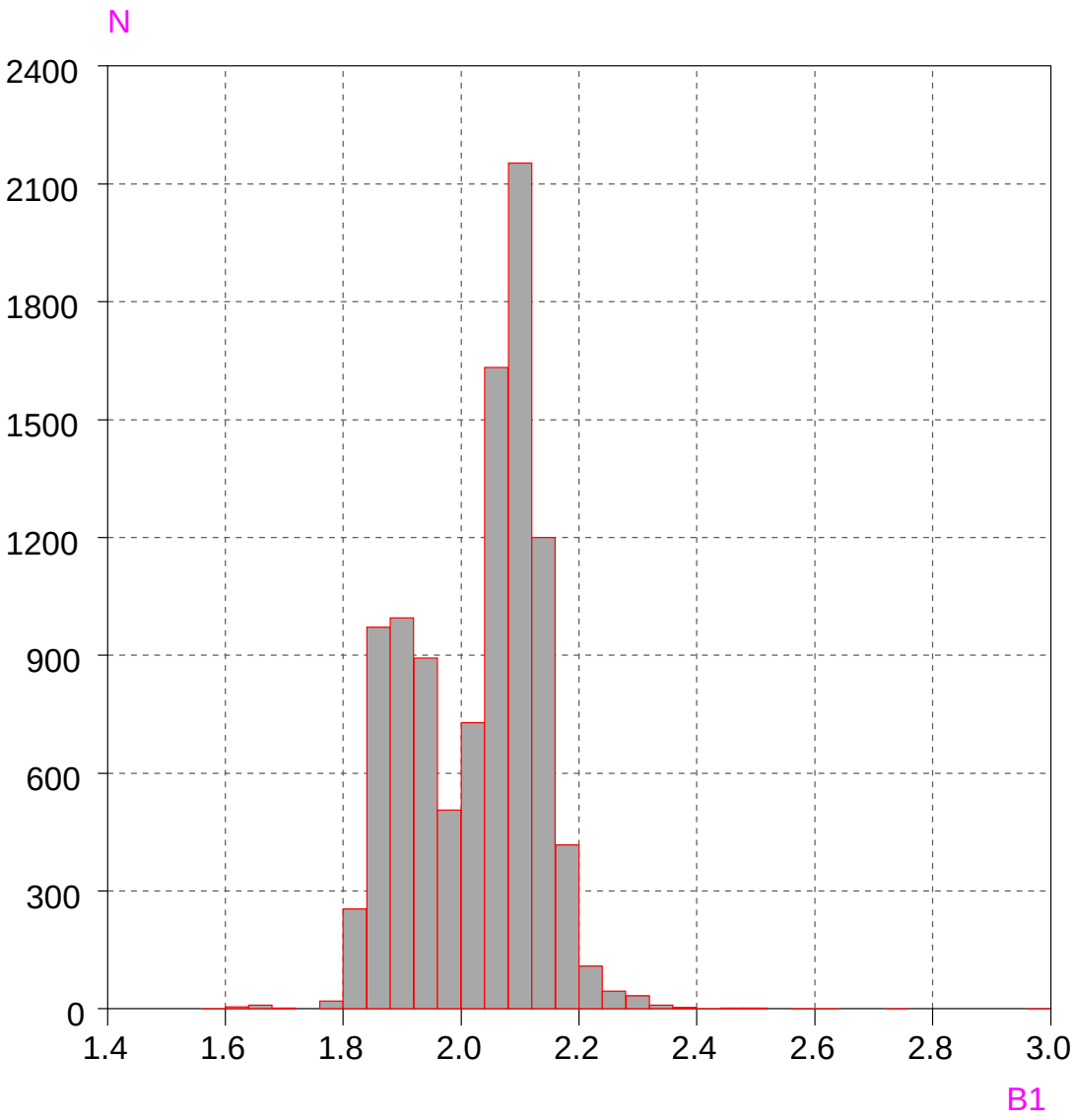


Plot Data
File=con
Test=1
Tot.Obs.=10000
Obs.=10000
Supp.=0

X-axis
Min.=1.590
Max.=2.732
Range=1.142
Mean=1.974
Mean SE=0.001
Sample SD=0.094

Histogram
Median=1.959
Skew=1.108
Quantile=10.000
LQ=1.880
HQ=2.119
Bin Width=0.035
Max. Bin =2246.000

B1 Figure S-4. Nickel-nitrogen bond lengths (Angstrom) in CSD Oct 2001. Histogram from VISTA v2.1.

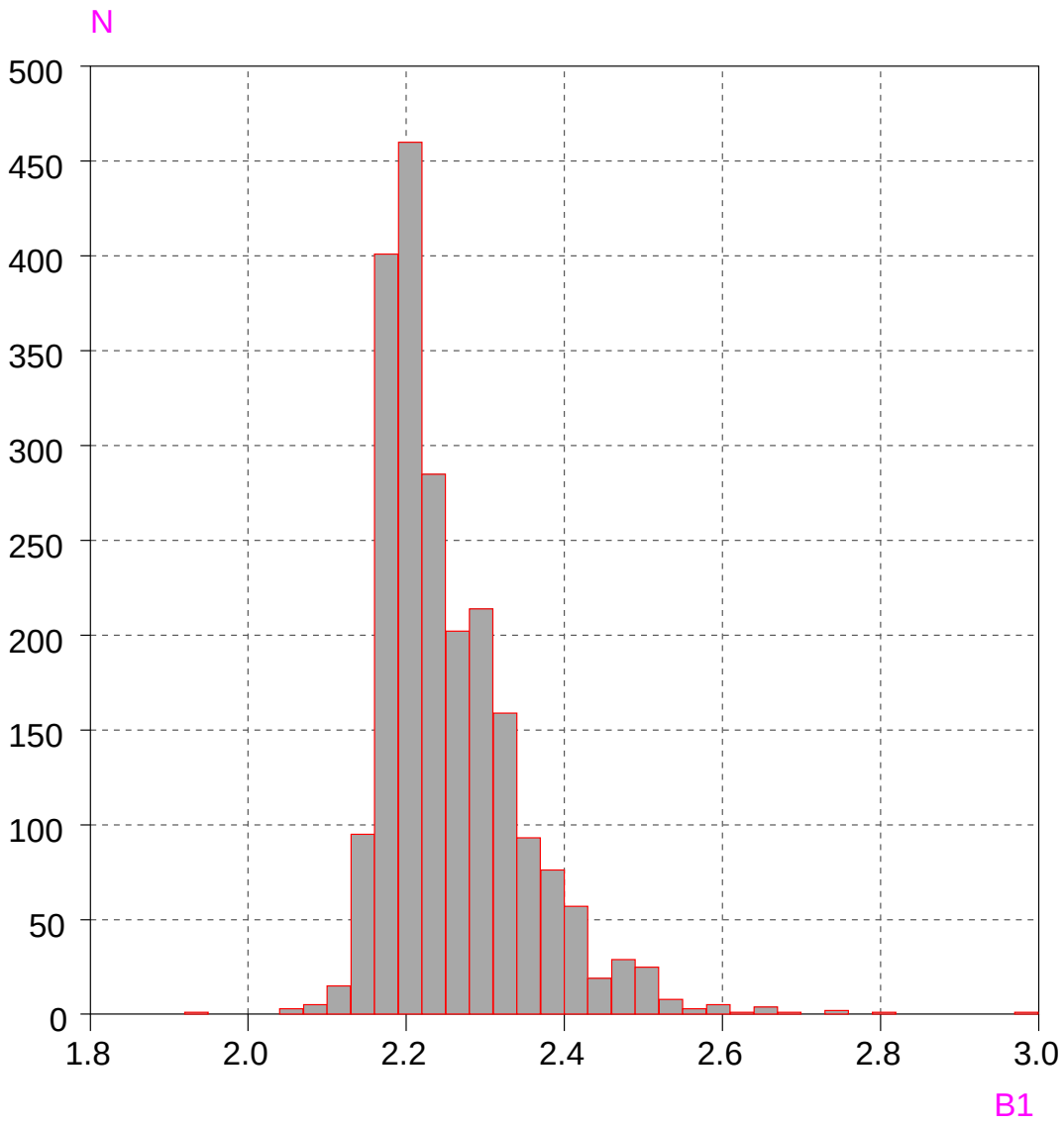


Plot Data
File=nin
Test=1
Tot.Obs.=10000
Obs.=10000
Supp.=0

X-axis
Min.=1.597
Max.=2.963
Range=1.366
Mean=2.027
Mean SE=0.001
Sample SD=0.108

Histogram
Median=2.059
Skew=-0.171
Quantile=10.000
LQ=1.870
HQ=2.142
Bin Width=0.040
Max. Bin =2153.000

B1 Figure S-5. Iron-chlorine bond lengths (Angstrom) in CSD Oct 2001. Histogram from VISTA v2.1.

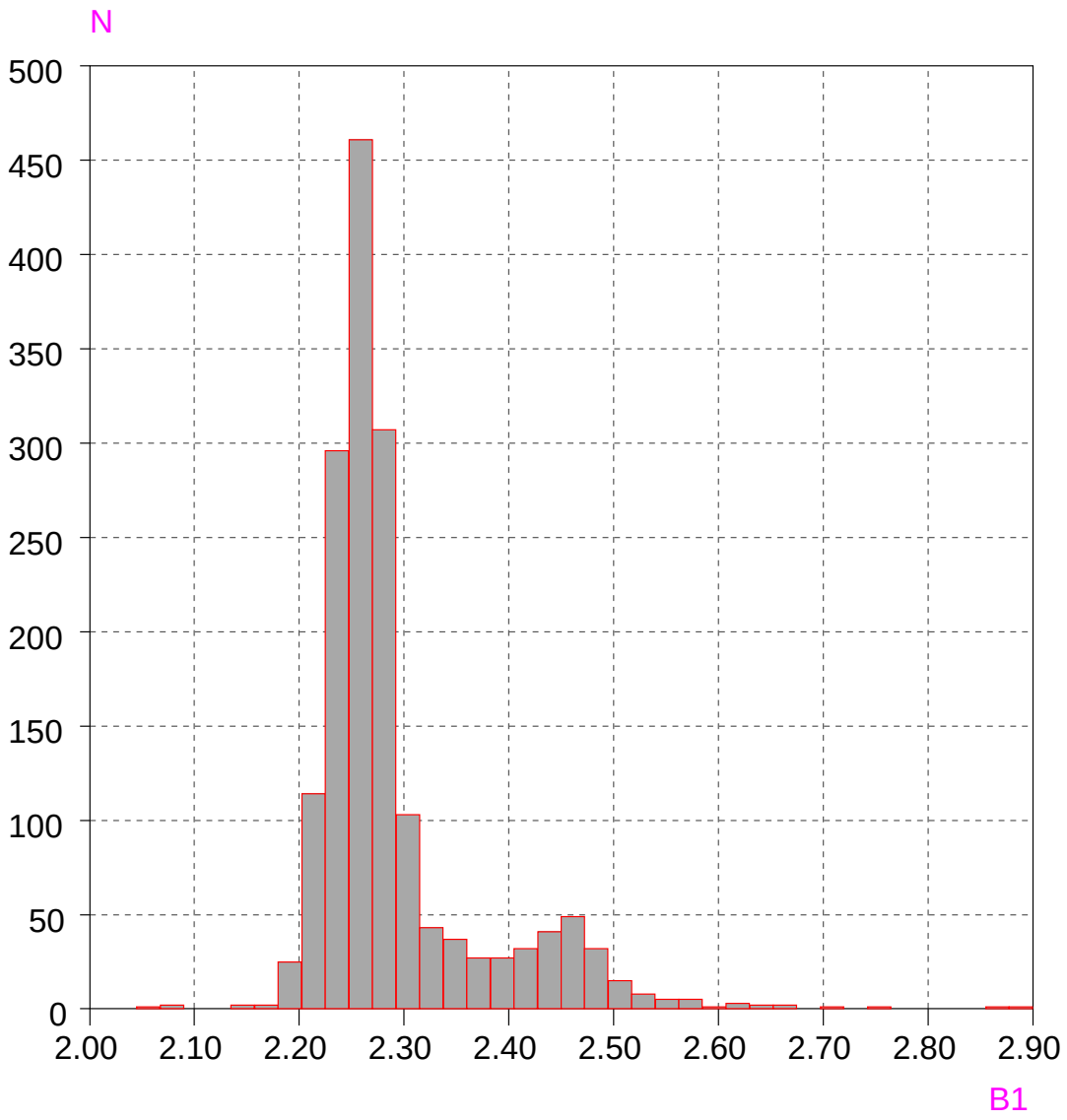


Plot Data
File=fecl
Test=1
Tot.Obs.=2165
Obs.=2165
Supp.=0

X-axis
Min.=1.937
Max.=2.978
Range=1.041
Mean=2.255
Mean SE=0.002
Sample SD=0.091

Histogram
Median=2.228
Skew=1.534
Quantile=10.000
LQ=2.171
HQ=2.377
Bin Width=0.030
Max. Bin =460.000

B1 Figure S-6. Cobalt-chlorine bond lengths (Angstrom) in CSD Oct 2001. Histogram from VISTA v2.1.

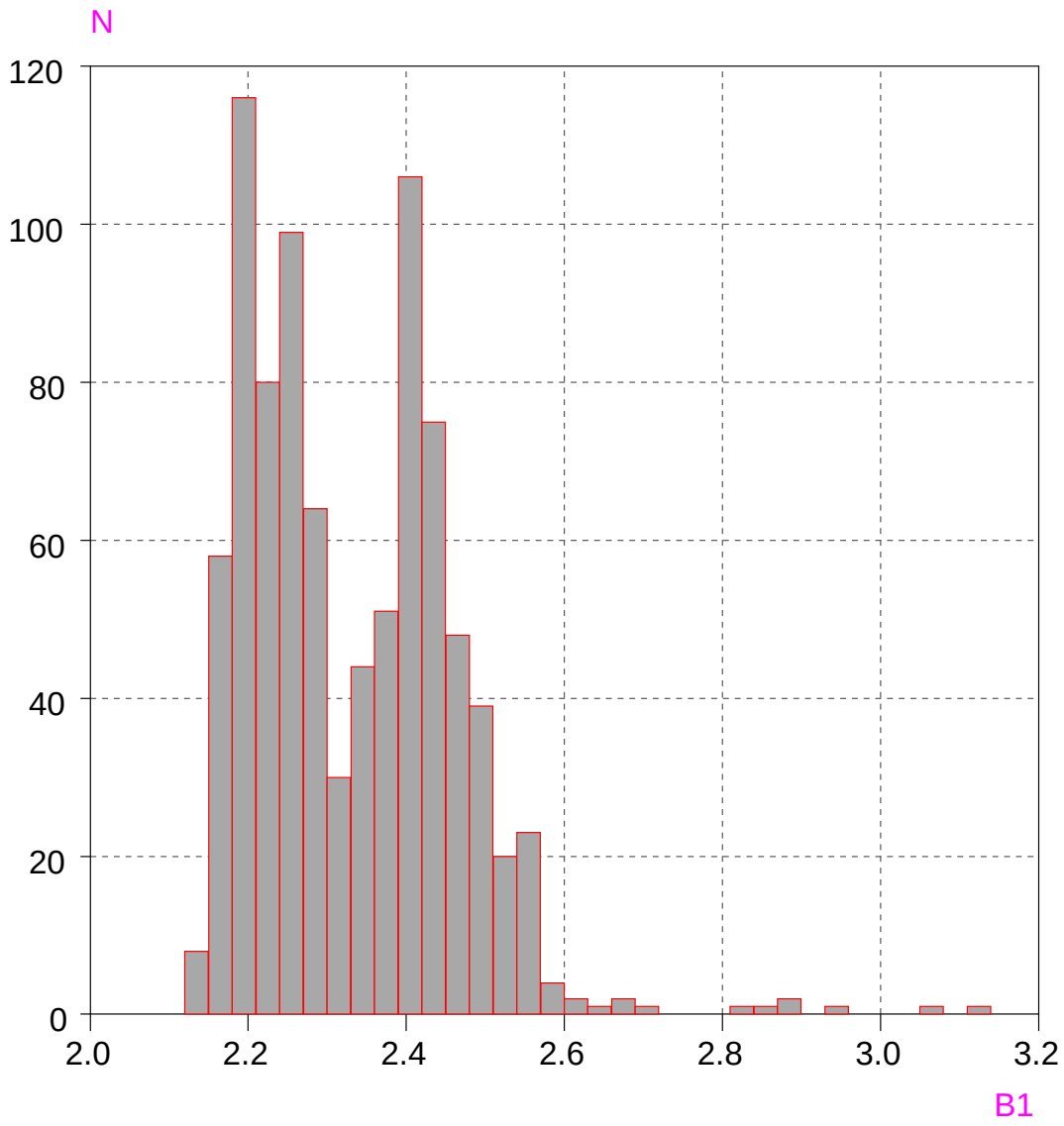


Plot Data
File=cocl
Test=1
Tot.Obs.=1646
Obs.=1646
Supp.=0

X-axis
Min.=2.047
Max.=2.894
Range=0.847
Mean=2.291
Mean SE=0.002
Sample SD=0.082

Histogram
Median=2.266
Skew=2.085
Quantile=10.000
LQ=2.227
HQ=2.431
Bin Width=0.023
Max. Bin =461.000

B1 Figure S-7. Nickel-chlorine bond lengths (Angstrom) in CSD Oct 2001. Histogram from VISTA v2.1.

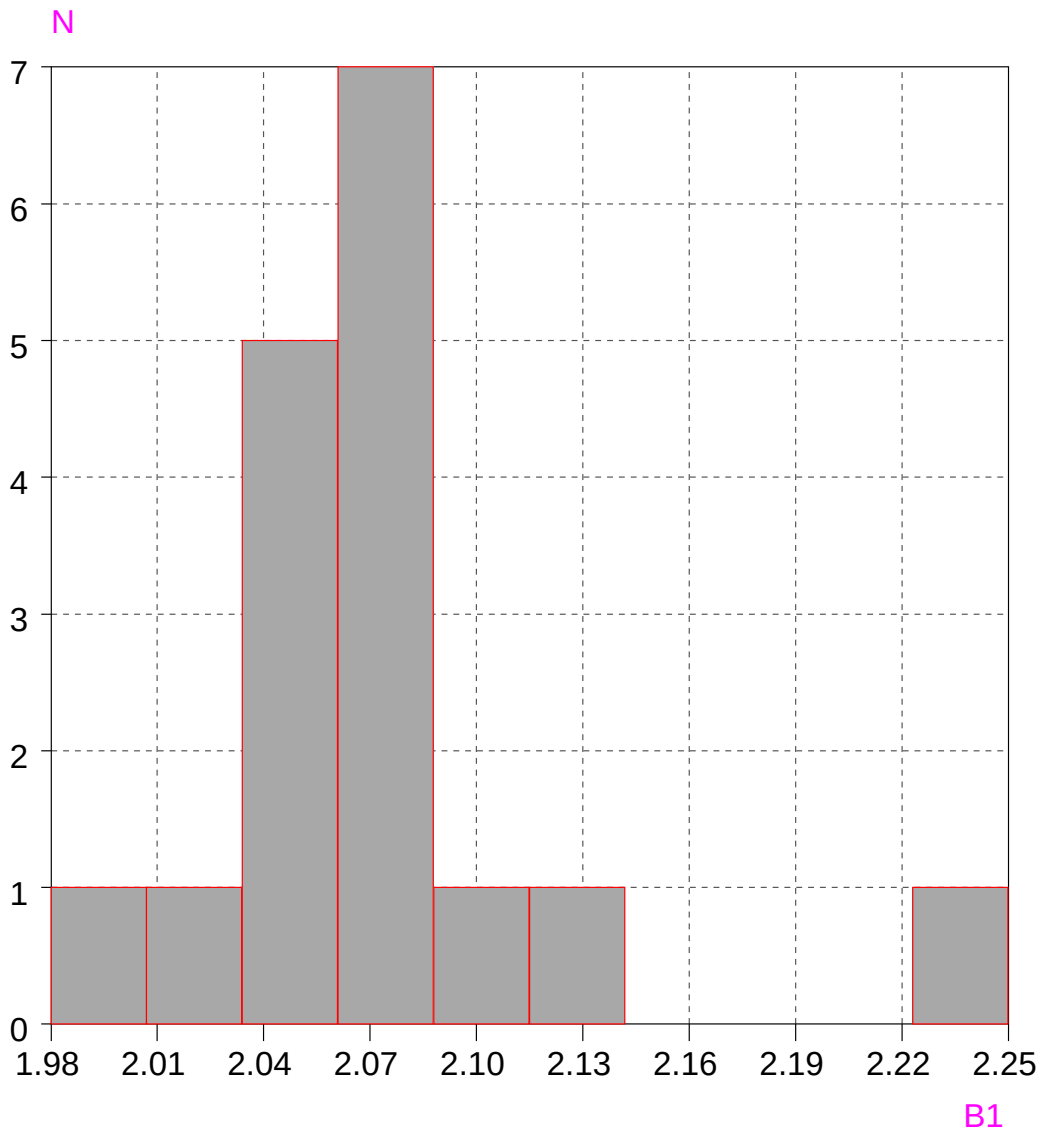


Plot Data
File=nicl
Test=1
Tot.Obs.=878
Obs.=878
Supp.=0

X-axis
Min.=2.121
Max.=3.126
Range=1.005
Mean=2.333
Mean SE=0.004
Sample SD=0.128

Histogram
Median=2.309
Skew=1.060
Quantile=10.000
LQ=2.187
HQ=2.488
Bin Width=0.030
Max. Bin =116.000

B1 Figure S-8. Iron-carbon bond lengths (Angstrom) in CSD Oct 2001. Histogram from VISTA v2.1.

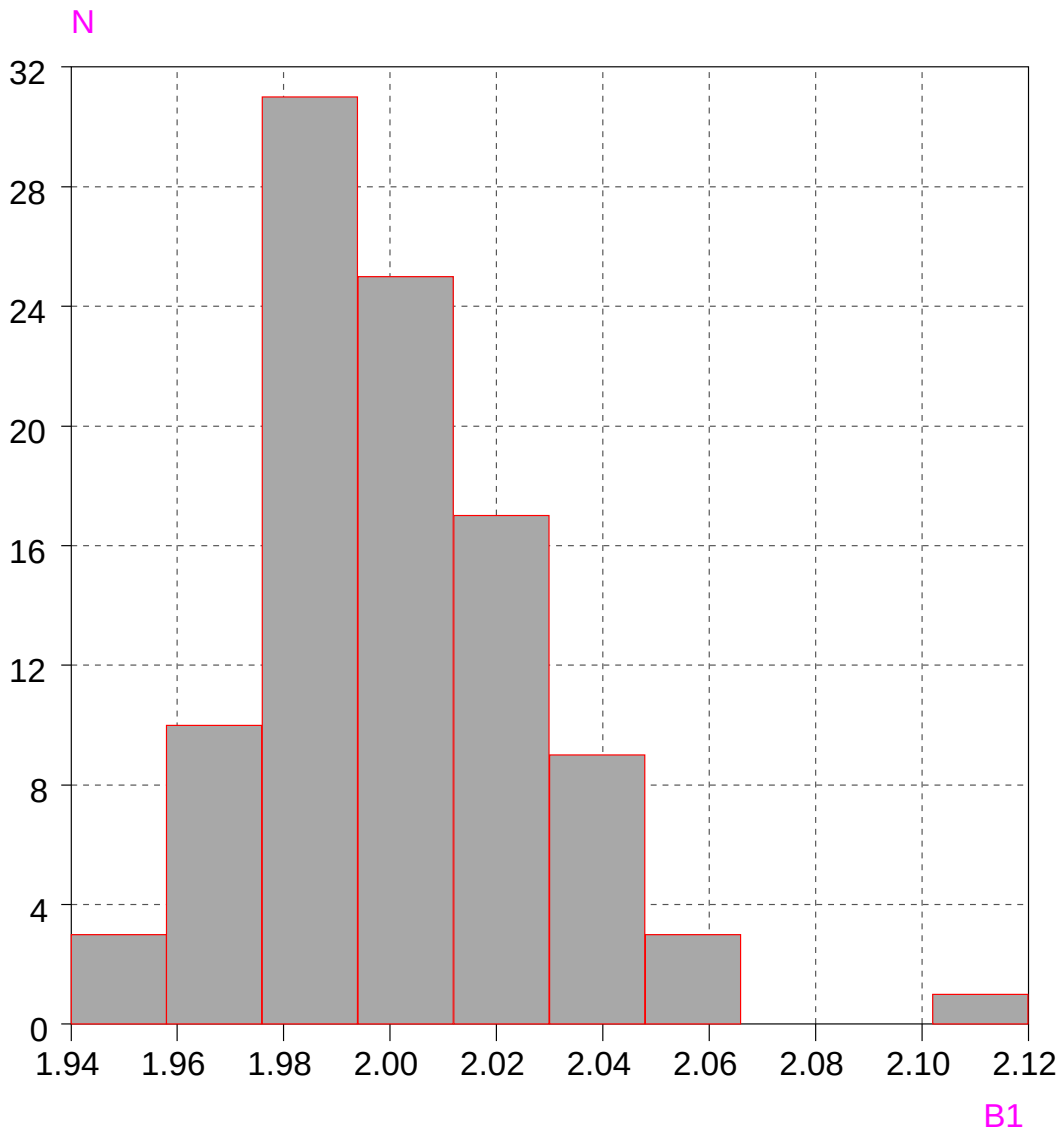


Plot Data
File=fec
Test=1
Tot.Obs.=17
Obs.=17
Supp.=0

X-axis
Min.=1.980
Max.=2.225
Range=0.245
Mean=2.072
Mean SE=0.012
Sample SD=0.050

Histogram
Median=2.064
Skew=1.325
Quantile=20.000
LQ=2.039
HQ=2.083
Bin Width=0.027
Max. Bin =7.000

B1 Figure S-9. Cobalt-carbon bond lengths (Angstrom) in CSD Oct 2001. Histogram from VISTA v2.1.



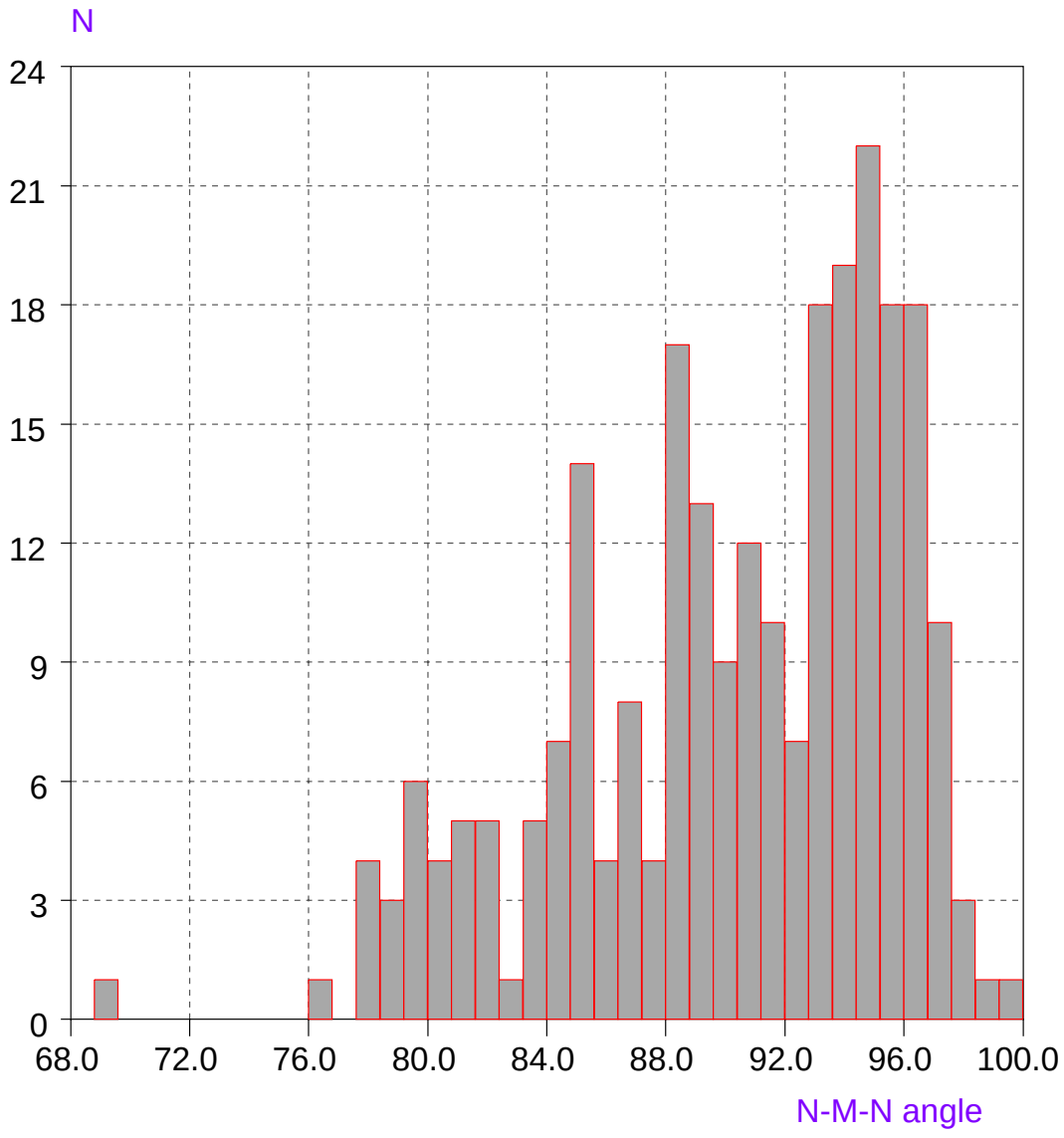
Plot Data
File=coc
Test=1
Tot.Obs.=99
Obs.=99
Supp.=0

X-axis
Min.=1.940
Max.=2.115
Range=0.175
Mean=2.000
Mean SE=0.003
Sample SD=0.026

Histogram
Median=1.998
Skew=0.896
Quantile=10.000
LQ=1.969
HQ=2.035
Bin Width=0.018
Max. Bin =31.000

N-M-N angles

Figure S-10. N-M-N angles (deg) for M(delocalized N2C3 chelate) in CSD (Oct 2001). Histogram from VISTA v2.1.



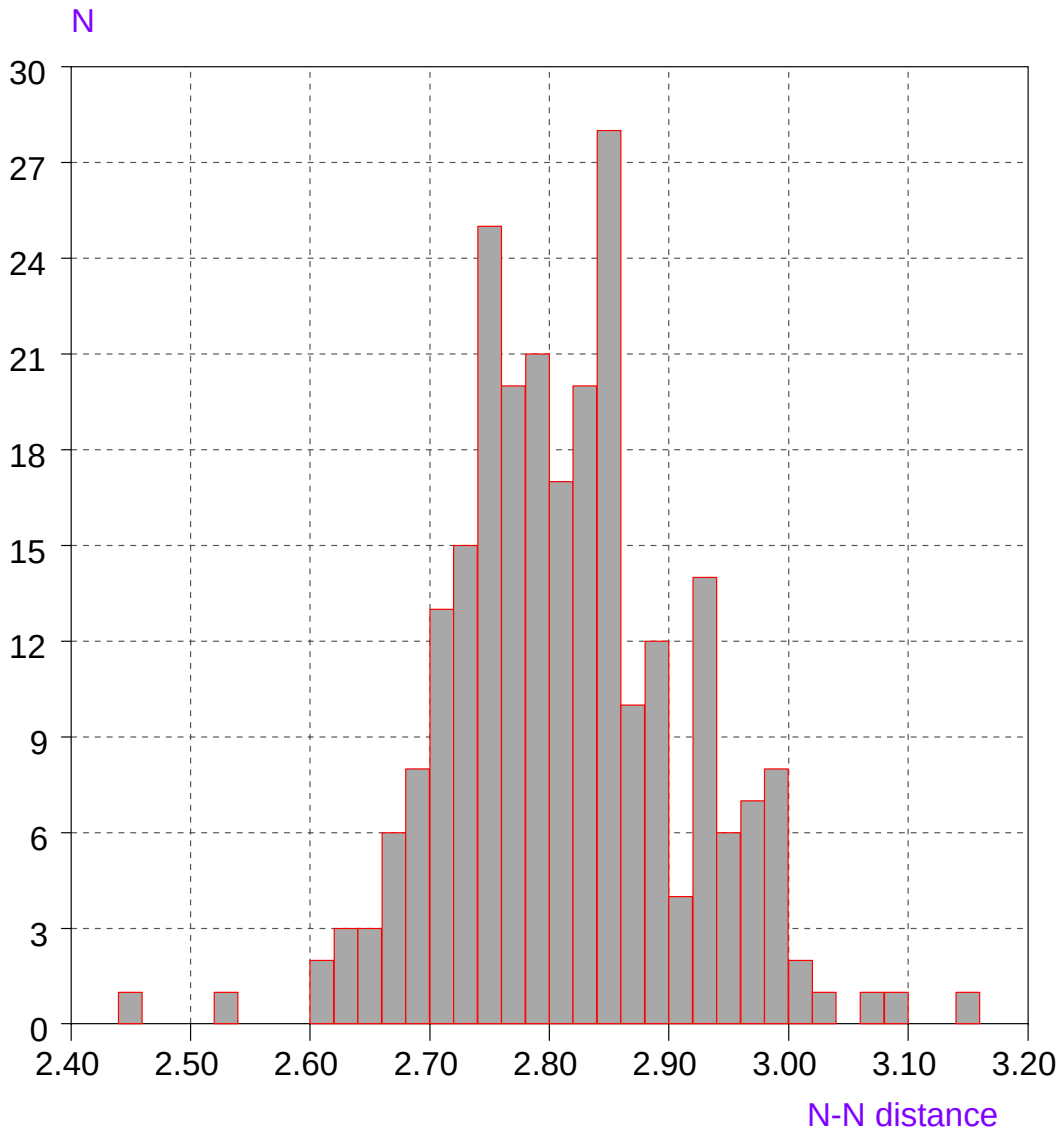
Plot Data
File=dik2
Test=1
Tot.Obs.=250
Obs.=250
Supp.=0

X-axis
Min.=69.064
Max.=99.401
Range=30.337
Mean=90.318
Mean SE=0.348
Sample SD=5.501

Histogram
Median=91.257
Skew=-0.762
Quantile=10.000
LQ=81.731
HQ=96.497
Bin Width=0.800
Max. Bin =22.000

N---N distances in cyclic -MNCCCN- complexes

Figure S-11. N---N distances (Å) for M(delocalized N2C3 chelate) in CSD (Oct 2001). Histogram from VISTA v2.1.



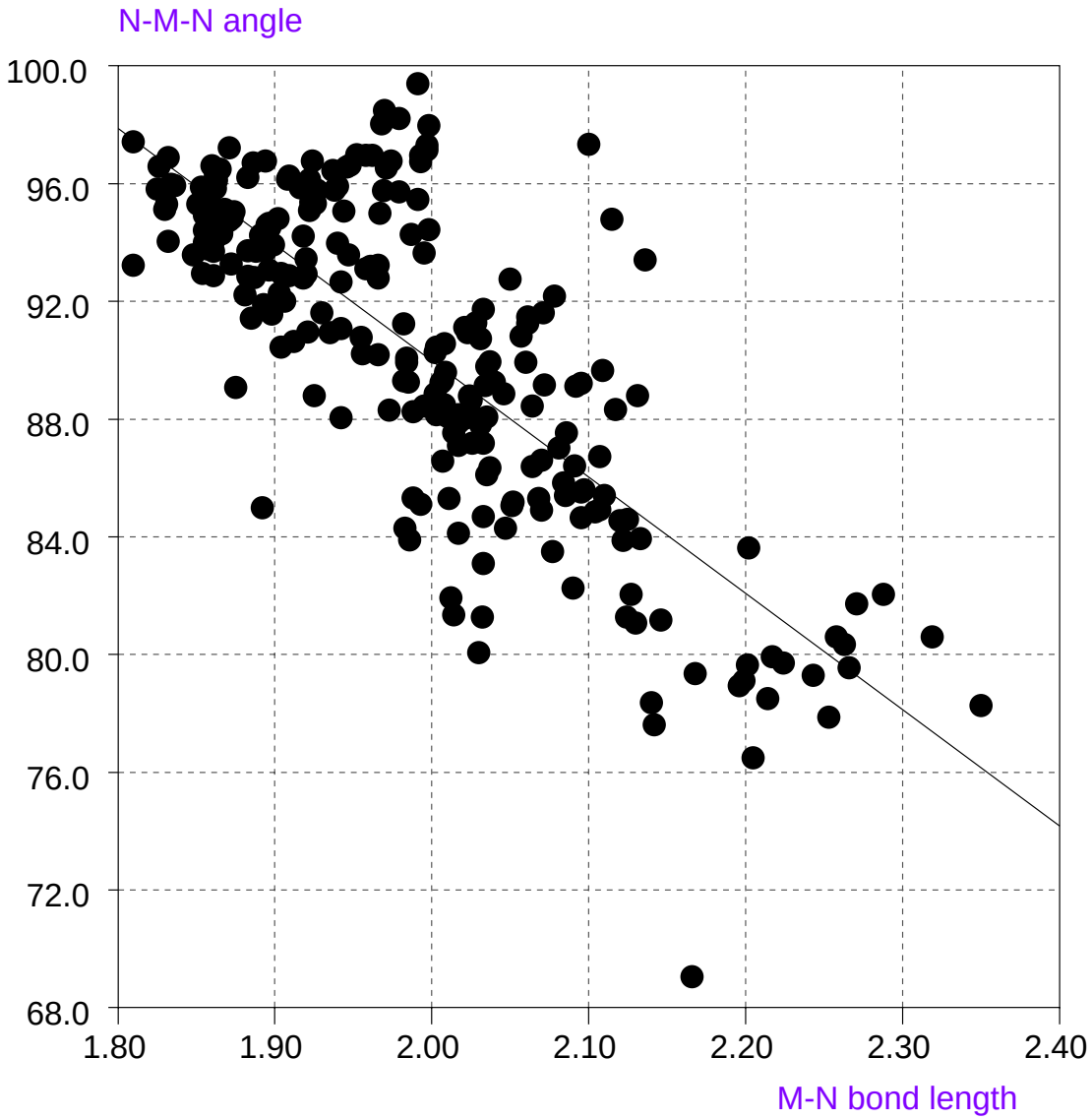
Plot Data
File=dik2
Test=1
Tot.Obs.=250
Obs.=250
Supp.=0

X-axis
Min.=2.443
Max.=3.147
Range=0.704
Mean=2.815
Mean SE=0.006
Sample SD=0.098

Histogram
Median=2.809
Skew=0.139
Quantile=10.000
LQ=2.702
HQ=2.943
Bin Width=0.020
Max. Bin =28.000

M-N bond length vs. N-M-N bond angle

Figure S-12. Scatter plot for M(delocalized N2C3 chelate) in CSD (Oct 2001). Generated by VISTA v2.1.



Plot Data
File=dik2
Test=1
Tot.Obs.=250
Obs.=250
Supp.=0

X-axis
Min.=1.810
Max.=2.350
Range=0.540
Mean=1.991
Mean SE=0.007
Sample SD=0.110

Y-axis
Min.=69.064
Max.=99.401
Range=30.337
Mean=90.318
Mean SE=0.348
Sample SD=5.501

Regression
Gradient=-39.480
Grad. SD.=1.968
Intercept=168.933
Int. SD.=3.925
Cor.Coeff.=-0.787
F stat.=402.441
Signif.=0.000

Table S-1. Optimized geometries reported in the text.

L'FeCl ($^5A_1$) ROB3LYP/6-311+G(d) optimized geometry
E(ROB+HF-LYP) = -1950.92562649

C	-1.434251	0.000000	-1.967598
N	-1.522682	0.000000	-0.645198
Fe	0.055563	0.000000	0.591243
N	1.375815	0.000000	-0.917591
C	1.042558	0.000000	-2.200362
C	-0.255673	0.000000	-2.720590
H	-2.368061	0.000000	-2.533170
H	-2.480873	0.000000	-0.313895
H	2.378955	0.000000	-0.770608
H	1.854647	0.000000	-2.930008
H	-0.356978	0.000000	-3.798564
Cl	0.261172	0.000000	2.779103

L'CoCl ($^4A_2$) ROB3LYP/6-311+G(d) optimized geometry
E(ROB+HF-LYP) = -2069.97123273

C	-1.426772	0.000000	-1.947743
N	-1.492561	0.000000	-0.624628
Co	0.053282	0.000000	0.566964
N	1.350055	0.000000	-0.891768
C	1.038909	0.000000	-2.179461
C	-0.254516	0.000000	-2.708281
H	-2.369241	0.000000	-2.497628
H	-2.443097	0.000000	-0.272006
H	2.349645	0.000000	-0.722414
H	1.862428	0.000000	-2.895308
H	-0.355814	0.000000	-3.786178
Cl	0.257017	0.000000	2.734894

L'NiCl ($^3A_2$)
E(ROB+HF-LYP) = -2195.50197732 ROB3LYP/6-311+G(d) optimized geometry

C	-1.418936	0.000000	-1.954715
N	-1.446562	0.000000	-0.632801
Ni	0.053571	0.000000	0.570045
N	1.303338	0.000000	-0.891228
C	1.029912	0.000000	-2.184851
C	-0.256494	0.000000	-2.729328
H	-2.373120	0.000000	-2.484084
H	-2.386672	0.000000	-0.251610
H	2.298007	0.000000	-0.691863
H	1.868763	0.000000	-2.882724
H	-0.357762	0.000000	-3.806901
Cl	0.254498	0.000000	2.708088

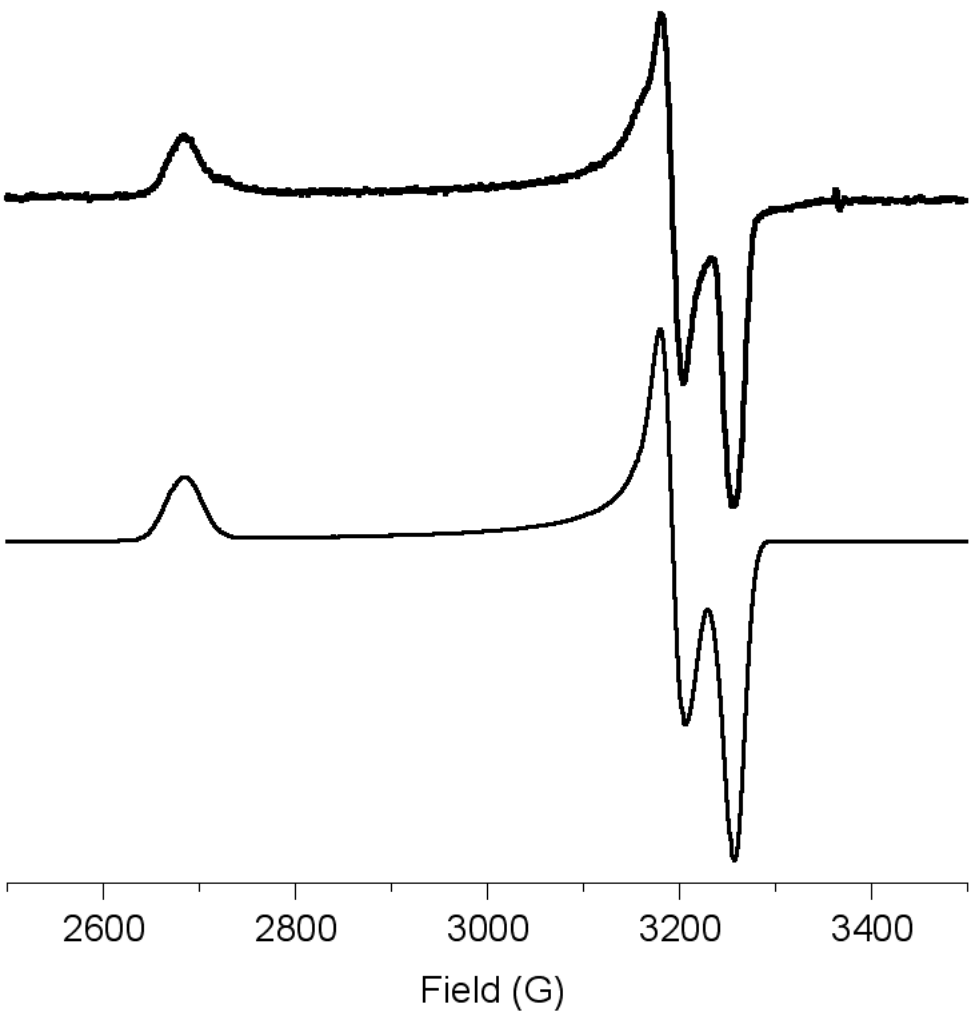
Figure S-13. Top: X-band EPR spectrum of LNi(THF), 1 mM solution in 2-methyltetrahydrofuran, glass at 77 K. Bottom: simulation from QPOWA (http://endor1.chem.nwu.edu/program1.htm)

Collection parameters:

Frequency: 9.425 GHz
microwave power: 10 mW
modulation: 100 kHz, 5 G
gain: 4K
time constant = conversion time = 82 ms

Simulation parameters:

$g_{x,y,z}$ = 2.068, 2.110, 2.510
A_N not included
$W_{x,y,z}$ = 35, 35, 75 MHz



```
new experiment

Pulse Sequence: dqcosy

 Solvent: d2o
 Temp. 30.0 C / 303.1 K
INOVA-500  "inova500"


 Relax. delay 0.400 sec
 Acq. time 0.043 sec
 Width    92699.9 Hz
 2D Width 92699.9 Hz
 24 repetitions
 2 x 512 increments
OBSERVE   H1, 499.8360615 MHz
DATA PROCESSING
 Sine bell 0.014 sec
  Shifted by 0.000 sec
F1 DATA PROCESSING
 Gauss apodization 0.026 sec
FT size 8192 x 2048
Total time 3 hr, 25 min, 0 sec
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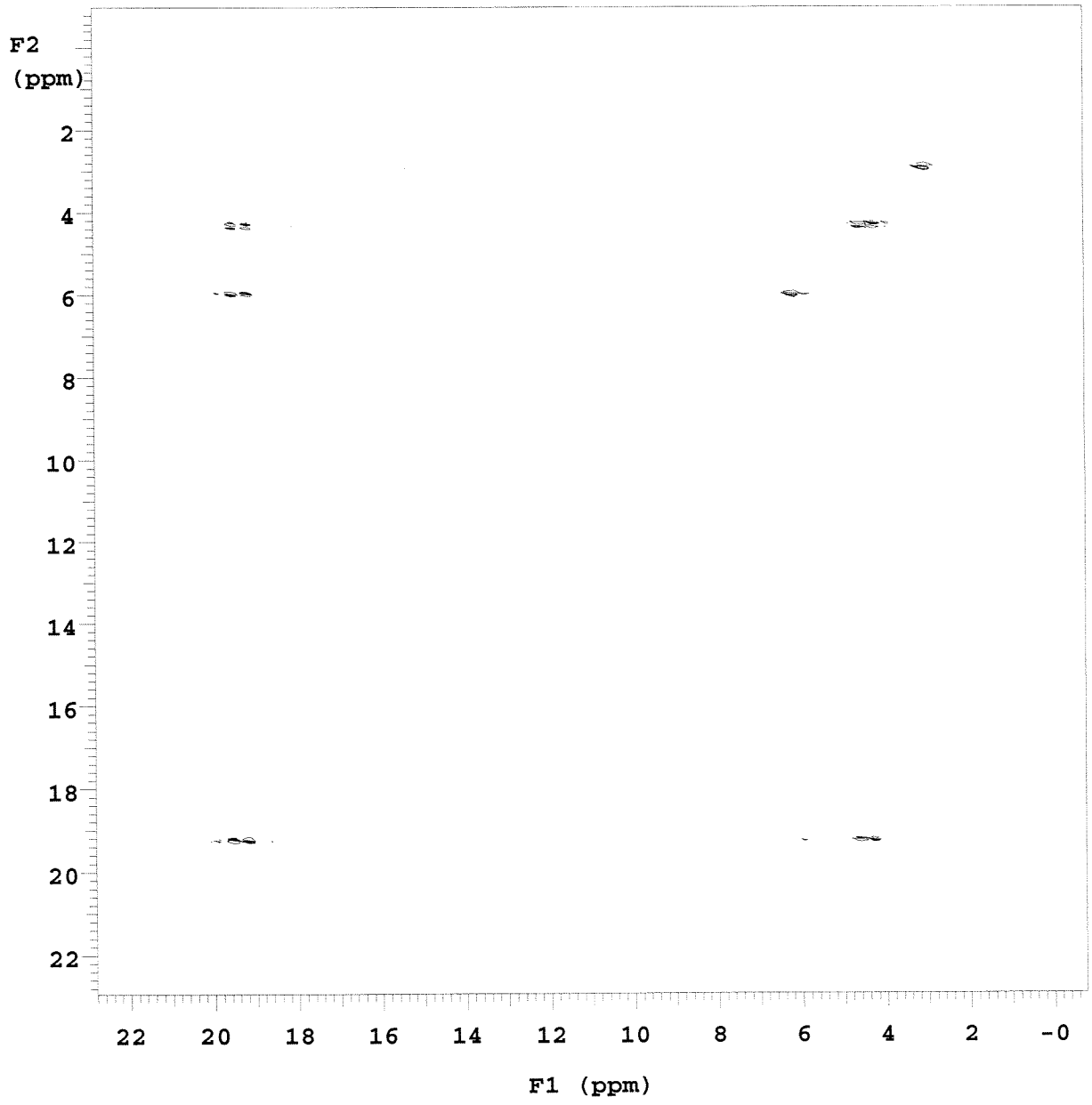

Figure S-14. A portion of the DQF-COSY spectrum (500 MHz) of LNiCl in methylene chloride-d2, showing correlation between the isopropyl methine resonance and the two inequivalent isopropyl methyl resonances.

```
new experiment

Pulse Sequence: dqcosy

 Solvent: d2o
 Temp. 30.0 C / 303.1 K
INOVA-500  "inova500"


 Relax. delay 0.400 sec
 Acq. time 0.043 sec
 Width    92699.9 Hz
 2D Width 92699.9 Hz
 24 repetitions
 2 x 512 increments
OBSERVE   H1, 499.8360615 MHz
DATA PROCESSING
 Sine bell 0.014 sec
  Shifted by 0.000 sec
F1 DATA PROCESSING
 Gauss apodization 0.026 sec
FT size 8192 x 2048
Total time 3 hr, 25 min, 0 sec
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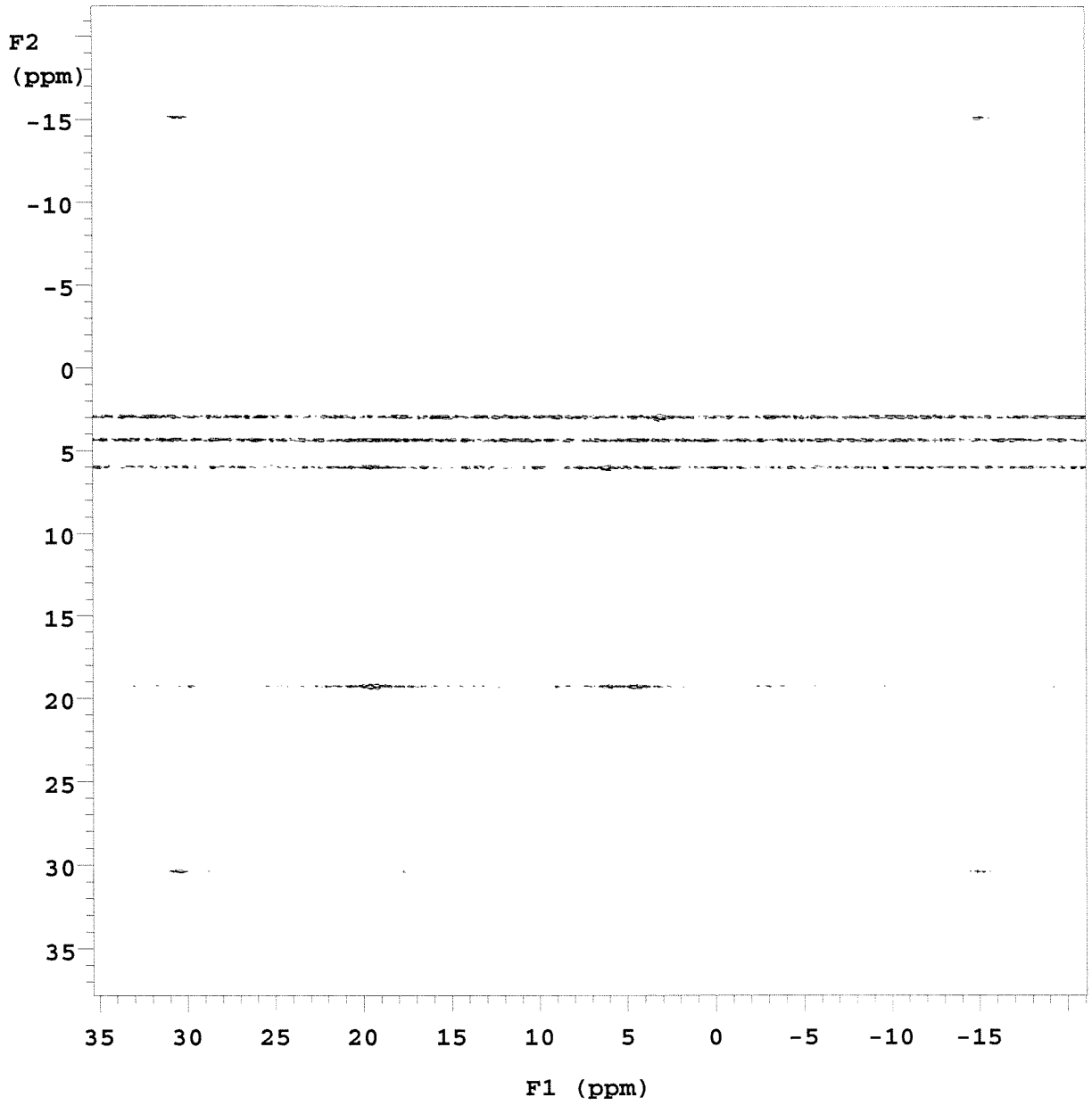

Figure S-15. A portion of the DQF-COSY spectrum (500 MHz) of LNiCl in methylene chloride-d2, showing correlation between the meta and para aryl resonances.