Supporting Information

Substantial exchange coupling for {Mo-NCS-M} combination: Illustration for 1-D $[\{Mo(NCS)_6\}\{NiL\}_2(NCS)]_n$.

Maliheh Mousavi,[1,2] Virgine Béreau,[1,2] Cédric Desplanches,[3] Carine Duhayon,[1,2] Jean-Pascal Sutter,*[1,2]

[1] *CNRS ; LCC (Laboratoire de Chimie de Coordination) ; 205, route de Narbonne, F-31077 Toulouse, France*
[2] *Université de Toulouse ; UPS, INPT ; LCC ; F-31077 Toulouse, France*
[3] *CNRS, Université de Bordeaux, ICMCB, 87 avenue du Dr A. Schweitzer, Pessac, F-33608, France*

* e-mail: sutter@lcc-toulouse.fr

Figure SI1. ORTEP view of the molecular structure of $(PPh_4)_3\{Mo(NCS)_6\}.2MeCN$, **1**. (thermal ellipsoids set at 30 % of probability).

Table SI1. Selected bond lengths and angles for **1**.

Figure SI2. Crystal packing for **1**.

Figure SI3. ORTEP view of the molecular structure of $[\{Mo(NCS)_6\}\{NiL^2\}_2(NCS)]_n\cdot MeCN$, **2**. (thermal ellipsoids set at 30 % of probability).

Table SI2. Selected bond lengths and angles for **2**.

Figure SI4. ORTEP view of the molecular structure of $[\{Cr(NCS)_6\}\{NiL^2\}_2(NCS)]_n\cdot MeCN$, **3**. (thermal ellipsoids set at 30 % of probability).

Table SI3. Selected bond lengths and angles for **3**.

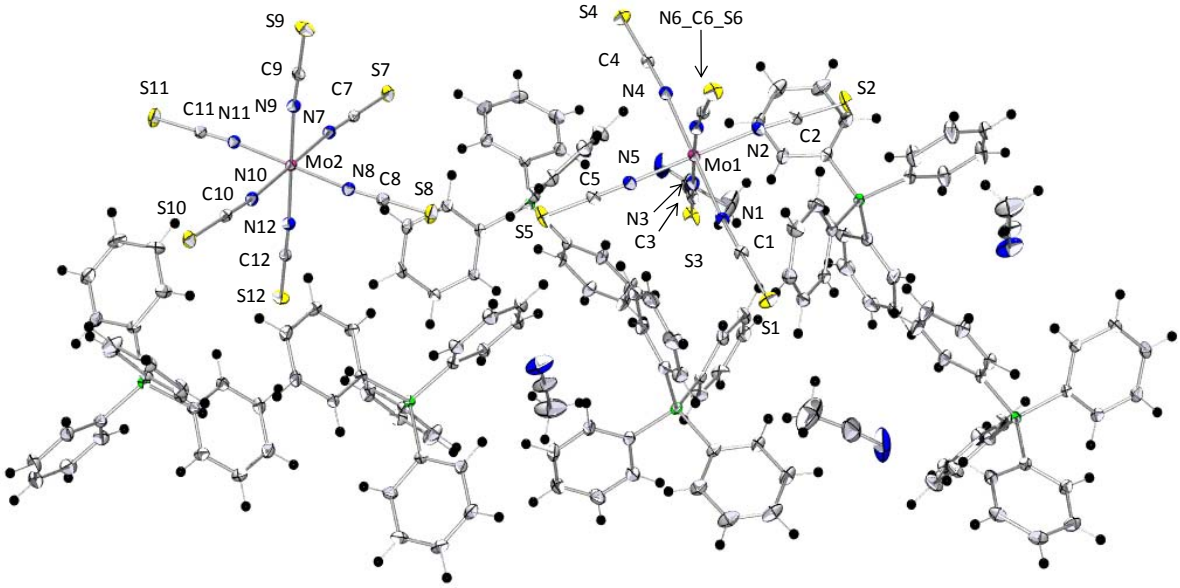
Table SI4. Spin density distribution for $\{Mo(NCS)_6\}^{3-}$ in **1** deduced from DFT calculations.

Table SI5. Spin distribution obtained for $\{Mo(NCS)_6\}^{3-}$ at crystallographic coordinates reported for $K_3\{MoNCS\}_6$.

Full reference for Gaussian03.

Figure SI5. Experimental and calculated (—) $\chi_M T$ versus T, and M versus H for $(PPh_4)_3\{Mo(NCS)_6\}.2MeCN$, **1**.

Figure SI1. ORTEP view of the molecular structure of $(PPh_4)_3\{Mo(NCS)_6\}.2MeCN$, **1**. (thermal ellipsoids set at 30 % of probability)



Supporting Information

Table SI1. Selected bond lengths and angles for **1**.

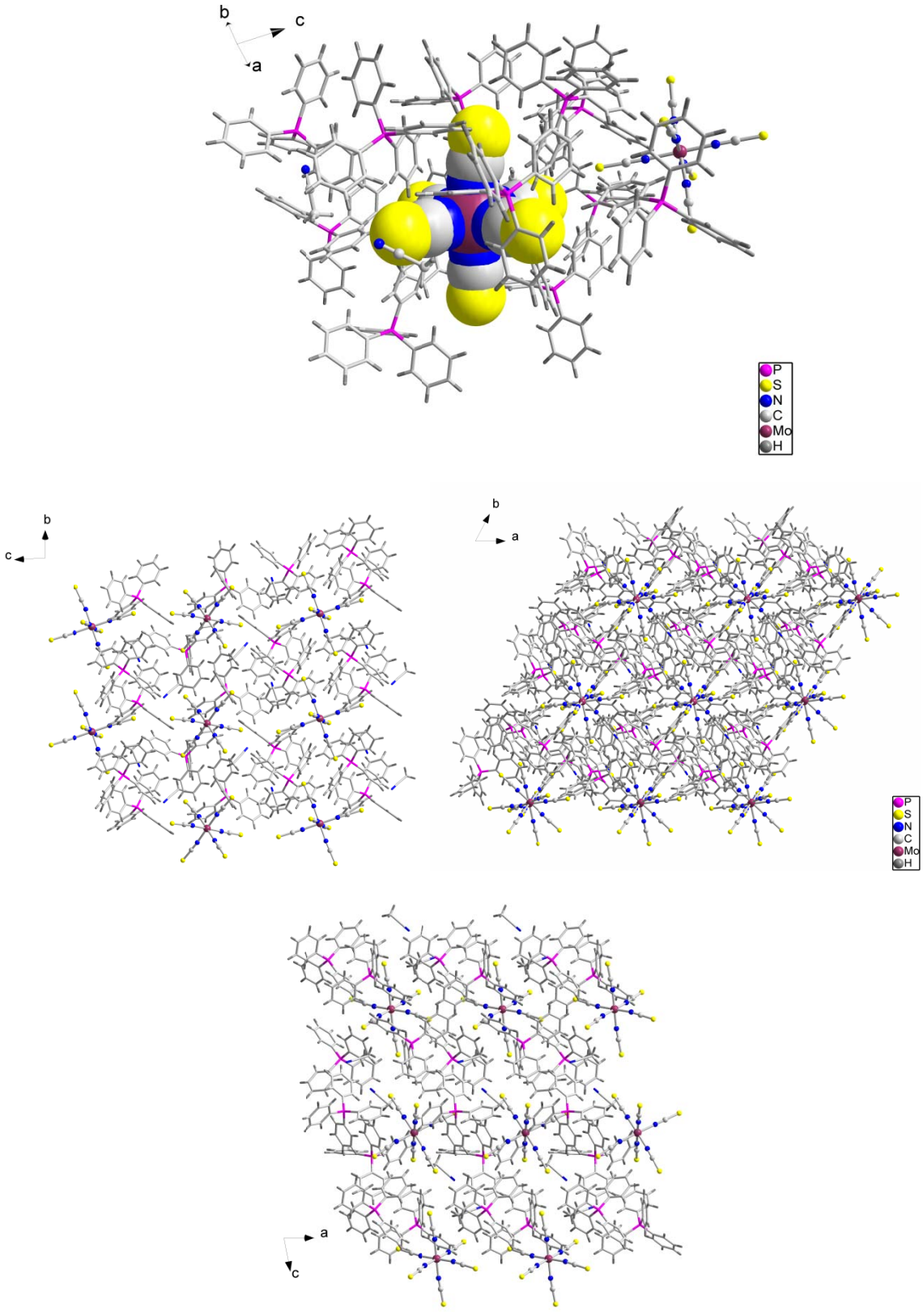
DISTANCES (Å)

S1	C1	1.6272(16)Å	S2	C2	1.6264(17)Å
S3	C3	1.6198(16)Å	S4	C4	1.6273(16)Å
S5	C5	1.6217(17)Å	S6	C6	1.6200(17)Å
S7	C7	1.6217(17)Å	S8	C8	1.6178(17)Å
S9	C9	1.6225(16)Å	S10	C10	1.6212(17)Å
S11	C11	1.6172(17)Å	S12	C12	1.6163(16)Å
N1	C1	1.161(2)Å	N1	Mo1	2.1135(13)Å
N2	C2	1.163(2)Å	N2	Mo1	2.1061(14)Å
N3	C3	1.163(2)Å	N3	Mo1	2.0948(14)Å
N4	C4	1.161(2)Å	N4	Mo1	2.1110(13)Å
N5	C5	1.164(2)Å	N5	Mo1	2.1079(14)Å
N6	C6	1.163(2)Å	N6	Mo1	2.0919(14)Å
N7	C7	1.165(2)Å	N7	Mo2	2.1018(15)Å
N8	C8	1.163(2)Å	N8	Mo2	2.0976(14)Å
N9	C9	1.156(2)Å	N9	Mo2	2.0923(14)Å
N10	C10	1.164(2)Å	N10	Mo2	2.1050(14)Å
N11	C11	1.165(2)Å	N11	Mo2	2.1003(14)Å
N12	C12	1.165(2)Å	N12	Mo2	2.0919(14)Å

ANGLES (°)

C1	N1	Mo1	175.15(13)°	C2	N2	Mo1	173.72(12)°
C3	N3	Mo1	179.55(13)°	C4	N4	Mo1	174.39(13)°
C5	N5	Mo1	178.51(12)°	C6	N6	Mo1	172.17(13)°
C7	N7	Mo2	172.30(13)°	C8	N8	Mo2	172.79(13)°
C9	N9	Mo2	174.42(13)°	C10	N10	Mo2	172.45(12)°
C11	N11	Mo2	173.11(13)°	C12	N12	Mo2	176.25(13)°
S1	C1	N1	179.42(16)°	S2	C2	N2	179.06(15)°
S3	C3	N3	179.48(15)°	S4	C4	N4	179.21(15)°
S5	C5	N5	179.70(15)°	S6	C6	N6	179.07(14)°
S7	C7	N7	179.66(13)°	S8	C8	N8	179.77(16)°
S9	C9	N9	178.99(16)°	S10	C10	N10	179.50(13)°
S11	C11	N11	179.70(15)°	S12	C12	N12	179.16(16)°
N1	Mo1	N2	88.95(5)°	N1	Mo1	N3	90.72(5)°
N2	Mo1	N3	90.45(5)°	N1	Mo1	N4	179.21(7)°
N2	Mo1	N4	90.96(5)°	N3	Mo1	N4	88.50(5)°
N1	Mo1	N5	90.47(5)°	N2	Mo1	N5	179.10(6)°
N3	Mo1	N5	90.25(5)°	N4	Mo1	N5	89.63(5)°
N1	Mo1	N6	89.10(5)°	N2	Mo1	N6	88.34(6)°
N3	Mo1	N6	178.78(7)°	N4	Mo1	N6	91.68(5)°
N5	Mo1	N6	90.95(6)°	N7	Mo2	N8	88.45(5)°
N7	Mo2	N9	89.82(6)°	N8	Mo2	N9	88.84(5)°
N7	Mo2	N10	179.81(6)°	N8	Mo2	N10	91.71(5)°
N9	Mo2	N10	90.08(6)°	N7	Mo2	N11	91.67(5)°
N8	Mo2	N11	179.82(6)°	N9	Mo2	N11	91.29(5)°
N10	Mo2	N11	88.17(5)°	N7	Mo2	N12	90.18(6)°
N8	Mo2	N12	90.79(5)°	N9	Mo2	N12	179.63(6)°
N10	Mo2	N12	89.92(6)°	N11	Mo2	N12	89.08(5)°

Figure SI2. Crystal packing for **1**.



Supporting Information

Figure SI3. ORTEP view of the molecular structure of [{Mo(NCS)$_6$}{NiL^2}$_2$(NCS)]$_n$·MeCN, **2**. (thermal ellipsoids set at 30 % of probability).

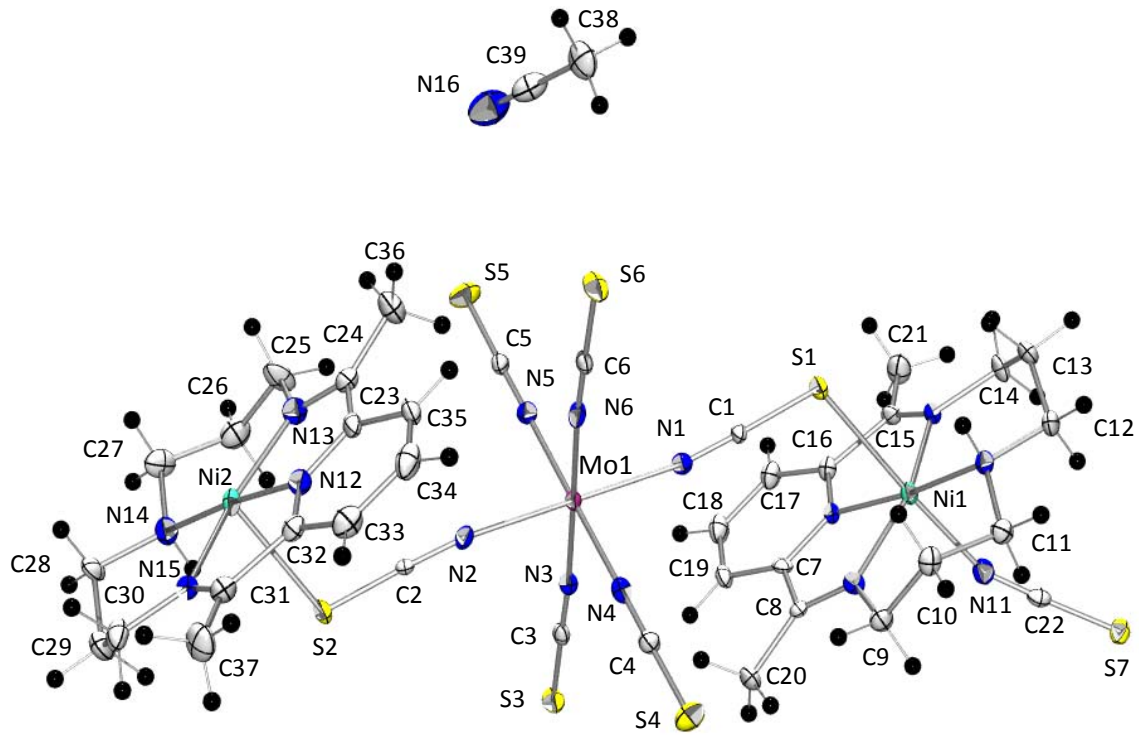


Table SI2. Selected bond lengths and angles for **2**.

DISTANCES (Å)

Mo1	N1	2.095(5)Å	Mo1	N2	2.086(5)Å
Mo1	N3	2.066(6)Å	Mo1	N4	2.086(6)Å
Mo1	N5	2.075(6)Å	Mo1	N6	2.076(6)Å
Ni1	N7	1.933(5)Å	Ni1	N8	2.039(5)Å
Ni1	N9	1.989(5)Å	Ni1	N10	2.057(5)Å
Ni1	N11	2.072(7)Å	Ni1	S1	2.619(2)Å
Ni2	N12	1.933(6)Å	Ni2	N13	2.004(6)Å
Ni2	N14	1.996(6)Å	Ni2	N15	2.099(6)Å
Ni2	S2	2.534(2)Å	Ni2	S7 2_645	2.519(2)Å
C1	N1	1.136(7)Å	C1	S1	1.628(6)Å
C2	N2	1.154(7)Å	C2	S2	1.616(6)Å
C3	N3	1.160(9)Å	C3	S3	1.612(8)Å
C4	N4	1.153(8)Å	C4	S4	1.606(7)Å
C5	N5	1.148(8)Å	C5	S5	1.613(7)Å
C6	N6	1.134(9)Å	C6	S6	1.619(8)Å
C22	S7	1.637(7)Å	C22	N11	1.422(9)Å

ANGLES (°)

N2	C2	S2	177.8(6)°	N1	C1	S1	178.2(6)°
N4	C4	S4	178.9(7)°	N3	C3	S3	177.8(6)°
N6	C6	S6	179.2(7)°	N5	C5	S5	178.5(6)°
N11	C22	S7	177.5(6)°	Mo1	N1	C1	166.5(6)°
Mo1	N2	C2	168.6(6)°	Mo1	N3	C3	172.6(5)°
Mo1	N4	C4	178.0(6)°	Mo1	N5	C5	175.9(6)°
Mo1	N6	C6	173.5(5)°	Ni2	S2	C2	104.6(2)°
Ni1	S1	C1	105.8(2)°	Ni2 2_655	S7	C22	103.9(2)°

Supporting Information

Figure SI4. ORTEP view of the molecular structure of $[\{Cr(NCS)_6\}\{NiL^2\}_2(NCS)]_n \cdot MeCN$, **3**. (thermal ellipsoids set at 30 % of probability).

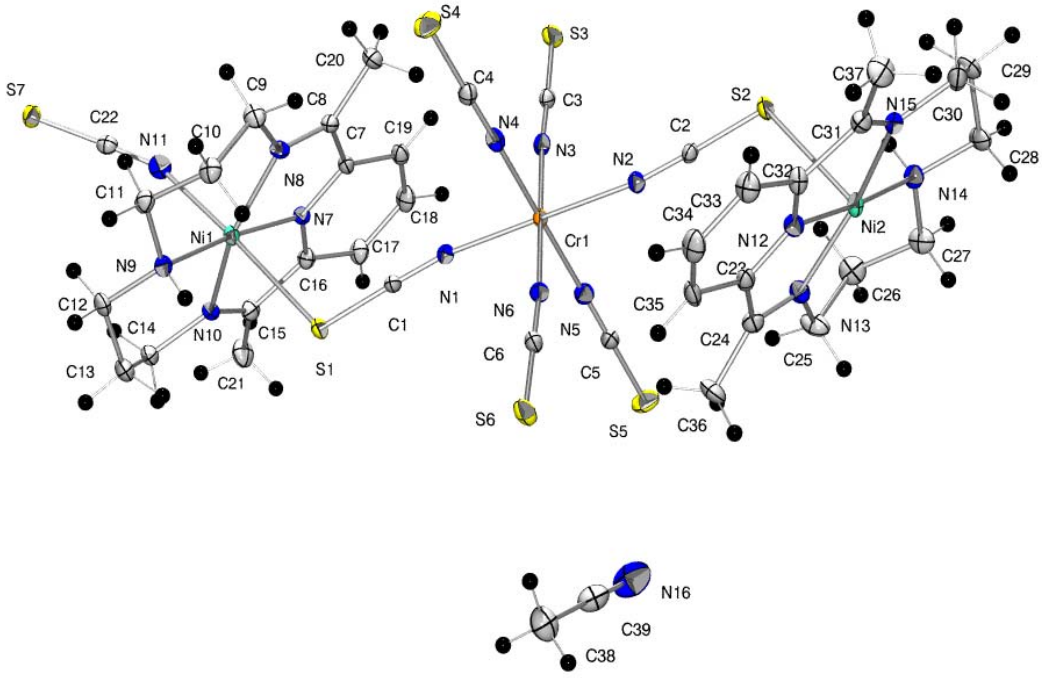


Table SI3. Selected bond lengths and angles for **3**.

DISTANCES (Å)

Cr1	N1	2.017(3)Å	Cr1	N2	2.015(3)Å
Cr1	N3	2.008(3)Å	Cr1	N4	2.005(3)Å
Cr1	N5	2.000(3)Å	Cr1	N6	1.987(3)Å
Ni1	N7	1.939(3)Å	Ni1	N8	2.039(3)Å
Ni1	N9	2.008(3)Å	Ni1	N10	2.062(3)Å
Ni1	N11	2.088(4)Å	Ni1	S1	2.6432(10)Å
Ni2	N12	1.936(3)Å	Ni2	N13	2.010(3)Å
Ni2	N14	2.009(3)Å	Ni2	N15	2.101(3)Å
Ni2	S2	2.5534(10)Å	Ni2	S7 2_645	2.5394(10)Å
C1	N1	1.158(4)Å	C1	S1	1.638(3)Å
C2	N2	1.149(4)Å	C2	S2	1.643(3)Å
C3	N3	1.147(4)Å	C3	S3	1.622(3)Å
C4	N4	1.129(5)Å	C4	S4	1.640(4)Å
C5	N5	1.150(5)Å	C5	S5	1.617(4)Å
C6	N6	1.156(5)Å	C6	S6	1.631(4)Å

ANGLES (°)

N2	C2	S2	178.1(3)°	N1	C1	S1	178.3(3)°
N4	C4	S4	179.3(3)°	N3	C3	S3	177.9(3)°
N6	C6	S6	178.8(4)°	N5	C5	S5	178.5(4)°
Cr1	N2	C2	167.3(3)°	Cr1	N1	C1	165.1(3)°
Cr1	N4	C4	176.9(3)°	Cr1	N3	C3	171.8(3)°
Cr1	N6	C6	171.9(3)°	Cr1	N5	C5	174.5(3)°
Ni1	S1	C1	106.33(11)°	Ni2	S2	C2	105.44(12)°
Ni2 2_655	S7	C22	103.37(12)°	Ni1	N11	C22	157.8(3)°

Table SI4. Spin density distribution for $\{Mo(NCS)_6\}^{3-}$ in **1** deduced from DFT calculations.

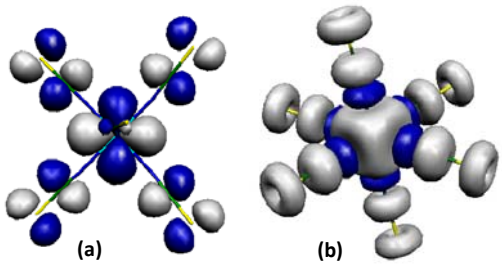
Atom (structure[1] label)	Atom (DFT labeling)	Spin density
Mo1	Mo1	2.521467
N1	N3	-0.075417
C1	C2	0.085085
S1	S1	0.064320
N2	N5	-0.076352
C2	C10	0.087830
S2	S15	0.065893
N3	N6	-0.078432
C3	C11	0.094175
S3	S16	0.069746
N4	N7	-0.076581
C4	C12	0.088087
S4	S17	0.064454
N5	N8	-0.077863
C5	C13	0.090577
S5	S18	0.066542
N6	N9	-0.078202
C6	C14	0.094561
S6	S19	0.070111
Mo2	Mo2	2.509164
N7	N3	-0.078071
C7	C2	0.091139
S7	S1	0.066833
N8	N5	-0.077622
C8	C10	0.091322
S8	S15	0.068098
N9	N6	-0.077002
C9	C11	0.092689
S9	N16	0.068006
N10	N7	-0.077303
C10	C12	0.089451
S10	N17	0.066049
N11	N8	-0.077923
C11	C13	0.091415
S11	N18	0.067781
N12	N9	-0.079453
C12	C14	0.095484
S12	N19	0.069942

[1] Label as in Figure SI1

Table SI5. Spin distribution obtained for $\{Mo(NCS)_6\}^{3-}$ at crystallographic coordinates reported for $K_3\{MoNCS\}_6$.[1]

Atom (structure[1] label)	Atom (DFT labeling)	Spin density
Mo	Mo	2.480367
N1	N6	-0.084097
C1	C1	0.096178
S1	S10	0.072329
N2	N7	-0.086545
C2	C2	0.126992
S2	S11	0.071795
N3	N14 / N8	-0.076586 / -0.076564
C3	C16 / C3	0.097820 / 0.097787
S3	S18 / S12	0.070462 / 0.070430
N4	N15 / N9	-0.076366 / -0.076364
C4	C17 / C4	0.085390 / 0.085401
S4	S19 / S13	0.060787 / 0.060785

[1] The atom labeling refers to Figure 1 in J. R. Knox and K. Eriks, *Inorg. Chem.*, **1968**, *7*, 84-90.

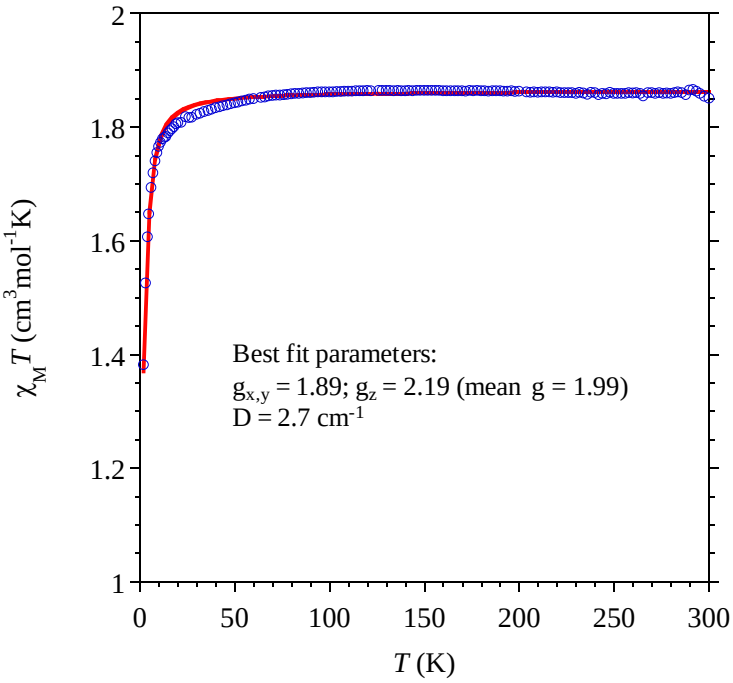


(a) One of the three HOMOs, and *(b)* distribution of spin density (positive in grey) and negative in (blue)

Full reference for Gaussian03:

Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian, Inc., Pittsburgh PA,* ***2003.***

Figure SI5. Experimental and calculated (—) $\chi_M T$ versus *T*, and M versus H for $(PPh_4)_3\{Mo(NCS)_6\}.2MeCN$, **1**.



Modeling has been performed with the expression of χ_M susceptibility for an ion with d^3 configuration in axially distorted octahedral surroundings given by O. Kahn *Molecular Magnetism*, Weiley-VCH, Weinheim **1993**.