Stabilization of Ni^{2+} dimers in Prussian Blue derivatives built up from hexacyano Mo_6 cluster based compounds: experimental and theoretical investigations of magnetic properties

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SUPPORTING INFORMATION

Table S1. Cartesian coordinates of the $[Ni_2(NH_3)_8]^{4+}$ dimer for which the atomic position of the Ni and N atoms are extracted from the X-ray structure and the hydrogen atom positions were optimized by DFT calculations.

Atom	x	y	z
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C	0.000001	0.000002	-3.411579
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H	1.736889	1.633165	4.112336
H	2.416877	1.312987	2.675822
N	1.517065	-1.517065	3.113974
H	2.421357	-1.308029	2.687340
H	1.263510	-2.454696	2.794883
H	1.727145	-1.642464	4.113287
N	-0.000002	-0.000001	5.516598
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H	2.454660	1.264142	0.398762
H	1.306617	2.420069	0.508212
H	-1.649522	1.722900	-0.919186
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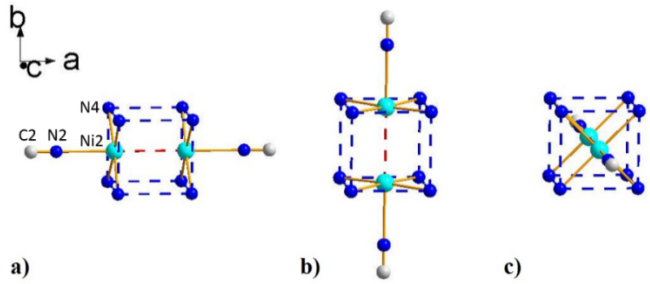


Figure S1. Representation of a Ni_2 dimer-based $[Ni_2(NH_3)_8]^{4+}$ cubic complex oriented along the a) *a* axis, b) *b* axis and c) *c* axis respectively.

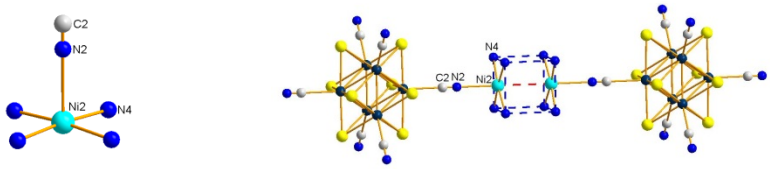


Figure S3. a) Representation of the Ni2 atom environment. b) Environment of the $[Ni_2(NH_3)_8]^{4+}$ cubic complex.

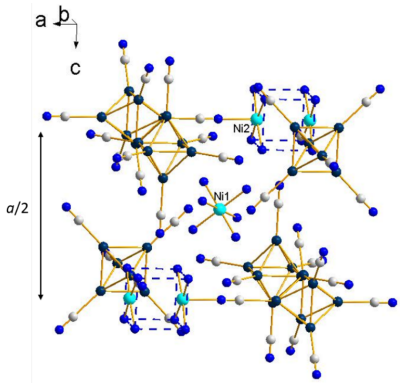


Figure S4. Representation of Ni1 environment. Inner ligands and crystallization water molecules have been omitted for clarity.

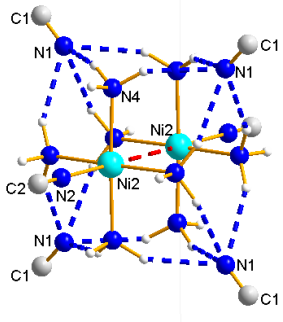


Figure S5. Representation of the $[\{Ni(CN)(NH_3)_4\}_2]^{2+}$ dimer after optimization of the hydrogen atoms positions by DFT calculations with the crystal structure environment of CN groups. It evidences that the stability of the dimer is due to hydrogen bonding between ammonia molecules and the surrounding cyanide ligands. Blue dashed lines represent the hydrogen bond network and the red dashed line represents the antiferromagnetic interaction between the monomers.

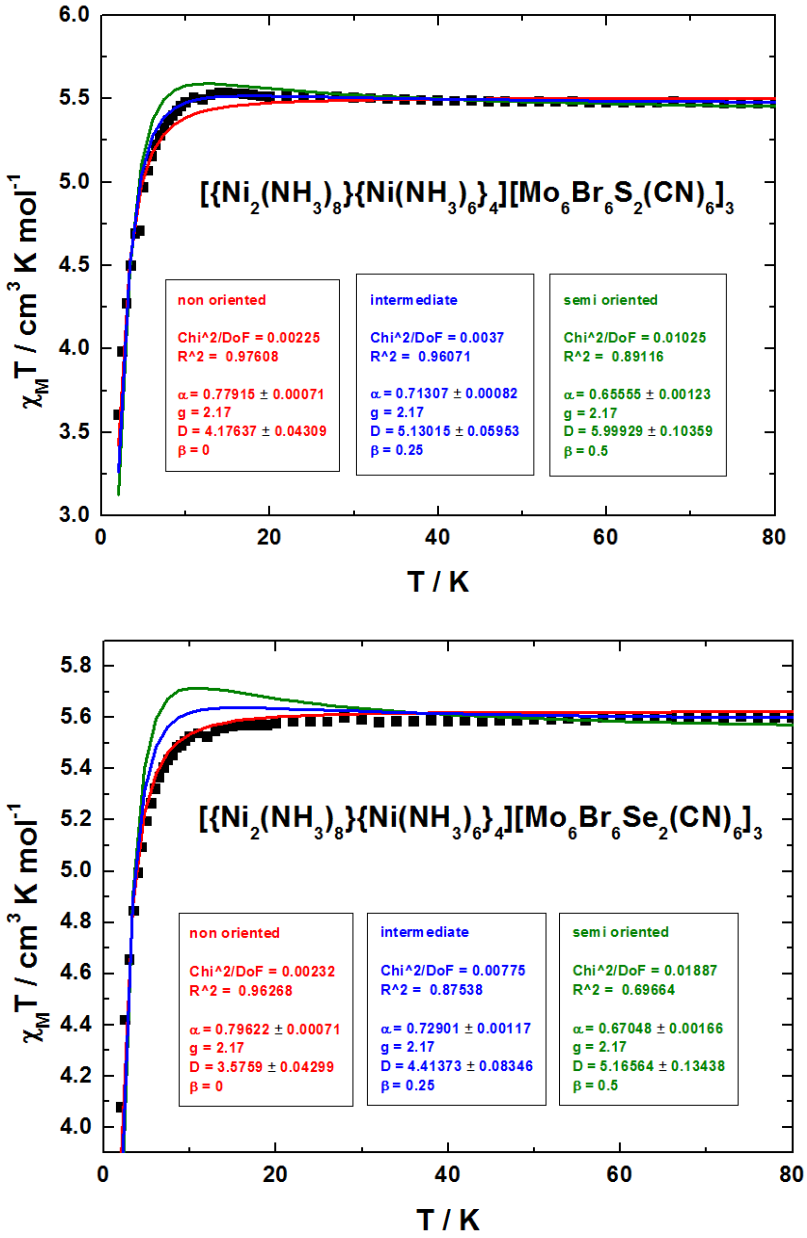
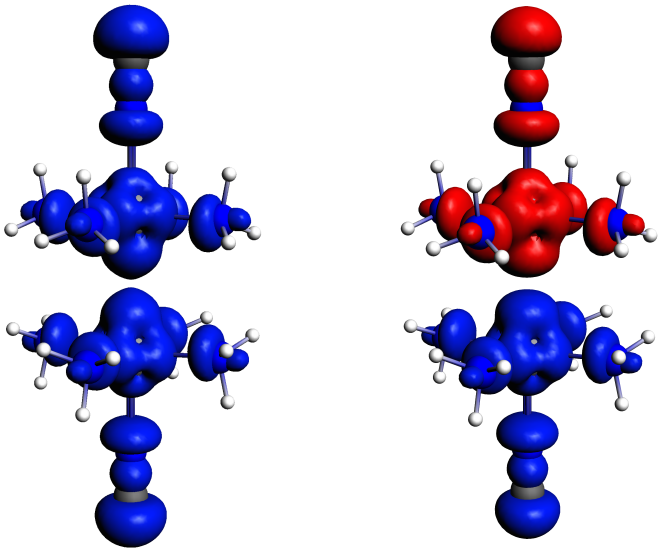


Figure S6. Thermal dependencies of $\chi_M T$ for **1** and **2** with their respective fitted curves considering only zero-field splitting effects, fixing *g* to 2.17, in three cases: non oriented microcrystalline powder, and two level of partly orientated powder (partial orientation of crystallites).



a) **b)**

Figure S7. Computed spin density plots: a) quintet spin state of $[\{Ni(CN)(NH_3)_4\}_2]^{2+}$, b) BS states of $[\{Ni(CN)(NH_3)_4\}_2]^{2+}$, (isosurface ± 0.002 e.bohr^{-3}). Only the results obtained using the B3LYP functional are given, the two other functional giving really similar features.

$[\{Ni(NH_3)_6\}_4\{Ni_2(NH_3)_8\}_1][Mo_6Br_6S_2(CN)_6]_3.12H_2O$ (1)

CSD-433371

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Br1 Mo1 S1 88.4 . 51 ?
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Br1 Mo2 Br1 89.971(4) 49_665 52_655 ?
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    shelx.res created by SHELXL-2014/7


TITL Im3m in Im-3m
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ZERR     6.00   0.0012   0.0012   0.0012    0.000    0.000    0.000
LATT   2
SYMM  - Y,   X,   Z
SYMM  - X, - Y,   Z
SYMM    Y, - X,   Z
SYMM    X, - Z,   Y
SYMM    X, - Y, - Z
SYMM    X,   Z, - Y
SYMM    Z,   Y, - X
SYMM  - X,   Y, - Z
SYMM  - Z,   Y,   X
SYMM    Z,   X,   Y
SYMM    Y,   Z,   X
SYMM  - Y, - Z,   X
SYMM    Z, - X, - Y
SYMM  - Y,   Z, - X
SYMM  - Z, - X,   Y
SYMM  - Z,   X, - Y
SYMM    Y, - Z, - X
SYMM    Y,   X, - Z
SYMM  - Y, - X, - Z
SYMM  - X,   Z,   Y
SYMM  - X, - Z, - Y
SYMM    Z, - Y,   X
SYMM  - Z, - Y, - X
SFAC  C    N    O    NI   S   BR   MO
UNIT  36 100 24 12 12 36 36
MERG   2
OMIT     0   1   3
EADP Br1 S1
EXYZ Br1 S1
DFIX NI2 N4 2.1
FMAP   2
PLAN   20
ACTA
LIST   4
L.S.  10
TEMP  -100.00
WGHT    0.099200  187.093002
EXTI    0.000381
FVAR       0.08865
MO1   7    0.427327    0.427327    0.000000    10.25000    0.02971    0.02971 =
         0.08216    0.00000    0.00000   -0.00152
MO2   7    0.500000    0.500000    0.102260    10.12500    0.05460    0.05460 =
         0.05218    0.00000    0.00000    0.00000
BR1   6    0.500000    0.355991   -0.099024    10.37500    0.05905    0.06299 =
         0.10556   -0.04460    0.00000    0.00000
S1    5    0.500000    0.355991   -0.099024    10.12500    0.05905    0.06299 =
         0.10556   -0.04460    0.00000    0.00000
NI4   4    0.250000    0.250000    0.250000    10.08333    0.09683    0.09683 =
         0.09683    0.04081    0.04081    0.04081
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         0.23648    0.00000    0.00000    0.00246
C2    1    0.500000    0.500000    0.225906    10.12500    0.24099    0.24099 =
         0.06477    0.00000    0.00000    0.00000
N2    2    0.500000    0.500000    0.271933    10.12500   -1.20000
N1    2    0.297341    0.297341    0.000000    10.25000    0.05247    0.05247 =
         0.31104    0.00000    0.00000   -0.01061
N3    2    0.292997    0.174514    0.174514    10.50000    0.18893    0.14973 =
         0.14973   -0.01395    0.05359    0.05359
NI2   4    0.500000    0.500000    0.413099    10.04167    0.17142    0.17142 =
         0.17040    0.00000    0.00000    0.00000
O1    3    0.193095    0.193095    0.000000    10.25000    0.26762    0.26762 =
         0.62927    0.00000    0.00000   -0.14207
N4    2    0.417962    0.417962    0.417962    10.16667    0.43527    0.43527 =
         0.43527   -0.12114   -0.12114   -0.12114
HKLF    4

REM  Im3m in Im-3m
REM R1 =  0.0693 for     433 Fo > 4sig(Fo)  and  0.0794 for all     512 data
REM     45 parameters refined using      1 restraints

END

WGHT      0.0923    184.9421

REM Highest difference peak  2.869,  deepest hole -1.088,  1-sigma level  0.270
Q1    1   0.5000  0.5000  0.5000  10.02083  0.05    2.87
Q2    1   0.1923  0.1923  0.1923  10.16667  0.05    1.41
Q3    1   0.5000  0.3489 -0.0664  10.50000  0.05    0.91
Q4    1   0.5000  0.3412 -0.0864  10.50000  0.05    0.89
Q5    1   0.4242  0.4242 -0.1481  10.50000  0.05    0.85
Q6    1   0.2642  0.1680  0.1680  10.50000  0.05    0.84
Q7    1   0.2798  0.1924  0.1785  11.00000  0.05    0.83
Q8    1   0.2441  0.2441  0.1785  10.50000  0.05    0.78
Q9    1   0.2433  0.1615  0.1615  10.50000  0.05    0.78
Q10   1   0.3487  0.3487 -0.0937  10.50000  0.05    0.78
Q11   1   0.3260  0.2500  0.1740  10.50000  0.05    0.76
Q12   1   0.3082  0.2147  0.2147  10.50000  0.05    0.73
Q13   1   0.3241  0.2001  0.2343  11.00000  0.05    0.70
Q14   1   0.3356  0.3356 -0.0825  10.50000  0.05    0.67
Q15   1   0.5000  0.5000  0.0538  10.12500  0.05    0.66
Q16   1   0.5000  0.5000  0.3219  10.12500  0.05    0.62
Q17   1   0.2803  0.4190  0.0000  10.50000  0.05    0.61
Q18   1   0.3219  0.1614  0.1614  10.50000  0.05    0.60
Q19   1   0.3593  0.1129  0.1129  10.50000  0.05    0.58
Q20   1   0.3156  0.3156 -0.0595  10.50000  0.05    0.52
;
_shelx_res_checksum   94699
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$[\{Ni(NH_3)_6\}_4\{Ni_2(NH_3)_8\}_1][Mo_6Br_6Se_2(CN)_6]_3.12H_2O$ (2)

CSD-433370

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 'C6 Br6 Mo6 N16.67 Ni2 O4 Se2'
_chemical_formula_weight          1700.00

loop_
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 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Ni'  'Ni'   0.3393   1.1124
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 'Se'  'Se'  -0.0929   2.2259
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Br'  'Br'  -0.2901   2.4595
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Mo'  'Mo'  -1.6832   0.6857
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_shelx_space_group_comment
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The symmetry employed for this shelxl refinement is uniquely defined
by the following loop, which should always be used as a source of
symmetry information in preference to the above space-group names.
They are only intended as comments.
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_cell_formula_units_Z             6
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_exptl_absorpt_process_details
;
  [Sheldrick, G.M. (2014). SADABS Bruker AXS Inc., Madison, Wisconsin, USA]
;
_exptl_absorpt_special_details    ?
_diffrn_ambient_temperature       298(2)
_diffrn_radiation_wavelength      0.71073
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_diffrn_measurement_device_type    'APEXII, Bruker-AXS'
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_reflns_special_details
;
 Reflections were merged by SHELXL according to the crystal
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 _reflns_Friedel_fraction is defined as the number of unique
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Br1 Br 0.500000 0.35664(8) -0.09987(9) 0.0767(5) Uani 0.75 2 d S T P . .
Se1 Se 0.500000 0.35664(8) -0.09987(9) 0.0767(5) Uani 0.25 2 d S T P . .
Ni4 Ni 0.250000 0.250000 0.250000 0.0809(14) Uani 1 12 d S T P . .
C1 C 0.3421(7) 0.3421(7) 0.000000 0.080(6) Uani 1 4 d S T P . .
C2 C 0.500000 0.500000 0.226(3) 0.126(14) Uani 1 8 d S T P . .
N2 N 0.500000 0.500000 0.283(2) 0.27(4) Uani 1 8 d S T P . .
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N3 N 0.2918(11) 0.1734(7) 0.1734(7) 0.143(7) Uani 1 2 d S T P . .
Ni2 Ni 0.500000 0.500000 0.4130(11) 0.146(7) Uani 0.3334 8 d DS T P . .
O1 O 0.1940(11) 0.1940(11) 0.000000 0.30(2) Uani 1 4 d S T P . .
N4 N 0.4155(16) 0.4155(16) 0.4155(16) 0.28(3) Uani 1 6 d DS T P . .

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Mo2 0.0547(7) 0.0547(7) 0.0542(11) 0.000 0.000 0.000
Br1 0.0631(8) 0.0620(8) 0.1048(12) -0.0371(7) 0.000 0.000
Se1 0.0631(8) 0.0620(8) 0.1048(12) -0.0371(7) 0.000 0.000
Ni4 0.0809(14) 0.0809(14) 0.0809(14) 0.0299(17) 0.0299(17) 0.0299(17)
C1 0.038(5) 0.038(5) 0.16(2) 0.000 0.000 0.004(7)
C2 0.14(2) 0.14(2) 0.10(3) 0.000 0.000 0.000
N2 0.38(6) 0.38(6) 0.05(2) 0.000 0.000 0.000
```

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N1 0.051(6) 0.051(6) 0.26(3) 0.000 0.000 -0.002(8)
N3 0.19(2) 0.118(8) 0.118(8) -0.012(10) 0.056(9) 0.056(9)
Ni2 0.166(11) 0.166(11) 0.107(13) 0.000 0.000 0.000
O1 0.18(2) 0.18(2) 0.53(7) 0.000 0.000 -0.08(3)
N4 0.28(3) 0.28(3) 0.28(3) 0.04(3) 0.04(3) 0.04(3)

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;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
;

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Mo1 Br1 2.5884(12) 50_565 ?
Mo1 Mo2 2.6342(17) 49_665 ?
Mo1 Mo2 2.6342(17) . ?
Mo1 Mo1 2.6435(17) 50_565 ?
Mo1 Mo1 2.6435(17) 2_655 ?
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Ni4 N3 2.111(15) 11 ?
Ni4 N3 2.111(15) 83 ?
Ni4 N3 2.112(15) . ?
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C2 N2 1.05(5) . ?
N2 Ni2 2.36(4) . ?
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Ni2 Ni2 2.24(3) 5_565 ?
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C1 Mo1 Br1 90.56(3) . 51 ?
Br1 Mo1 Br1 89.14(7) . 51 ?
Br1 Mo1 Br1 178.87(7) 4_565 51 ?
C1 Mo1 Br1 90.56(3) . 50_565 ?
Br1 Mo1 Br1 178.87(7) . 50_565 ?
Br1 Mo1 Br1 89.14(7) 4_565 50_565 ?
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Br1 Mo1 Mo2 119.18(4) 50_565 49_665 ?
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Br1 Mo2 Br1 178.26(12) 51 49_665 ?
Br1 Mo2 Br1 89.987(2) 50_565 49_665 ?
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Br1 Mo2 Mo1 59.18(4) 51 2_655 ?
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Br1 Mo2 Mo1 119.41(6) 49_665 2_655 ?
Mo1 Mo2 Mo1 60.23(4) . 2_655 ?
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C2 Mo2 Mo1 134.80(4) . 49_665 ?
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Br1 Mo2 Mo1 119.41(6) 50_565 49_665 ?
Br1 Mo2 Mo1 59.18(4) 49_665 49_665 ?
Mo1 Mo2 Mo1 90.40(8) . 49_665 ?
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```

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Ni2 Ni2 Ni2 60.001(1) 53_656 8_556 ?
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Ni2 N4 Ni2 62.0(16) 8_556 53_656 ?

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_refine_diff_density_rms    0.155

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TITL Im3m in Im-3m
    shelx.res
    created by SHELXL-2017/1 at 15:05:50 on 20-Jul-2017
CELL  0.71073  18.1877  18.1877  18.1877   90.000   90.000   90.000
ZERR     6.00   0.0019   0.0019   0.0019    0.000    0.000    0.000
LATT   2
SYMM  - Y,   X,   Z
SYMM  - X, - Y,   Z
SYMM    Y, - X,   Z
SYMM    X, - Z,   Y
SYMM    X, - Y, - Z
SYMM    X,   Z, - Y
SYMM    Z,   Y, - X
SYMM  - X,   Y, - Z
SYMM  - Z,   Y,   X
SYMM    Z,   X,   Y
SYMM    Y,   Z,   X
SYMM  - Y, - Z,   X
SYMM    Z, - X, - Y
SYMM  - Y,   Z, - X
SYMM  - Z, - X,   Y
SYMM  - Z,   X, - Y
SYMM    Y, - Z, - X
SYMM    Y,   X, - Z
SYMM  - Y, - X, - Z
SYMM  - X,   Z,   Y
SYMM  - X, - Z, - Y
SYMM    Z, - Y,   X
SYMM  - Z, - Y, - X
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UNIT  36 100 24 12 12 36 36
MERG   2
OMIT     0   1   3
EADP Br1 Se1
EXYZ Br1 Se1
DFIX 2.1 0.05  NI2 N4
FMAP   2
PLAN   20
ACTA
LIST   4
L.S.  10
TEMP  -100.00
WGHT    0.053600   91.586395
FVAR       0.08910
MO1   7    0.427330    0.427330    0.000000    10.25000    0.03277    0.03277 =
         0.07605    0.00000    0.00000   -0.00116
MO2   7    0.500000    0.500000    0.102057    10.12500    0.05473    0.05473 =
         0.05416    0.00000    0.00000    0.00000
BR1   6    0.500000    0.356641   -0.099874    10.37500    0.06311    0.06201 =
         0.10484   -0.03709    0.00000    0.00000
SE1   5    0.500000    0.356641   -0.099874    10.12500    0.06311    0.06201 =
         0.10484   -0.03709    0.00000    0.00000
NI4   4    0.250000    0.250000    0.250000    10.08333    0.08091    0.08091 =
         0.08091    0.02988    0.02988    0.02988
C1    1    0.342132    0.342132    0.000000    10.25000    0.03849    0.03849 =
         0.16269    0.00000    0.00000    0.00381
C2    1    0.500000    0.500000    0.225772    10.12500    0.13784    0.13784 =
         0.10259    0.00000    0.00000    0.00000
N2    2    0.500000    0.500000    0.283290    10.12500    0.38171    0.38171 =
         0.05099    0.00000    0.00000    0.00000
N1    2    0.298063    0.298063    0.000000    10.25000    0.05133    0.05133 =
         0.25986    0.00000    0.00000   -0.00228
N3    2    0.291823    0.173420    0.173420    10.50000    0.19340    0.11803 =
         0.11803   -0.01174    0.05586    0.05586
NI2   4    0.500000    0.500000    0.413036    10.04167    0.16585    0.16585 =
         0.10671    0.00000    0.00000    0.00000
O1    3    0.194043    0.194043    0.000000    10.25000    0.18156    0.18156 =
         0.52794    0.00000    0.00000   -0.07539
N4    2    0.415548    0.415548    0.415548    10.16667    0.28174    0.28174 =
         0.28174    0.03542    0.03542    0.03542
HKLF    4



REM  Im3m in Im-3m
REM R1 =  0.0545 for     577 Fo > 4sig(Fo)  and  0.0996 for all     906 data
REM     46 parameters refined using      1 restraints

END

WGHT      0.0548     61.4444

REM Highest difference peak  1.786,  deepest hole -1.025,  1-sigma level  0.155
Q1    1   0.5000  0.5000  0.5000  10.02083  0.05    1.79
Q2    1   0.1940  0.1940  0.1940  10.16667  0.05    1.10
Q3    1   0.4284  0.5000  0.0000  10.25000  0.05    0.96
Q4    1   0.4220  0.5000  0.4220  10.25000  0.05    0.93
Q5    1   0.2777  0.4292  0.0000  10.50000  0.05    0.54
Q6    1   0.5000  0.5000  0.1749  10.12500  0.05    0.51
Q7    1   0.4623  0.3892  0.0000  10.50000  0.05    0.50
Q8    1   0.4710  0.4710  0.0000  10.25000  0.05    0.48
Q9    1   0.2021  0.2022  0.2359  10.50000  0.05    0.48
Q10   1   0.4261  0.3718 -0.1113  11.00000  0.05    0.47
Q11   1   0.5000  0.3968 -0.1379  10.50000  0.05    0.46
Q12   1   0.4281  0.4281  0.0782  10.50000  0.05    0.46
Q13   1   0.4290  0.5710  0.1434  10.50000  0.05    0.45
Q14   1   0.4428  0.4428  0.0255  10.50000  0.05    0.44
Q15   1   0.3583  0.4217  0.0000  10.50000  0.05    0.43
Q16   1   0.3473  0.4076  0.5000  10.50000  0.05    0.42
Q17   1   0.4288  0.5712  0.3120  10.50000  0.05    0.42
Q18   1   0.3237  0.4611  0.0000  10.50000  0.05    0.42
Q19   1   0.3437  0.2093  0.2093  10.50000  0.05    0.41
Q20   1   0.5000  0.5000  0.2968  10.12500  0.05    0.41
;
_shelx_res_checksum   66612
```