Synthesis of $(Me_4N)_2[Cr(N)(NCS)_4]$

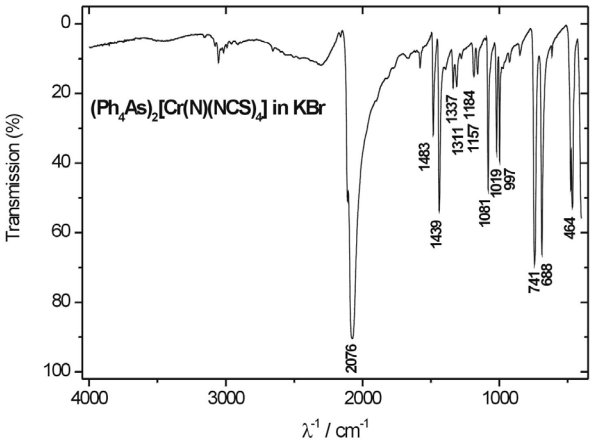
Tetramethylammoniumhydroxide in methanol (25% w/w, Sigma) and ammoniumthiocyanate (Riedel-de Haën) were used as received. Solvents: diethyl ether (Lab-Scan), acetonitrile (Lab-Scan), dichlormethane (Lab-Scan) and methanol (Lab-Scan) were HPLC grade and were used without purification.

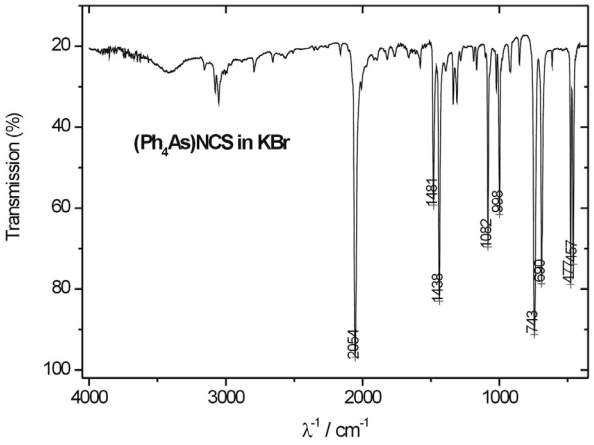
Synthesis of tetramethylammoniumthiocyanate. To a stirred solution of ammoniumthiocyanate (11.513g; 0.15mol) in water (50ml), was added tetramethylammoniumhydroxide (55.1g; 0.15mol) in methanol with precipitation of a white product commencing immediately. This was redissolved by heating and addition of methanol. Slow cooling yielded white needle shaped crystal. Yield: 12.68g (63.9%)

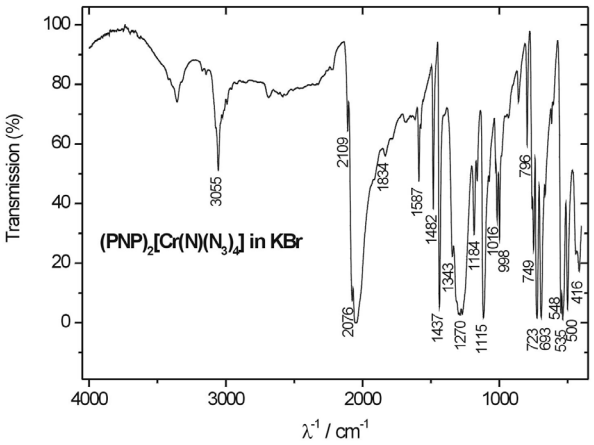
Synthesis of tetramethylammoniumnitridotetrakisisothiocyanatochromate(V) by nitrogen atom transfer.
This salt can be synthesized without isolating $[Cr(N)Cl_4]^{2-}$: The following procedure (cf. T. Birk, J. Bendix *Inorg. Chem.* **2003**, 42, 7608) was used for preparing a solution containing $\{Cr{\equiv}N\}^{2+}$ complexed by labile auxiliary ligands: $CrCl_3(THF)_3$ (0.906 g; 2.42 mmol) was dissolved in acetonitrile (20 ml) to give a purple solution. Addition of solid Mn(N)(salen) (0.810 g; 2.42 mmol) was accompanied by an immediate color change to yield a dark brown solution with suspended solid material. The reaction mixture was stirred for 30 min. under a N_2 atmosphere and filtered to give a dark brown crystalline precipitate and a yellow-brown solution. To the filtrate, a solution of $(Me_4N)NCS$ (2.560g; 19.36mmol) dissolved in methanol (10ml) was added rapidly. After 2 min. diethylether (100ml) was added to the solution causing immediate precipitation of a yellow-green product. After filtration and washing with diethylether (avoiding drying of the product), the product was extracted with acetonitrile (40ml).Dichloromethane (500ml) was added to the extract, and the resulting solution was left for crystallisation. Yield: 0.360g (33.3%) of green crystals.
Anal. Calcd for $C_{12}H_{24}N_7S_4Cr$: C, 32.27; H, 5.42; N, 21.95. Found: C, 31.37; H, 5.27; N, 20.99.

IR spectra

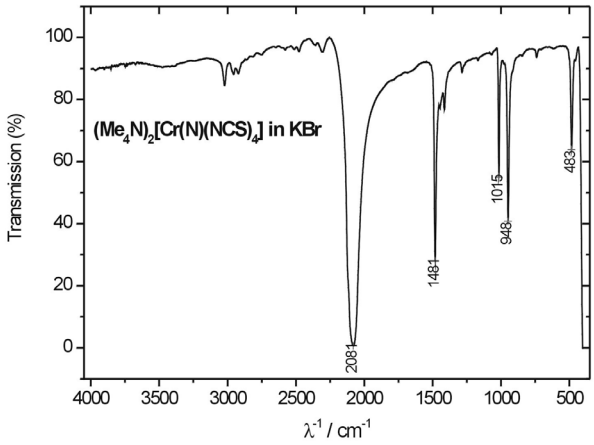
Nitrido complexes:

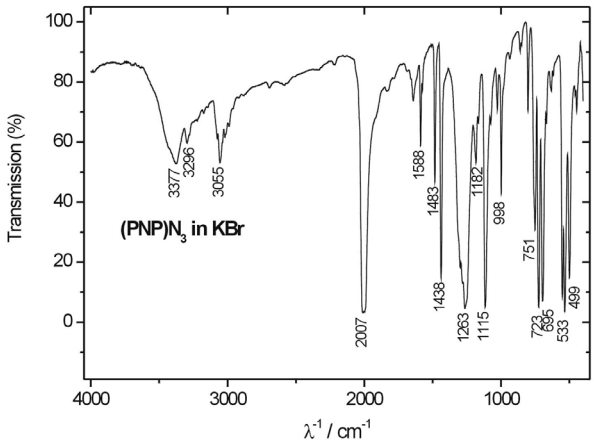






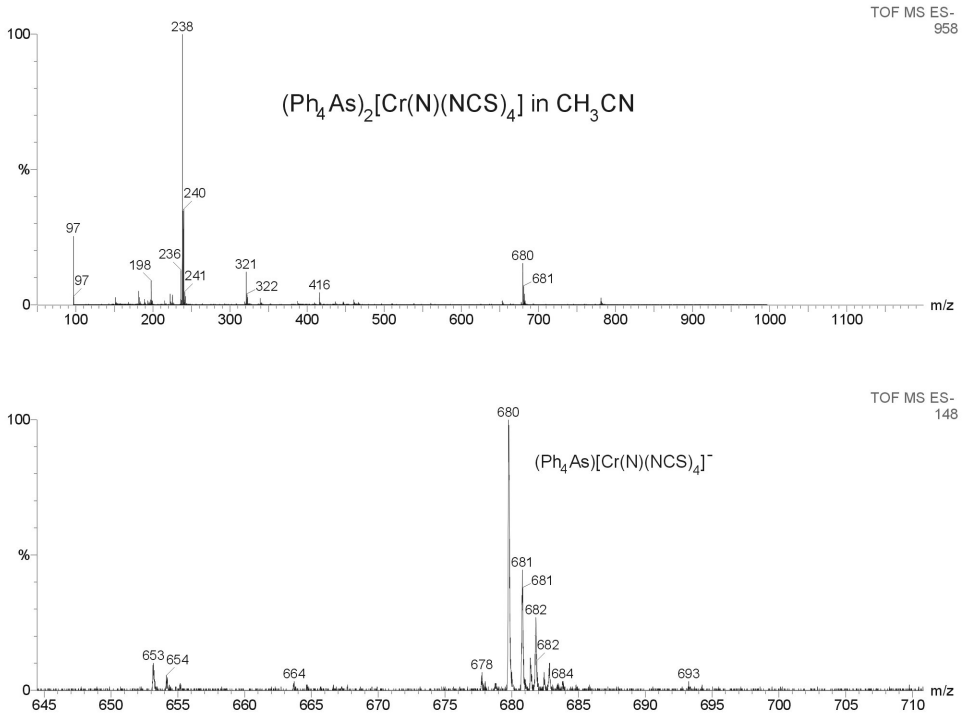
Reference spectra:



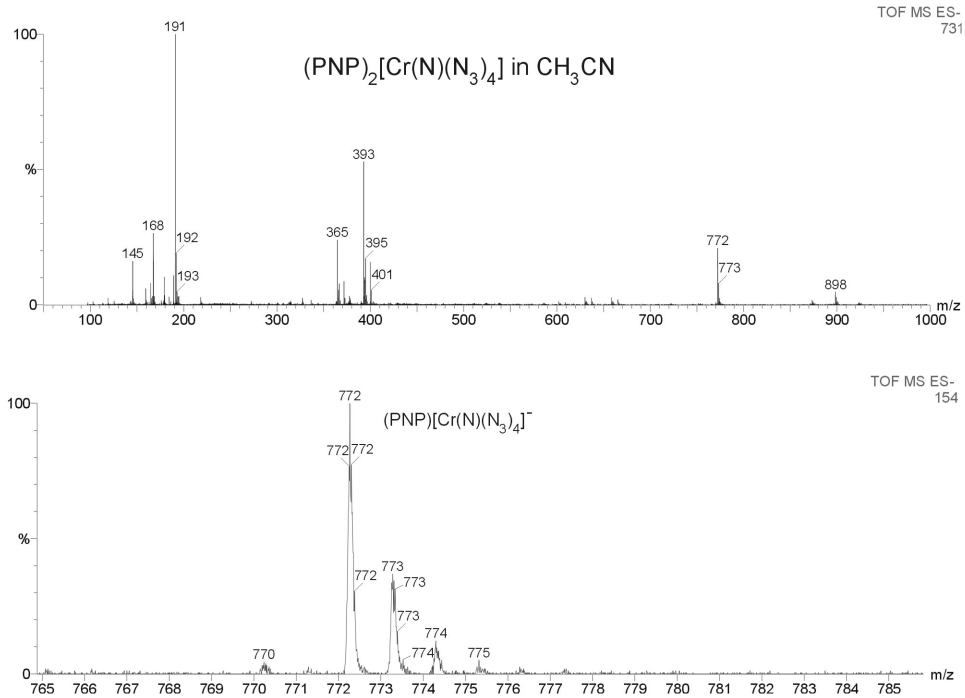


Mass spectrometric data

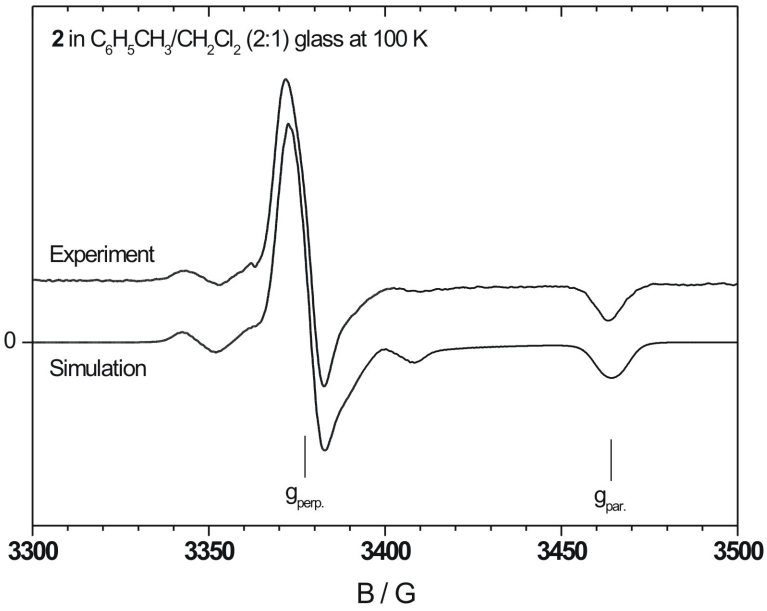
1:



2:



Low temperature EPR spectrum of 2



Simulation parameters:

$g_{\perp}$ =1.9895, $g_{\parallel}$ =1.9385, $A_{\perp}^{Cr}$ =17.5·10^{-4} cm^{-1},
$A_{\perp}^{N(nitrido)}$ =2.90·10^{-4} cm^{-1}, $A_{\parallel}^{N(nitrido)}$ =2.0·10^{-4} cm^{-1},
$A^{N(azido)}$ =1.20·10^{-4} cm^{-1}, line width (FWHH)=1.5 G.

Simulation software: SIM & ASIM, H. Weihe Univ. of Copenhagen (1992-2004): C. J. H. Jacobsen; E. Pedersen;J.. Villadsen; H. Weihe *Inorg. Chem.* 1993, **32**, 1216.

Some input and results from DFT calculations:

DFT calculations were performed with the Amsterdam Density Functional (ADF) program suite version 2002.03.[i,ii,iii] Slater-type orbital basis sets of triple-ζ quality for the valence orbitals were employed with polarization functions on the ligand atoms and additional valence p orbitals on Cr (ADF basis set TZ2P). Calculations were all-electron calculations with no frozen cores. The GGA calculations employed the exchange functional proposed by Becke (B88)[iv] and the correlation functional due to Perdew (P86)[v]. No use of symmetry was made. All charge and spin densities were based on Mulliken analyses.[vi] Transition energies were evaluated by Slater's transition state method.[vii]

(i) ADF 2.3.0, Theoretical Chemistry, Vrije Universitet , Amsterdam
(ii) Baerends, E. J. et.al. *Chem. Phys.* **1973**, *2*, 41.
(iii) te Velde, G.; Baerends, E. J. *J. Comp. Phys.* **1992**, *99*, 84.
(iv) Becke, A. D. *Phys. Rev.* **1988***, A38*, 3098.
(v) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822; Perdew, J. P. *Phys. Rev.* **1987**, *B34*, 7406 (erratum).
(vi) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.
(vii) Slater, J.C. *Quantum Theory of Molecules and Solids* McGraw-Hill, NY, **1974**

Input:

```
title [Cr(N)(NCS)4]2- all electron geometry opt

atoms cartesian
  N        0.12894       -0.00001       -2.01380
 Cr        0.02445        0.00000       -0.47213
  N       -1.92198        0.00010       -0.18292
  N        0.00070        1.92889       -0.01355
  N        0.00051       -1.92889       -0.01355
  C       -3.05395        0.00015        0.08742
  N        1.93757       -0.00010        0.06170
  C        3.09572       -0.00015        0.19879
  C       -0.04459       -3.06625        0.22020
  C       -0.04429        3.06625        0.22020
  S        4.70574       -0.00023        0.38561
  S       -4.62022        0.00023        0.48375
  S       -0.10454       -4.66278        0.51914
  S       -0.10407        4.66279        0.51914
end

charge -2 1

unrestricted

symmetry NOSYM

BASIS
  TYPE TZ2P
  CORE NONE
END

xc
  LDA vwn
  GGA becke perdew
```

```
end

geometry
end

noprint Computation
noprint Scf
print OrbPop

EPRINT
SFO NOEIG, NOOVL
ORBPOPER -10 1
SUBEND
END

end input
```

Output (partial):

```
Coordinates (Cartesian)
 ======================

   Atom                    bohr                                  angstrom                Geometric Variables
                 X           Y           Z             X           Y           Z       (0:frozen, *:LT par.)
 ------------------------------------------------------------------------------------------------------------
   1 N        0.055171   -0.000213   -3.853271       0.029195   -0.000113   -2.039063      1       2       3
   2 Cr       0.020041   -0.000066   -0.954385       0.010605   -0.000035   -0.505038      4       5       6
   3 N       -3.644858    0.000420   -0.145448      -1.928775    0.000222   -0.076968      7       8       9
   4 N       -0.000796    3.642142   -0.065751      -0.000421    1.927338   -0.034794     10      11      12
   5 N       -0.001706   -3.642185   -0.066030      -0.000903   -1.927361   -0.034941     13      14      15
   6 C       -5.849511    0.000478    0.230437      -3.095427    0.000253    0.121942     16      17      18
   7 N        3.662964   -0.000611   -0.063833       1.938357   -0.000323   -0.033779     19      20      21
   8 C        5.874112   -0.000484    0.272552       3.108445   -0.000256    0.144228     22      23      24
   9 C       -0.034079   -5.821078    0.436657      -0.018034   -3.080381    0.231069     25      26      27
  10 C       -0.033210    5.821145    0.436393      -0.017574    3.080416    0.230929     28      29      30
  11 S        8.918265   -0.000231    0.749505       4.719341   -0.000122    0.396621     31      32      33
  12 S       -8.885932    0.000492    0.760263      -4.702232    0.000260    0.402314     34      35      36
  13 S       -0.075451   -8.825336    1.121176      -0.039927   -4.670165    0.593301     37      38      39
  14 S       -0.074826    8.825366    1.121247      -0.039596    4.670181    0.593338     40      41      42
 ------------------------------------------------------------------------------------------


========================================
 M U L L I K E N   P O P U L A T I O N S
 ========================================

 The survey below gives for each atom:
 a) the total charge (Z minus electrons)
 b) the net spin polarization (nr of electrons spin-A minus spin-B)
 c) for each spin the atomic electron valence density (integrated) per L-value.

 Atom              Charge     Spin density          S         P         D         F
 ----              ------     ------------        ------    ------    ------    ------
 1 N              -0.2985         -0.2409    A:   1.9312    1.5770    0.0181    0.0025
                                             B:   1.9358    1.8155    0.0162    0.0021
 2 Cr              0.8663          1.1072    A:   3.0834    6.2171    2.7970    0.0229
                                             B:   3.0470    6.1859    1.7567    0.0237
 3 N              -0.2780         -0.0248    A:   1.7813    1.8190    0.0235    0.0029
                                             B:   1.7870    1.8413    0.0202    0.0028
 4 N              -0.2774         -0.0251    A:   1.7812    1.8186    0.0235    0.0029
                                             B:   1.7870    1.8413    0.0202    0.0028
 5 N              -0.2777         -0.0251    A:   1.7813    1.8187    0.0235    0.0029
                                             B:   1.7870    1.8414    0.0202    0.0028
 6 C               0.0604          0.0210    A:   1.5805    1.3501    0.0455    0.0043
                                             B:   1.5805    1.3293    0.0452    0.0043
 7 N              -0.2793         -0.0250    A:   1.7819    1.8189    0.0235    0.0029
                                             B:   1.7876    1.8415    0.0202    0.0028
 8 C               0.0613          0.0216    A:   1.5803    1.3502    0.0455    0.0043
                                             B:   1.5802    1.3288    0.0452    0.0043
```

9 C	0.0589	0.0215	A:	1.5809	1.3506	0.0455	0.0043
			B:	1.5809	1.3294	0.0452	0.0043
10 C	0.0586	0.0215	A:	1.5810	1.3507	0.0455	0.0043
			B:	1.5810	1.3295	0.0452	0.0043
11 S	-0.4237	0.0370	A:	2.9275	5.2555	0.0402	0.0072
			B:	2.9268	5.2194	0.0397	0.0073
12 S	-0.4244	0.0368	A:	2.9276	5.2558	0.0401	0.0072
			B:	2.9269	5.2198	0.0397	0.0073
13 S	-0.4232	0.0371	A:	2.9275	5.2554	0.0401	0.0072
			B:	2.9268	5.2192	0.0397	0.0073
14 S	-0.4232	0.0371	A:	2.9274	5.2554	0.0401	0.0072
			B:	2.9268	5.2192	0.0397	0.0073

*** SPIN 1 ***

E(eV)	Occ	MO	%	SFO (first member)	E(eV)	Occ	Fragment
.							
.							
.							
0.012	1.00	71 A	21.51%	2 P:z	-7.116	1.33	11 S
			17.31%	2 P:z	-7.116	1.33	14 S
			17.31%	2 P:z	-7.116	1.33	13 S
			14.14%	2 P:z	-7.116	1.33	12 S
			7.29%	1 P:z	-7.213	1.00	5 N
			5.80%	1 P:z	-7.213	1.00	3 N
			5.80%	1 P:z	-7.213	1.00	4 N
			4.74%	1 P:z	-7.213	1.00	2 N
0.099	1.00	72 A	27.57%	2 P:z	-7.116	1.33	14 S
			27.57%	2 P:z	-7.116	1.33	13 S
			9.46%	1 P:z	-7.213	1.00	3 N
			9.46%	1 P:z	-7.213	1.00	4 N
			5.50%	1 P:y	-7.213	1.00	1 N
			5.44%	2 P:y	-7.116	1.33	11 S
			4.17%	2 P:y	-7.116	1.33	12 S
			1.95%	1 P:y	-7.213	1.00	5 N
			1.49%	1 P:y	-7.213	1.00	2 N
			1.35%	1 D:yz	-2.737	1.00	6 Cr
			1.27%	2 P:y	-7.116	1.33	14 S
			1.27%	2 P:y	-7.116	1.33	13 S
0.104	1.00	73 A	33.62%	2 P:z	-7.116	1.33	12 S
			24.92%	2 P:z	-7.116	1.33	11 S
			11.68%	1 P:z	-7.213	1.00	2 N
			8.72%	1 P:z	-7.213	1.00	5 N
			5.40%	1 P:x	-7.213	1.00	1 N
			3.55%	2 P:x	-7.116	1.33	13 S
			3.55%	2 P:x	-7.116	1.33	14 S
			1.48%	1 D:xz	-2.737	1.00	6 Cr
			1.29%	1 P:x	-7.213	1.00	4 N
			1.29%	1 P:x	-7.213	1.00	3 N
0.207	1.00	74 A	20.07%	2 P:y	-7.116	1.33	12 S
			17.87%	2 P:x	-7.116	1.33	14 S
			17.86%	2 P:x	-7.116	1.33	13 S
			15.76%	2 P:y	-7.116	1.33	11 S
			7.30%	1 P:y	-7.213	1.00	2 N
			6.52%	1 P:x	-7.213	1.00	3 N
			6.52%	1 P:x	-7.213	1.00	4 N
			5.75%	1 P:y	-7.213	1.00	5 N
0.809	1.00	75 A	48.98%	1 D:xy	-2.737	1.00	6 Cr
			8.17%	2 P:y	-7.116	1.33	12 S
			8.15%	2 P:y	-7.116	1.33	11 S
			8.08%	2 P:x	-7.116	1.33	13 S
			8.07%	2 P:x	-7.116	1.33	14 S
			2.79%	2 D:xy	11.078	0.00	6 Cr
			2.48%	1 P:y	-7.213	1.00	2 N
			2.48%	1 P:y	-7.213	1.00	5 N
			2.43%	1 P:x	-7.213	1.00	4 N

			2.43%	1	P:x	-7.213	1.00	3 N
			1.22%	1	P:y	-5.392	0.67	8 C
			1.19%	1	P:x	-5.392	0.67	9 C
			1.19%	1	P:x	-5.392	0.67	10 C
			1.17%	1	P:y	-5.392	0.67	7 C
3.500	0.00	76 A	46.39%	1	P:x	-7.213	1.00	1 N
			40.85%	1	D:xz	-2.737	1.00	6 Cr
			3.71%	2	D:xz	11.078	0.00	6 Cr
			1.39%	1	P:z	-5.392	0.67	8 C
			1.35%	1	P:z	-5.392	0.67	7 C
			1.25%	2	S	-18.690	2.00	2 N
3.505	0.00	77 A	46.31%	1	P:y	-7.213	1.00	1 N
			40.77%	1	D:yz	-2.737	1.00	6 Cr
			3.75%	2	D:yz	11.078	0.00	6 Cr
			1.60%	1	P:z	-5.392	0.67	9 C
			1.59%	1	P:z	-5.392	0.67	10 C
			1.04%	2	S	-18.690	2.00	4 N
			1.03%	2	S	-18.690	2.00	3 N
3.573	0.00	78 A	60.68%	1	D:x2-y2	-2.737	1.00	6 Cr
			8.29%	2	D:x2-y2	11.078	0.00	6 Cr
			3.36%	2	S	-18.690	2.00	5 N
			3.10%	2	S	-18.690	2.00	3 N
			3.10%	2	S	-18.690	2.00	4 N
			2.94%	2	S	-18.690	2.00	2 N
			2.10%	1	P:x	-7.213	1.00	5 N
			1.84%	1	P:y	-7.213	1.00	3 N
			1.84%	1	P:y	-7.213	1.00	4 N
			1.81%	1	P:x	-7.213	1.00	2 N
3.905	0.00	79 A	22.83%	1	P:z	-7.213	1.00	1 N
			19.15%	1	D:z2	-2.737	1.00	6 Cr
			9.70%	3	P:z	-0.116	0.00	6 Cr
			6.38%	1	P:z	-5.392	0.67	8 C
			5.98%	1	P:z	-5.392	0.67	10 C
			5.98%	1	P:z	-5.392	0.67	9 C
			5.90%	1	P:z	-5.392	0.67	7 C
			3.02%	2	P:z	-7.116	1.33	11 S
			2.81%	2	P:z	-7.116	1.33	12 S
			2.76%	2	P:z	-7.116	1.33	14 S
			2.76%	2	P:z	-7.116	1.33	13 S
			1.31%	5	S	1.359	0.00	6 Cr
			1.16%	1	P:z	-7.213	1.00	5 N
			1.04%	1	P:z	-7.213	1.00	2 N
			1.01%	1	P:z	-7.213	1.00	3 N
			1.01%	1	P:z	-7.213	1.00	4 N

*** SPIN 2 ***

E(eV)	Occ	MO	%	SFO (first member)	E(eV)	Occ	Fragment
.							
.							
.							
0.017	1.00	71 A	20.36%	2 P:z	-7.116	1.33	11 S
			17.29%	2 P:z	-7.116	1.33	14 S
			17.27%	2 P:z	-7.116	1.33	13 S
			15.06%	2 P:z	-7.116	1.33	12 S
			6.90%	1 P:z	-7.213	1.00	5 N
			5.81%	1 P:z	-7.213	1.00	3 N
			5.81%	1 P:z	-7.213	1.00	4 N
			5.09%	1 P:z	-7.213	1.00	2 N
0.099	1.00	72 A	23.55%	2 P:z	-7.116	1.33	14 S
			23.55%	2 P:z	-7.116	1.33	13 S
			10.01%	2 P:y	-7.116	1.33	11 S
			8.53%	2 P:y	-7.116	1.33	12 S
			8.04%	1 P:z	-7.213	1.00	3 N
			8.04%	1 P:z	-7.213	1.00	4 N
			5.54%	1 P:y	-7.213	1.00	1 N

			3.59%	1	P:y	-7.213	1.00	5 N
			3.04%	1	P:y	-7.213	1.00	2 N
			1.06%	2	P:y	-7.116	1.33	14 S
			1.05%	2	P:y	-7.116	1.33	13 S
0.103	1.00	73 A	30.19%	2	P:z	-7.116	1.33	12 S
			21.86%	2	P:z	-7.116	1.33	11 S
			10.47%	1	P:z	-7.213	1.00	2 N
			7.64%	1	P:z	-7.213	1.00	5 N
			7.04%	2	P:x	-7.116	1.33	13 S
			7.04%	2	P:x	-7.116	1.33	14 S
			5.70%	1	P:x	-7.213	1.00	1 N
			2.54%	1	P:x	-7.213	1.00	4 N
			2.54%	1	P:x	-7.213	1.00	3 N
0.248	1.00	74 A	20.02%	2	P:y	-7.116	1.33	12 S
			17.74%	2	P:x	-7.116	1.33	14 S
			17.73%	2	P:x	-7.116	1.33	13 S
			15.93%	2	P:y	-7.116	1.33	11 S
			7.37%	1	P:y	-7.213	1.00	2 N
			6.56%	1	P:x	-7.213	1.00	3 N
			6.55%	1	P:x	-7.213	1.00	4 N
			5.89%	1	P:y	-7.213	1.00	5 N
2.199	0.00	75 A	68.58%	1	D:xy	-2.737	1.00	6 Cr
			3.95%	2	P:y	-7.116	1.33	11 S
			3.93%	2	P:x	-7.116	1.33	13 S
			3.93%	2	P:x	-7.116	1.33	14 S
			3.90%	2	P:y	-7.116	1.33	12 S
			3.22%	1	P:y	-5.392	0.67	8 C
			3.19%	1	P:x	-5.392	0.67	9 C
			3.19%	1	P:x	-5.392	0.67	10 C
			3.15%	1	P:y	-5.392	0.67	7 C
			1.11%	2	D:xy	11.078	0.00	6 Cr
3.768	0.00	76 A	47.49%	1	D:xz	-2.737	1.00	6 Cr
			37.55%	1	P:x	-7.213	1.00	1 N
			2.95%	2	D:xz	11.078	0.00	6 Cr
			2.45%	1	P:z	-5.392	0.67	7 C
			2.42%	1	P:z	-5.392	0.67	8 C
			1.28%	2	P:z	-7.116	1.33	12 S
			1.22%	2	P:z	-7.116	1.33	11 S
			1.12%	2	S	-18.690	2.00	2 N
3.771	0.00	77 A	47.09%	1	D:yz	-2.737	1.00	6 Cr
			37.41%	1	P:y	-7.213	1.00	1 N
			2.97%	2	D:yz	11.078	0.00	6 Cr
			2.73%	1	P:z	-5.392	0.67	9 C
			2.72%	1	P:z	-5.392	0.67	10 C
			1.44%	2	P:z	-7.116	1.33	13 S
			1.44%	2	P:z	-7.116	1.33	14 S
3.898	0.00	78 A	61.38%	1	D:x2-y2	-2.737	1.00	6 Cr
			7.48%	2	D:x2-y2	11.078	0.00	6 Cr
			3.14%	2	S	-18.690	2.00	5 N
			2.85%	2	S	-18.690	2.00	2 N
			2.80%	2	S	-18.690	2.00	3 N
			2.80%	2	S	-18.690	2.00	4 N
			1.98%	1	P:x	-7.213	1.00	5 N
			1.76%	1	P:x	-7.213	1.00	2 N
			1.62%	1	P:y	-7.213	1.00	3 N
			1.62%	1	P:y	-7.213	1.00	4 N
			1.24%	1	P:z	-5.392	0.67	8 C
			1.11%	1	P:z	-5.392	0.67	7 C
			1.06%	2	P:x	-7.116	1.33	11 S
			1.03%	2	S	-13.865	2.00	8 C
4.042	0.00	79 A	18.76%	1	D:z2	-2.737	1.00	6 Cr
			17.77%	1	P:z	-7.213	1.00	1 N
			10.28%	3	P:z	-0.116	0.00	6 Cr
			6.92%	1	P:z	-5.392	0.67	10 C
			6.91%	1	P:z	-5.392	0.67	9 C
			6.73%	1	P:z	-5.392	0.67	8 C
			6.22%	1	P:z	-5.392	0.67	7 C
			3.10%	2	P:z	-7.116	1.33	11 S
			3.03%	2	P:z	-7.116	1.33	14 S
			3.02%	2	P:z	-7.116	1.33	13 S

2.89%	2	P:z	-7.116	1.33	12 S
1.49%	1	P:z	-7.213	1.00	5 N
1.37%	1	P:z	-7.213	1.00	3 N
1.36%	1	P:z	-7.213	1.00	4 N
1.35%	1	P:z	-7.213	1.00	2 N
1.16%	5	S	1.359	0.00	6 Cr
-1.14%	2	P:z	4.718	0.00	10 C
-1.14%	2	P:z	4.718	0.00	9 C
-1.07%	2	P:z	4.718	0.00	8 C

Input:

```
title [Cr(N)(N3)4]2- all electron geometry opt

atoms cartesian
N         0.793818    2.905285   -2.822880
N         0.744027    1.878388   -2.256966
N         0.740525    0.796905   -1.744057
N        -1.816693    0.173258   -0.934761
N        -2.952892    0.167444   -0.555727
N        -4.090984    0.156964   -0.275505
Cr       -0.013374    0.079765    0.001723
N         1.707481   -0.970004    0.158202
N         4.021059   -0.529214    0.402521
N         2.868367   -0.701821    0.274030
N         0.070678    1.265885    0.976984
N        -0.848507   -1.426879    1.092559
N        -0.668715   -1.773682    2.225242
N        -0.556462   -2.163985    3.325076
end

charge -2 1

unrestricted

symmetry NOSYM

xc
  LDA vwn
  GGA becke perdew
end

Geometry
  Converge Rad=5e-3 E=5e-4
End

Integration 6.0

SCF
  Mixing 0.1
  DIIS
  ITERATIONS 200
END

noprint Computation
noprint Scf
print OrbPop

EPRINT
SFO NOEIG, NOOVL
ORBPOPER -10 1
SUBEND
END

Fragments
Cr t21.Cr
N t21.N
End
end input
```

Output (partial)**:**

Coordinates (Cartesian)

Atom	bohr X	bohr Y	bohr Z	angstrom X	angstrom Y	angstrom Z	Geometric Variables (0:frozen, *:LT par.)		
1 N	1.468281	5.469642	-5.339910	0.776981	2.894409	-2.825758	1	2	3
2 N	1.399467	3.529564	-4.271830	0.740566	1.867764	-2.260555	4	5	6
3 N	1.417857	1.489262	-3.298814	0.750298	0.788083	-1.745657	7	8	9
4 N	-3.424369	0.326047	-1.764245	-1.812098	0.172537	-0.933598	10	11	12
5 N	-5.574084	0.333364	-1.055382	-2.949677	0.176408	-0.558484	13	14	15
6 N	-7.724045	0.334159	-0.520574	-4.087387	0.176829	-0.275476	16	17	18
7 Cr	-0.022627	0.149979	0.009815	-0.011974	0.079366	0.005194	19	20	21
8 N	3.231522	-1.833763	0.317142	1.710047	-0.970385	0.167824	22	23	24
9 N	7.600505	-0.962570	0.744942	4.022013	-0.509370	0.394206	25	26	27
10 N	5.423523	-1.313324	0.519929	2.870004	-0.694981	0.275135	28	29	30
11 N	0.139111	2.395266	1.851861	0.073615	1.267520	0.979963	31	32	33
12 N	-1.601454	-2.696595	2.064587	-0.847453	-1.426976	1.092532	34	35	36
13 N	-1.272618	-3.366664	4.200160	-0.673440	-1.781561	2.222628	37	38	39
14 N	-1.071380	-4.120085	6.272201	-0.566950	-2.180254	3.319105	40	41	42

M U L L I K E N P O P U L A T I O N S

The survey below gives for each atom:
a) the total charge (Z minus electrons)
b) the net spin polarization (nr of electrons spin-A minus spin-B)
c) for each spin the atomic electron valence density (integrated) per L-value.

Atom	Charge	Spin density		S	P	D	F
1 N	-0.3831	0.0323	A:	1.8419	1.8291	0.0335	0.0032
			B:	1.8408	1.7978	0.0336	0.0032
2 N	0.1777	0.0042	A:	1.6190	1.7081	0.0805	0.0056
			B:	1.6188	1.7052	0.0794	0.0056
3 N	-0.3828	-0.0126	A:	1.8242	1.8247	0.0327	0.0034
			B:	1.8277	1.8360	0.0306	0.0033
4 N	-0.3826	-0.0115	A:	1.8235	1.8262	0.0324	0.0034
			B:	1.8264	1.8368	0.0305	0.0033
5 N	0.1755	0.0042	A:	1.6205	1.7082	0.0801	0.0056
			B:	1.6200	1.7051	0.0795	0.0056
6 N	-0.3776	0.0185	A:	1.8426	1.8188	0.0335	0.0032
			B:	1.8420	1.8007	0.0336	0.0032
7 Cr	0.7025	1.1825	A:	3.1133	6.2526	2.8528	0.0213
			B:	3.0903	6.2245	1.7207	0.0220
8 N	-0.3814	-0.0130	A:	1.8223	1.8259	0.0326	0.0034
			B:	1.8256	1.8378	0.0305	0.0033
9 N	-0.3785	0.0282	A:	1.8428	1.8239	0.0335	0.0032
			B:	1.8419	1.7964	0.0336	0.0032
10 N	0.1759	0.0044	A:	1.6204	1.7080	0.0802	0.0056
			B:	1.6200	1.7050	0.0793	0.0056
11 N	-0.3628	-0.2557	A:	1.9211	1.6124	0.0176	0.0025
			B:	1.9263	1.8655	0.0154	0.0021
12 N	-0.3841	-0.0116	A:	1.8244	1.8257	0.0328	0.0034
			B:	1.8274	1.8364	0.0308	0.0033
13 N	0.1795	0.0042	A:	1.6191	1.7073	0.0803	0.0056
			B:	1.6187	1.7044	0.0794	0.0056
14 N	-0.3782	0.0260	A:	1.8422	1.8232	0.0336	0.0032
			B:	1.8414	1.7978	0.0337	0.0032

*** SPIN 1 ***

E(eV)	Occ	MO	%	SFO (first member)	E(eV)	Occ	Fragment
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1.248	1.00	58 A	18.82%	1 P:z	-7.213	1.00	7 N
			18.16%	1 P:z	-7.213	1.00	8 N
			10.97%	1 P:x	-7.213	1.00	3 N
			10.77%	1 P:x	-7.213	1.00	1 N
			9.74%	1 P:x	-7.213	1.00	11 N
			8.53%	1 P:x	-7.213	1.00	13 N
			2.76%	1 P:z	-7.213	1.00	4 N
			2.52%	1 P:y	-7.213	1.00	7 N
			2.21%	1 P:y	-7.213	1.00	8 N
			2.08%	1 P:y	-7.213	1.00	4 N
			2.07%	1 P:z	-7.213	1.00	6 N
			1.80%	1 P:y	-7.213	1.00	6 N
			1.32%	1 D:xz	33.695	0.00	9 N
			1.10%	1 P:z	-7.213	1.00	3 N
2.113	1.00	59 A	20.96%	1 D:xz	-2.737	1.00	14 Cr
			13.20%	1 D:x2-y2	-2.737	1.00	14 Cr
			11.40%	1 D:xy	-2.737	1.00	14 Cr
			6.50%	1 D:yz	-2.737	1.00	14 Cr
			6.13%	1 P:x	-7.213	1.00	1 N
			5.44%	1 D:z2	-2.737	1.00	14 Cr
			4.73%	1 P:z	-7.213	1.00	8 N
			4.42%	1 P:x	-7.213	1.00	3 N
			4.36%	1 P:x	-7.213	1.00	13 N
			3.37%	1 P:x	-7.213	1.00	11 N
			2.92%	1 P:y	-7.213	1.00	6 N
			2.90%	1 P:z	-7.213	1.00	7 N
			1.81%	1 P:y	-7.213	1.00	4 N
			1.24%	2 D:xz	11.078	0.00	14 Cr
4.133	0.00	60 A	13.64%	1 D:xz	-2.737	1.00	14 Cr
			11.99%	1 D:x2-y2	-2.737	1.00	14 Cr
			11.17%	1 D:xy	-2.737	1.00	14 Cr
			7.69%	1 D:z2	-2.737	1.00	14 Cr
			6.78%	1 P:y	-7.213	1.00	8 N
			6.47%	1 P:z	-7.213	1.00	6 N
			4.47%	1 D:yz	-2.737	1.00	14 Cr
			2.92%	1 P:y	-7.213	1.00	13 N
			2.89%	1 P:z	-7.213	1.00	1 N
			2.70%	1 P:x	-7.213	1.00	13 N
			2.68%	1 P:y	-7.213	1.00	9 N
			2.48%	1 P:z	-7.213	1.00	5 N
			1.64%	1 P:y	-7.213	1.00	1 N
			1.47%	2 S	-18.690	2.00	4 N
			1.43%	2 S	-18.690	2.00	7 N
			1.42%	2 D:xz	11.078	0.00	14 Cr
			1.40%	1 P:x	-7.213	1.00	1 N
			1.40%	2 S	-18.690	2.00	3 N
			1.38%	2 S	-18.690	2.00	11 N
			1.31%	1 P:z	-7.213	1.00	2 N
			1.28%	1 P:y	-7.213	1.00	12 N
			1.12%	2 D:xy	11.078	0.00	14 Cr
			1.04%	2 D:x2-y2	11.078	0.00	14 Cr
			1.03%	1 P:x	-7.213	1.00	12 N
4.668	0.00	61 A	25.20%	1 D:z2	-2.737	1.00	14 Cr
			21.11%	1 P:z	-7.213	1.00	10 N
			12.67%	1 P:y	-7.213	1.00	10 N
			10.20%	1 P:x	-7.213	1.00	10 N
			6.96%	1 D:xy	-2.737	1.00	14 Cr
			6.34%	1 D:x2-y2	-2.737	1.00	14 Cr
			3.04%	1 D:xz	-2.737	1.00	14 Cr
			2.09%	2 D:z2	11.078	0.00	14 Cr
			1.68%	1 D:yz	-2.737	1.00	14 Cr
			1.60%	1 P:x	-7.213	1.00	13 N
4.720	0.00	62 A	32.24%	1 P:x	-7.213	1.00	10 N

			18.61%	1	D:xy	-2.737	1.00	14	Cr
			13.45%	1	D:xz	-2.737	1.00	14	Cr
			6.45%	1	D:z2	-2.737	1.00	14	Cr
			5.34%	1	P:y	-7.213	1.00	10	N
			5.15%	1	P:z	-7.213	1.00	10	N
			4.06%	1	D:x2-y2	-2.737	1.00	14	Cr
			1.68%	2	D:xy	11.078	0.00	14	Cr
			1.44%	1	P:z	-7.213	1.00	6	N
			1.22%	2	D:xz	11.078	0.00	14	Cr
			1.21%	1	P:y	-7.213	1.00	8	N
			1.10%	1	P:y	-7.213	1.00	6	N
			1.04%	2	S	-18.690	2.00	7	N
5.054	0.00	63 A	15.64%	1	D:yz	-2.737	1.00	14	Cr
			13.01%	1	P:y	-7.213	1.00	10	N
			9.19%	1	P:z	-7.213	1.00	10	N
			6.15%	1	P:y	-7.213	1.00	13	N
			5.74%	1	P:z	-7.213	1.00	1	N
			4.98%	1	D:x2-y2	-2.737	1.00	14	Cr
			4.33%	1	P:y	-7.213	1.00	8	N
			3.63%	1	P:y	-7.213	1.00	12	N
			3.45%	3	P:y	-0.116	0.00	14	Cr
			3.44%	1	P:z	-7.213	1.00	2	N
			3.34%	1	P:z	-7.213	1.00	6	N
			2.92%	5	S	1.359	0.00	14	Cr
			2.84%	1	P:y	-7.213	1.00	6	N
			2.46%	1	P:y	-7.213	1.00	9	N
			2.40%	3	P:z	-0.116	0.00	14	Cr
			1.96%	1	P:z	-7.213	1.00	8	N
			1.87%	1	P:z	-7.213	1.00	5	N
			1.66%	1	P:y	-7.213	1.00	1	N
			1.66%	1	P:y	-7.213	1.00	5	N
			1.15%	1	P:z	-7.213	1.00	9	N
6.362	0.00	64 A	50.56%	5	S	1.359	0.00	14	Cr
			20.27%	4	S	-3.903	1.00	14	Cr
			2.78%	1	P:x	-7.213	1.00	13	N
			2.70%	1	P:y	-7.213	1.00	6	N
			2.67%	1	P:x	-7.213	1.00	12	N
			2.55%	1	P:y	-7.213	1.00	5	N
			2.31%	1	P:y	-7.213	1.00	10	N
			1.88%	1	P:z	-7.213	1.00	8	N
			1.88%	1	P:z	-7.213	1.00	5	N
			1.73%	1	P:y	-7.213	1.00	4	N
			1.71%	1	P:x	-7.213	1.00	11	N
			1.64%	1	P:z	-7.213	1.00	9	N
			1.62%	1	P:z	-7.213	1.00	6	N
			1.51%	1	P:y	-7.213	1.00	9	N
			1.46%	1	P:y	-7.213	1.00	8	N
			-1.43%	3	S	14.025	0.00	6	N
			1.41%	1	P:x	-7.213	1.00	1	N
			1.40%	1	P:z	-7.213	1.00	10	N
			1.32%	1	P:z	-7.213	1.00	7	N
			-1.27%	3	S	14.025	0.00	8	N
			1.23%	1	P:x	-7.213	1.00	2	N
			-1.23%	3	S	14.025	0.00	13	N
			-1.17%	3	S	14.025	0.00	1	N
			1.01%	3	S	14.025	0.00	10	N

*** SPIN 2 ***

E(eV)	Occ	MO	%	SFO (first member)		E(eV)	Occ	Fragment	
.									
.									
.									
1.302	1.00	58 A	15.96%	1	P:z	-7.213	1.00	7	N
			15.11%	1	P:z	-7.213	1.00	8	N
			13.15%	1	P:x	-7.213	1.00	3	N

			12.65%	1	P:x	-7.213	1.00	1 N
			10.48%	1	P:x	-7.213	1.00	11 N
			9.15%	1	P:x	-7.213	1.00	13 N
			2.80%	1	P:y	-7.213	1.00	7 N
			2.67%	1	P:z	-7.213	1.00	4 N
			2.44%	1	P:y	-7.213	1.00	8 N
			2.08%	1	P:y	-7.213	1.00	4 N
			2.02%	1	P:z	-7.213	1.00	6 N
			1.78%	1	P:y	-7.213	1.00	6 N
			1.13%	1	P:z	-7.213	1.00	3 N
			1.11%	1	D:xz	33.695	0.00	9 N
3.773	0.00	59 A	22.71%	1	D:x2-y2	-2.737	1.00	14 Cr
			21.64%	1	D:xz	-2.737	1.00	14 Cr
			11.07%	1	D:xy	-2.737	1.00	14 Cr
			10.88%	1	D:yz	-2.737	1.00	14 Cr
			9.76%	1	D:z2	-2.737	1.00	14 Cr
			4.16%	1	P:x	-7.213	1.00	1 N
			3.34%	1	P:x	-7.213	1.00	13 N
			3.04%	1	P:z	-7.213	1.00	8 N
			1.64%	1	P:y	-7.213	1.00	6 N
			1.23%	1	P:z	-7.213	1.00	6 N
			1.21%	1	P:x	-7.213	1.00	2 N
4.443	0.00	60 A	19.67%	1	D:xz	-2.737	1.00	14 Cr
			14.95%	1	D:xy	-2.737	1.00	14 Cr
			7.97%	1	D:x2-y2	-2.737	1.00	14 Cr
			6.31%	1	P:y	-7.213	1.00	8 N
			5.88%	1	P:z	-7.213	1.00	6 N
			5.53%	1	D:z2	-2.737	1.00	14 Cr
			3.20%	1	P:y	-7.213	1.00	13 N
			3.10%	1	P:z	-7.213	1.00	1 N
			2.92%	1	P:y	-7.213	1.00	9 N
			2.66%	1	D:yz	-2.737	1.00	14 Cr
			2.63%	1	P:z	-7.213	1.00	5 N
			1.97%	1	P:x	-7.213	1.00	13 N
			1.72%	1	P:y	-7.213	1.00	1 N
			1.66%	1	P:y	-7.213	1.00	12 N
			1.66%	1	P:z	-7.213	1.00	2 N
			1.48%	2	S	-18.690	2.00	4 N
			1.44%	2	D:xz	11.078	0.00	14 Cr
			1.41%	2	S	-18.690	2.00	7 N
			1.40%	2	S	-18.690	2.00	3 N
			1.38%	2	S	-18.690	2.00	11 N
			1.11%	2	D:xy	11.078	0.00	14 Cr
5.012	0.00	61 A	28.10%	1	D:z2	-2.737	1.00	14 Cr
			15.35%	1	P:z	-7.213	1.00	10 N
			10.44%	1	D:xy	-2.737	1.00	14 Cr
			10.23%	1	P:x	-7.213	1.00	10 N
			9.00%	1	P:y	-7.213	1.00	10 N
			6.61%	1	D:x2-y2	-2.737	1.00	14 Cr
			4.61%	1	D:xz	-2.737	1.00	14 Cr
			1.93%	1	P:x	-7.213	1.00	13 N
			1.90%	1	D:yz	-2.737	1.00	14 Cr
			1.55%	2	D:z2	11.078	0.00	14 Cr
			1.18%	1	P:x	-7.213	1.00	1 N
			1.07%	1	P:x	-7.213	1.00	12 N
5.060	0.00	62 A	23.02%	1	P:x	-7.213	1.00	10 N
			19.75%	1	D:xy	-2.737	1.00	14 Cr
			14.76%	1	D:xz	-2.737	1.00	14 Cr
			10.10%	1	D:z2	-2.737	1.00	14 Cr
			5.74%	1	P:y	-7.213	1.00	10 N
			5.32%	1	D:x2-y2	-2.737	1.00	14 Cr
			4.99%	1	P:z	-7.213	1.00	10 N
			1.82%	1	P:y	-7.213	1.00	6 N
			1.32%	1	P:y	-7.213	1.00	8 N
			1.30%	1	P:z	-7.213	1.00	6 N
			1.22%	2	D:xy	11.078	0.00	14 Cr
			1.15%	1	P:y	-7.213	1.00	5 N
			1.04%	2	S	-18.690	2.00	7 N
5.221	0.00	63 A	15.37%	1	D:yz	-2.737	1.00	14 Cr
			9.32%	1	P:y	-7.213	1.00	10 N

```
                                    7.40%     1 P:z           -7.213  1.00    10 N
                                    6.62%     1 P:y           -7.213  1.00    13 N
                                    6.19%     1 P:z           -7.213  1.00     1 N
                                    5.31%     1 D:x2-y2       -2.737  1.00    14 Cr
                                    4.40%     1 P:y           -7.213  1.00     8 N
                                    4.14%     1 P:y           -7.213  1.00    12 N
                                    3.94%     1 P:z           -7.213  1.00     2 N
                                    3.86%     3 P:y           -0.116  0.00    14 Cr
                                    3.63%     1 P:z           -7.213  1.00     6 N
                                    3.36%     5 S              1.359  0.00    14 Cr
                                    2.97%     1 P:y           -7.213  1.00     6 N
                                    2.70%     1 P:y           -7.213  1.00     9 N
                                    2.68%     3 P:z           -0.116  0.00    14 Cr
                                    2.25%     1 P:z           -7.213  1.00     8 N
                                    2.19%     1 P:z           -7.213  1.00     5 N
                                    1.83%     1 P:y           -7.213  1.00     5 N
                                    1.73%     1 P:y           -7.213  1.00     1 N
                                    1.39%     1 P:z           -7.213  1.00     9 N
       6.374  0.00    64 A        52.82%     5 S              1.359  0.00    14 Cr
                                   21.78%     4 S             -3.903  1.00    14 Cr
                                    2.58%     1 P:y           -7.213  1.00     6 N
                                    2.57%     1 P:x           -7.213  1.00    13 N
                                    2.40%     1 P:x           -7.213  1.00    12 N
                                    2.36%     1 P:y           -7.213  1.00     5 N
                                    2.26%     1 P:y           -7.213  1.00    10 N
                                    1.81%     1 P:z           -7.213  1.00     8 N
                                    1.57%     1 P:y           -7.213  1.00     4 N
                                    1.51%     1 P:z           -7.213  1.00     9 N
                                   -1.49%     3 S             14.025  0.00     6 N
                                    1.48%     1 P:x           -7.213  1.00    11 N
                                    1.47%     1 P:x           -7.213  1.00     1 N
                                    1.37%     1 P:z           -7.213  1.00    10 N
                                    1.37%     1 P:z           -7.213  1.00     5 N
                                   -1.35%     3 S             14.025  0.00     8 N
                                   -1.31%     3 S             14.025  0.00    13 N
                                   -1.24%     3 S             14.025  0.00     1 N
                                    1.23%     1 P:x           -7.213  1.00     2 N
                                    1.21%     1 P:y           -7.213  1.00     9 N
                                    1.20%     1 P:z           -7.213  1.00     7 N
                                    1.17%     1 P:y           -7.213  1.00     8 N
                                    1.15%     1 P:z           -7.213  1.00     6 N
                                    1.04%     3 S             14.025  0.00    10 N
                                    1.01%     1 D:yz          -2.737  1.00    14 Cr
```

.

Input:

```
title slater TS [Cr(N)(NCS)4]2- optim geometry

atoms cartesian
  N        0.029195   -0.000113   -2.039063
 Cr        0.010605   -0.000035   -0.505038
  N       -1.928775    0.000222   -0.076968
  N       -0.000421    1.927338   -0.034794
  N       -0.000903   -1.927361   -0.034941
  C       -3.095427    0.000253    0.121942
  N        1.938357   -0.000323   -0.033779
  C        3.108445   -0.000256    0.144228
  C       -0.018034   -3.080381    0.231069
  C       -0.017574    3.080416    0.230929
  S        4.719341   -0.000122    0.396621
  S       -4.702232    0.000260    0.402314
  S       -0.039927   -4.670165    0.593301
  S       -0.039596    4.670181    0.593338
end

charge -2 1

unrestricted

symmetry NOSYM
```

```
BASIS
  TYPE TZ2P
  CORE NONE
END

xc
  LDA vwn
  GGA becke perdew
end

scf
  Mixing 0.1
  Iterations 70
end

occupations
  A  74 0.5 0.5 // 74
end

noprint Computation
noprint Scf
print OrbPop

EPRINT
SFO NOEIG, NOOVL
ORBPOPER -10 1
SUBEND
END

end input
```

Output (partial)**:**

```
                                   *** SPIN 1 ***

      E(eV)  Occ       MO          %     SFO (first member)   E(eV)  Occ   Fragment
 ------------------------------------------------------------------------------------
.
.
.
      0.220  1.00    74 A        19.97%     2 P:y            -7.116  1.33    12 S
                                 17.67%     2 P:x            -7.116  1.33    14 S
                                 17.66%     2 P:x            -7.116  1.33    13 S
                                 15.73%     2 P:y            -7.116  1.33    11 S
                                  7.41%     1 P:y            -7.213  1.00     2 N
                                  6.58%     1 P:x            -7.213  1.00     3 N
                                  6.58%     1 P:x            -7.213  1.00     4 N
                                  5.85%     1 P:y            -7.213  1.00     5 N
      1.161  0.50    75 A        58.76%     1 D:xy           -2.737  1.00     6 Cr
                                  6.21%     2 P:y            -7.116  1.33    11 S
                                  6.17%     2 P:y            -7.116  1.33    12 S
                                  6.11%     2 P:x            -7.116  1.33    13 S
                                  6.11%     2 P:x            -7.116  1.33    14 S
                                  2.35%     2 D:xy           11.078  0.00     6 Cr
                                  1.79%     1 P:y            -5.392  0.67     8 C
                                  1.76%     1 P:x            -5.392  0.67     9 C
                                  1.76%     1 P:x            -5.392  0.67    10 C
                                  1.74%     1 P:y            -5.392  0.67     7 C
                                  1.55%     1 P:y            -7.213  1.00     5 N
                                  1.54%     1 P:y            -7.213  1.00     2 N
                                  1.50%     1 P:x            -7.213  1.00     4 N
                                  1.50%     1 P:x            -7.213  1.00     3 N
      3.434  0.50    76 A        60.01%     1 D:x2-y2        -2.737  1.00     6 Cr
                                  8.82%     2 D:x2-y2        11.078  0.00     6 Cr
                                  3.34%     2 S             -18.690  2.00     2 N
```

```
                                    3.23%     2 S           -18.690  2.00     4 N
                                    3.23%     2 S           -18.690  2.00     3 N
                                    3.14%     2 S           -18.690  2.00     5 N
                                    2.07%     1 P:x          -7.213  1.00     2 N
                                    2.00%     1 P:x          -7.213  1.00     5 N
                                    1.95%     1 P:y          -7.213  1.00     4 N
                                    1.95%     1 P:y          -7.213  1.00     3 N
       3.692  0.00    77 A        46.31%     1 P:x          -7.213  1.00     1 N
                                   40.82%     1 D:xz         -2.737  1.00     6 Cr
                                    3.53%     2 D:xz         11.078  0.00     6 Cr
                                    1.68%     1 P:z          -5.392  0.67     7 C
                                    1.40%     1 P:z          -5.392  0.67     8 C
                                    1.13%     2 S           -18.690  2.00     5 N
```

Input:

```
title [Cr(N)(N3)4]2- all electron geometry opt

atoms cartesian
  N        0.71084        2.84826       -2.42021
  N        0.71331        1.79359       -2.13301
  N        0.80632        0.64070       -1.86152
  N       -1.81346        0.48332       -0.89352
  N       -2.93356        0.19205       -0.55083
  N       -3.97135       -0.05927       -0.29851
 Cr       -0.01400        0.02734       -0.04769
  N        1.60870       -1.14163        0.23795
  N        3.80309       -0.46640        0.46684
  N        2.74119       -0.72152        0.35943
  N        0.18618        1.22563        0.90182
  N       -1.03026       -1.33209        1.01055
  N       -0.56992       -1.63559        2.13392
  N       -0.23706       -1.85439        3.09477
end

charge -2 1

unrestricted

symmetry NOSYM

BASIS
  TYPE TZ2P
  CORE NONE
END

xc
  LDA vwn
  GGA becke perdew
end

scf
  Mixing 0.1
  Iterations 70
end

occupations
  A  58 0.5 0.5 // 58
end

noprint Computation
noprint Scf
print OrbPop

EPRINT
SFO NOEIG, NOOVL
ORBPOPER -10 1
SUBEND
END
```

```
end input
```

Output (partial)**:**

```
                                    *** SPIN 1 ***

      E(eV)  Occ       MO          %     SFO (first member)   E(eV)  Occ   Fragment
 ------------------------------------------------------------------------------------
.
.
.
      1.863  1.00    58 A        21.24%     1 P:y            -7.213  1.00     4 N
                                 15.67%     1 P:y            -7.213  1.00     6 N
                                 12.54%     1 P:z            -7.213  1.00     4 N
                                  9.04%     1 P:z            -7.213  1.00     6 N
                                  6.88%     1 P:z            -7.213  1.00     7 N
                                  6.24%     1 P:x            -7.213  1.00    10 N
                                  5.89%     1 P:x            -7.213  1.00     3 N
                                  4.82%     1 P:x            -7.213  1.00     1 N
                                  4.81%     1 P:z            -7.213  1.00     8 N
                                  1.67%     1 P:z            -7.213  1.00     3 N
                                  1.42%     1 D:xz           -2.737  1.00    14 Cr
                                  1.37%     1 P:z            -7.213  1.00     1 N
                                  1.37%     1 P:y            -7.213  1.00    10 N
                                  1.31%     1 D:xy           33.695  0.00     5 N
      2.914  0.50    59 A        22.28%     1 D:xz           -2.737  1.00    14 Cr
                                 20.40%     1 D:x2-y2        -2.737  1.00    14 Cr
                                 11.26%     1 D:yz           -2.737  1.00    14 Cr
                                  7.27%     1 D:z2           -2.737  1.00    14 Cr
                                  6.54%     1 D:xy           -2.737  1.00    14 Cr
                                  4.05%     1 P:z            -7.213  1.00     8 N
                                  3.84%     1 P:x            -7.213  1.00     3 N
                                  3.70%     1 P:x            -7.213  1.00     1 N
                                  3.11%     1 P:z            -7.213  1.00     7 N
                                  2.35%     1 P:x            -7.213  1.00    11 N
                                  1.20%     2 D:xz           11.078  0.00    14 Cr
                                  1.16%     1 P:y            -7.213  1.00    13 N
                                  1.08%     1 P:x            -7.213  1.00    13 N
      4.724  0.50    60 A        17.44%     1 D:xz           -2.737  1.00    14 Cr
                                 10.75%     1 D:z2           -2.737  1.00    14 Cr
                                 10.18%     1 D:xy           -2.737  1.00    14 Cr
                                  6.36%     1 P:y            -7.213  1.00     8 N
                                  5.52%     1 D:x2-y2        -2.737  1.00    14 Cr
                                  4.75%     1 P:z            -7.213  1.00     1 N
                                  4.38%     1 P:z            -7.213  1.00     6 N
                                  3.18%     1 P:y            -7.213  1.00    13 N
                                  2.93%     1 P:x            -7.213  1.00    13 N
                                  2.87%     1 D:yz           -2.737  1.00    14 Cr
                                  2.70%     1 P:y            -7.213  1.00     9 N
                                  1.95%     2 D:xz           11.078  0.00    14 Cr
                                  1.84%     1 P:z            -7.213  1.00     2 N
                                  1.62%     1 P:z            -7.213  1.00     5 N
                                  1.55%     2 S             -18.690  2.00     4 N
                                  1.52%     1 P:y            -7.213  1.00    12 N
                                  1.27%     1 P:y            -7.213  1.00     6 N
                                  1.25%     2 D:z2           11.078  0.00    14 Cr
                                  1.25%     1 P:x            -7.213  1.00    12 N
                                  1.22%     1 P:z            -7.213  1.00     3 N
                                  1.21%     2 D:xy           11.078  0.00    14 Cr
                                  1.20%     1 P:x            -7.213  1.00     1 N
                                  1.17%     1 P:x            -7.213  1.00     4 N
                                  1.14%     2 S             -18.690  2.00     3 N
                                  1.11%     2 S             -18.690  2.00     7 N
                                  1.01%     1 P:x            -7.213  1.00     7 N
```

```
       5.260  0.00    61 A         20.88%     1 P:x           -7.213  1.00    10 N
                                   12.97%     1 D:z2          -2.737  1.00    14 Cr
                                   11.56%     1 P:y           -7.213  1.00    10 N
                                   11.21%     1 P:z           -7.213  1.00    10 N
                                   10.07%     1 D:x2-y2       -2.737  1.00    14 Cr
                                    9.84%     1 D:xz          -2.737  1.00    14 Cr
                                    9.52%     1 D:xy          -2.737  1.00    14 Cr
                                    1.79%     1 P:y           -7.213  1.00     6 N
                                    1.05%     2 D:z2          11.078  0.00    14 Cr
```

Frequencies calculations

Input for $[Cr(N)(NCS)_4]^{2-}$:

```
title frequencies[Cr(N)(NCS)4]2- optim geometry

restart t13

atoms cartesian
  N        0.029195   -0.000113   -2.039063
 Cr        0.010605   -0.000035   -0.505038
  N       -1.928775    0.000222   -0.076968
  N       -0.000421    1.927338   -0.034794
  N       -0.000903   -1.927361   -0.034941
  C       -3.095427    0.000253    0.121942
  N        1.938357   -0.000323   -0.033779
  C        3.108445   -0.000256    0.144228
  C       -0.018034   -3.080381    0.231069
  C       -0.017574    3.080416    0.230929
  S        4.719341   -0.000122    0.396621
  S       -4.702232    0.000260    0.402314
  S       -0.039927   -4.670165    0.593301
  S       -0.039596    4.670181    0.593338
end

charge -2 1

unrestricted

symmetry NOSYM

xc
  LDA vwn
  GGA becke perdew
end

Geometry
  Frequencies
End

noprint Computation
noprint Scf
print OrbPop

EPRINT
SFO NOEIG, NOOVL
ORBPOPER -10 1
SUBEND
END

Fragments
Cr t21.Cr
N t21.N
S t21.S
C t21.C
End
end input
```

Output (partial):

```
Intensities
 ===========

              Frequency       Dipole Strength        Absorption Intensity (degeneracy not counted)
                cm-1            1e-40 esu2 cm2             km/mole
              ----------        ----------             ----------
               11.018420      4272383.988034        11799.610543
               21.776282       941517.979315         5139.139610
               22.206375       716221.034858         3986.601362
               34.696113      2167336.329564        18848.864880
               38.968629     12194437.859237       119111.853944
               78.055133        55016.316368         1076.393446
               78.687341        27149.796264          535.487717
               96.126368           51.317682            1.236482
              129.635267       123631.187323         4017.253859
              200.599625      4120120.187594       207165.805319
              210.164660      3715151.678824       195710.582776
              228.652267        82126.101813         4706.898032
              229.573237      1425098.107687        82005.709784
              248.650797      1530054.064519        95361.857841
              253.815244        35150.861945         2236.308692
              266.706974          721.469468           48.231459
              286.877154      1117999.794592        80392.541478
              393.595975         4816.148834          475.147686
              395.937453       809486.171742        80336.718790
              449.036456         1023.787007          115.230988
              454.146325         3486.381928          396.870516
              460.264191        83952.933426         9685.479669
              460.875887          343.324323           39.661271
              463.197964         2704.631661          314.016768
              466.989504          614.086168           71.881065
              468.280103        16126.503770         1892.883989
              474.901386         1074.158488          127.864467
              836.724933       597427.974532       125298.633628
              843.011497        35521.938298         7505.994183
              843.645377      1207930.364012       255434.703144
              846.389828       614826.099663       130436.999677
             1120.655359         9508.836617         2671.022385
             2081.546458         2189.758890         1142.511227
             2090.883808          412.842721          216.367786
             2091.963734         6324.310736         3316.235941
             2122.459126         1610.109172          856.589467
```

Input for $[Cr(N)(N_3)_4]^{2-}$:

```
title frequencies[Cr(N)(N3)4]2- optim geometry

atoms cartesian
N         0.776981    2.894409   -2.825758
N         0.740566    1.867764   -2.260555
N         0.750298    0.788083   -1.745657
N        -1.812098    0.172537   -0.933598
N        -2.949677    0.176408   -0.558484
N        -4.087387    0.176829   -0.275476
Cr       -0.011974    0.079366    0.005194
N         1.710047   -0.970385    0.167824
N         4.022013   -0.509370    0.394206
N         2.870004   -0.694981    0.275135
N         0.073615    1.267520    0.979963
N        -0.847453   -1.426976    1.092532
N        -0.673440   -1.781561    2.222628
N        -0.566950   -2.180254    3.319105
end

charge -2 1
```

```
unrestricted

symmetry NOSYM

xc
  LDA vwn
  GGA becke perdew
end

Geometry
  Frequencies Numdif=2 Disrad=0.007 Disang=0.5

End

Integration 6.0

SCF
  Mixing 0.1
  DIIS
  ITERATIONS 200
END

noprint Computation
noprint Scf
print OrbPop

EPRINT
SFO NOEIG, NOOVL
ORBPOPER -10 1
SUBEND
END

Fragments
Cr t21.Cr
N t21.N
End
end input
```

Output (partial):

```
 Intensities
 ===========

              Frequency       Dipole Strength        Absorption Intensity (degeneracy not counted)
                cm-1            1e-40 esu2 cm2          km/mole
             ----------          ----------          ----------
             -13.006497       566937.036594        -1848.303307
               5.885142       231366.391925          341.299214
              26.058775        11437.033696           74.704277
              28.763825         5914.668433           42.643723
              35.800268        56170.449760          504.048412
              79.128170         1742.604643           34.562732
              85.464912        50440.445650         1080.549913
              88.295752         2965.765562           65.637903
             114.304167        11950.535474          342.395066
             201.579726         6844.212549          345.818648
             204.931697         1336.704547           68.662978
             213.498350          807.662496           43.221766
             233.858530         4435.031237          259.972834
             278.449402          370.907401           25.887485
             283.960196         1998.572258          142.251021
             289.237287         1840.378281          133.425687
             352.373211         2038.969529          180.090867
             390.672135          811.177950           79.434039
             402.694353          702.752293           70.934234
             592.534806         7101.196755         1054.686732
             594.190359           37.822010            5.633111
             595.968311           31.406540            4.691604
             601.058666          508.871516           76.666048
```

636.957194	826.824745	132.008465
639.191521	1099.278402	176.123282
640.256522	1173.224157	188.283853
642.048022	244.970604	39.423897
1113.725289	71.515128	19.964299
1345.057730	2011.351829	678.120759
1346.524780	216.312800	73.008704
1347.612171	5632.770192	1902.676822
1351.159886	5514.563751	1867.652077
2089.527109	2644.865417	1385.254782
2091.776040	128.980638	67.626634
2097.335757	7691.980835	4043.749319
2126.550317	3306.720665	1762.589761