Supporting Information

Synthesis of Ni(II)-Mn(II) complexes using a new mononuclear Ni(II) complex of an N_2O_3 donor unsymmetrical ligand: structures, magnetic properties and catalytic oxidase activity

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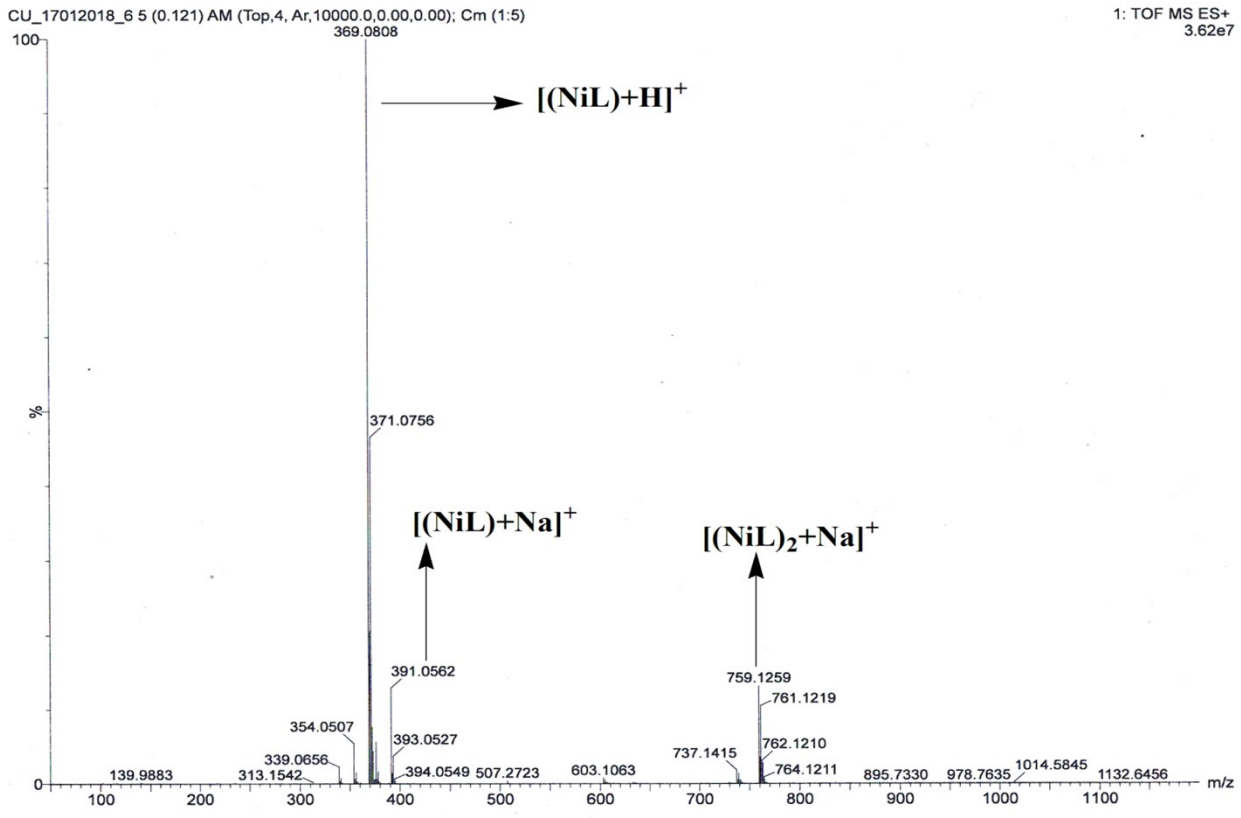


Fig. S1 ESI-mass spectrum of complex **1**.

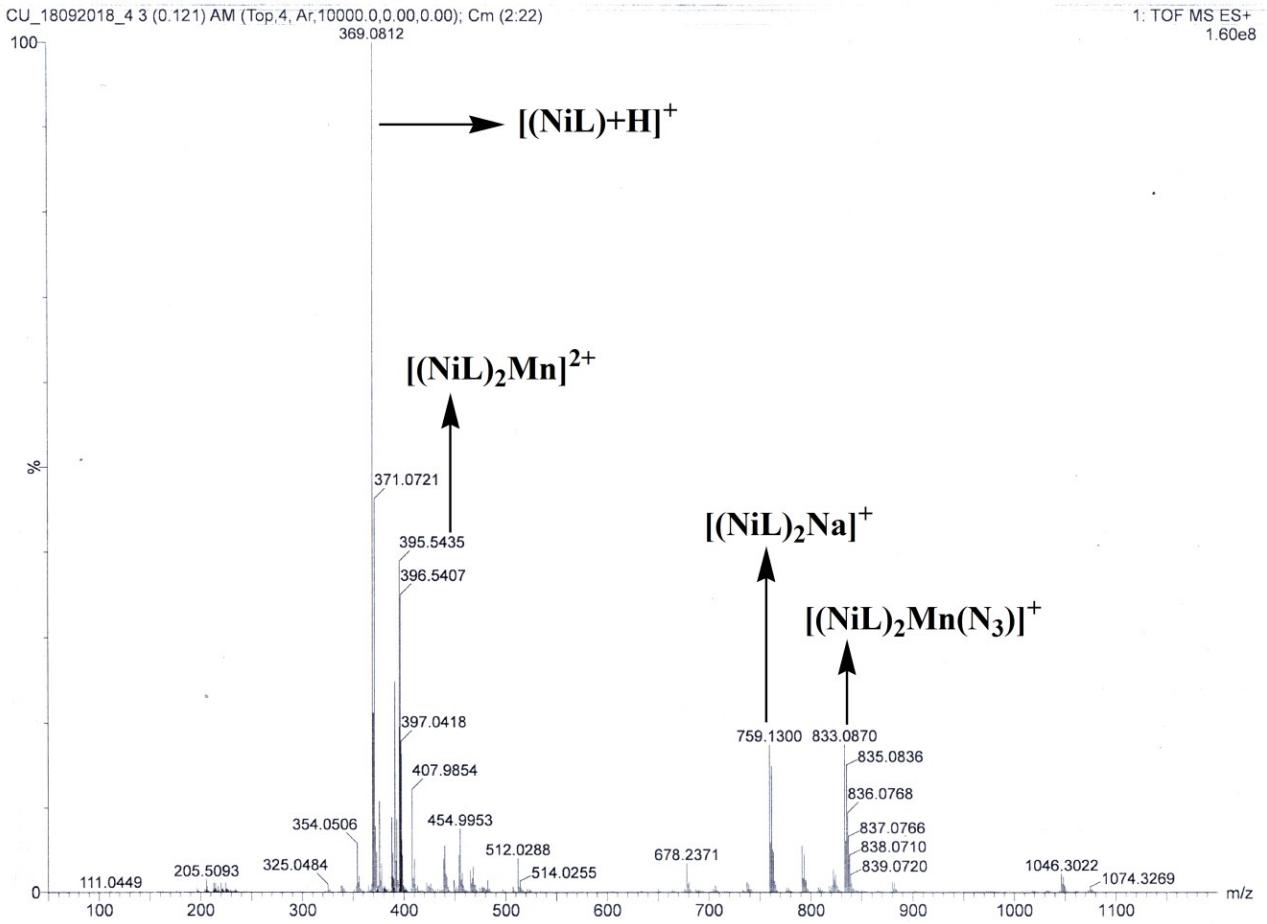


Fig. S2 ESI-mass spectrum of complex **4**.

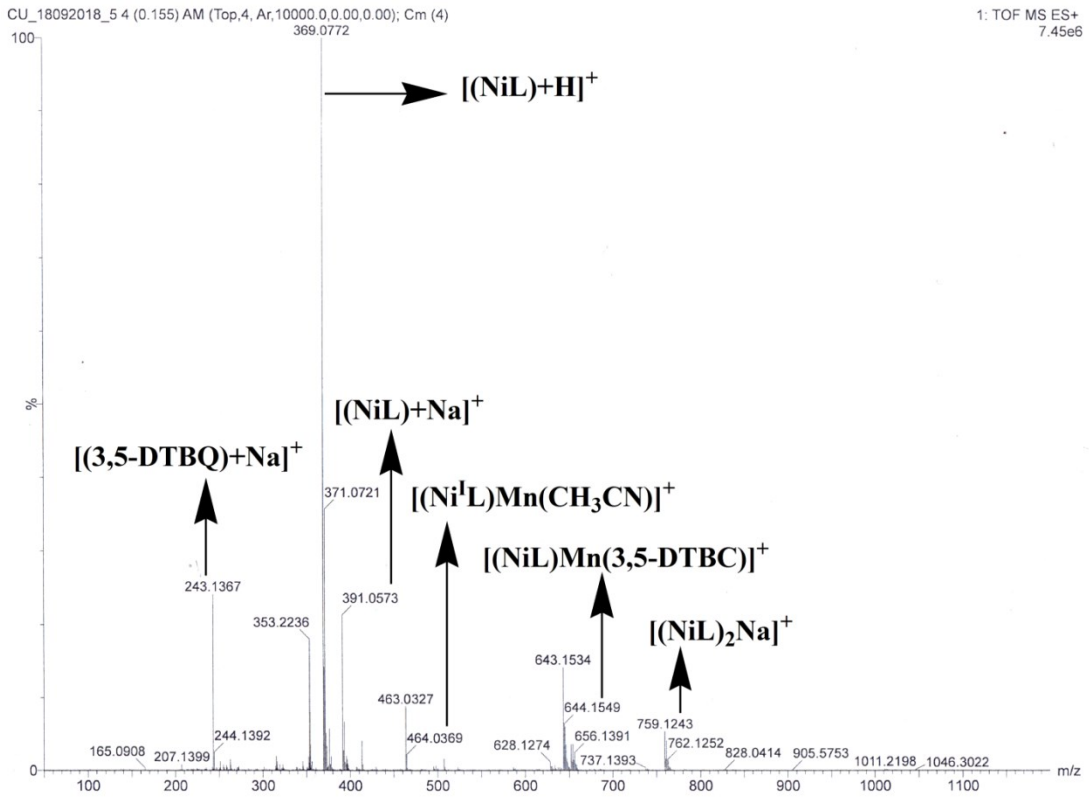


Fig. S3 ESI-mass spectrum of complex **4** with 3,5-DTBC.

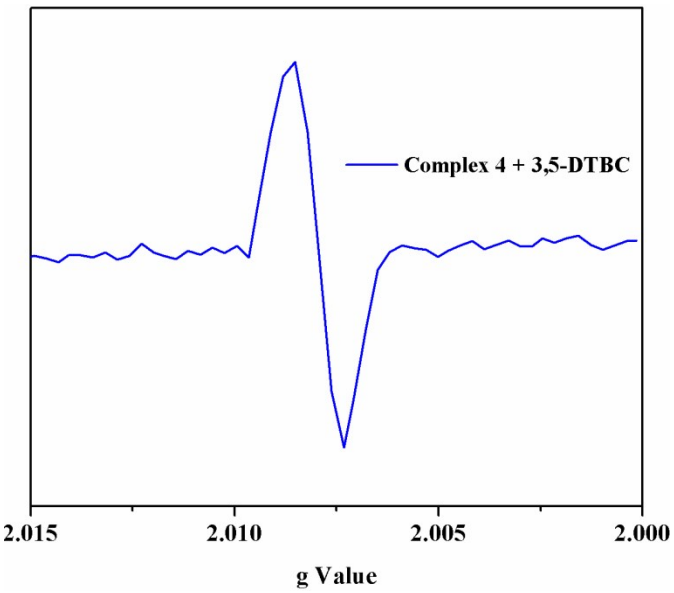


Fig. S4 EPR spectrum of complex **4** with 3,5-DTBC in acetonitrile at 113 K.

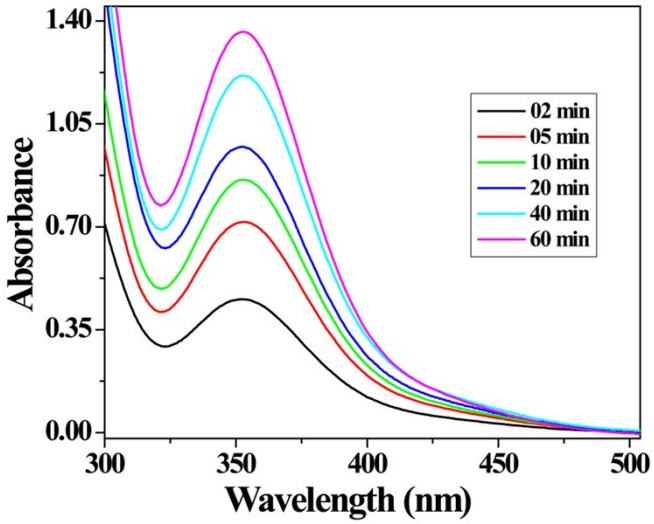


Fig. S5 Increase of the absorption band at around 353 nm during H_2O_2 estimation.

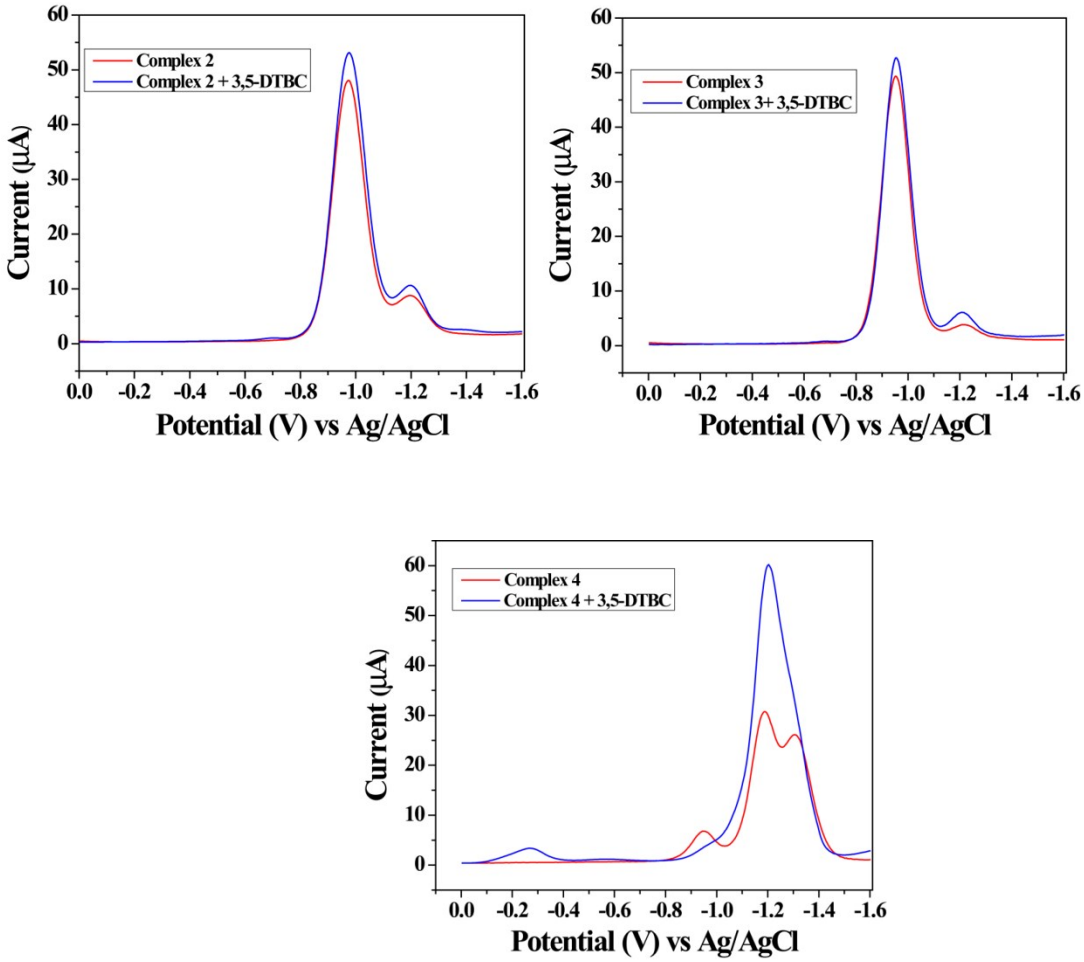


Fig. S6 Differential Pulse Voltammograms (DPVs) of complexes **2** (left), **3** (right) and **4** (middle) and the 1:1 mixture of the complexes with 3,5-DTBC in deoxygenated acetronitrile.

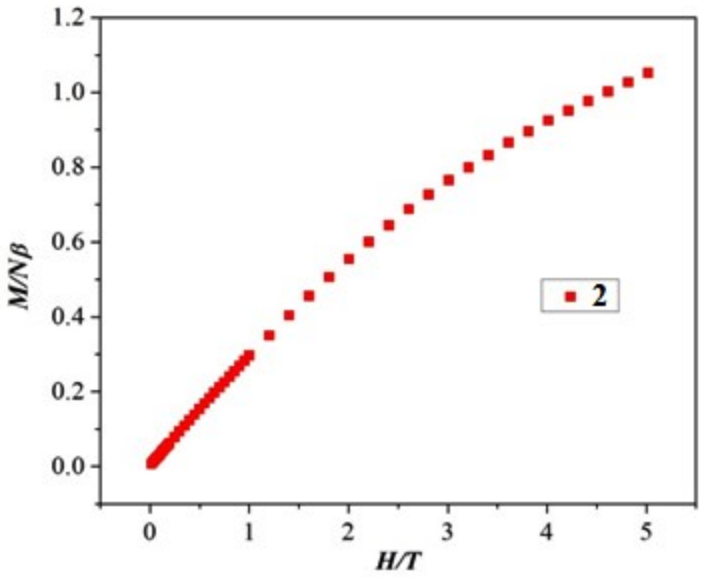


Fig. S7 Isothermal magnetizations at 2 K for complex **2**.

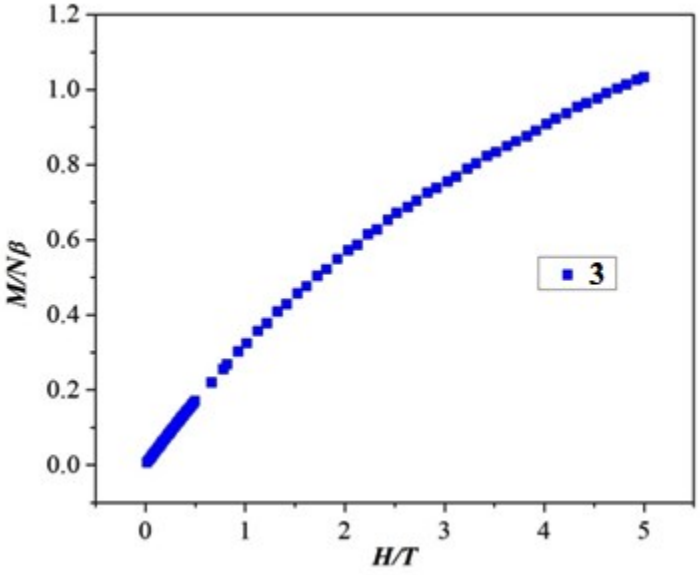


Fig. S8 Isothermal magnetizations at 2.5 K for complex **3**.

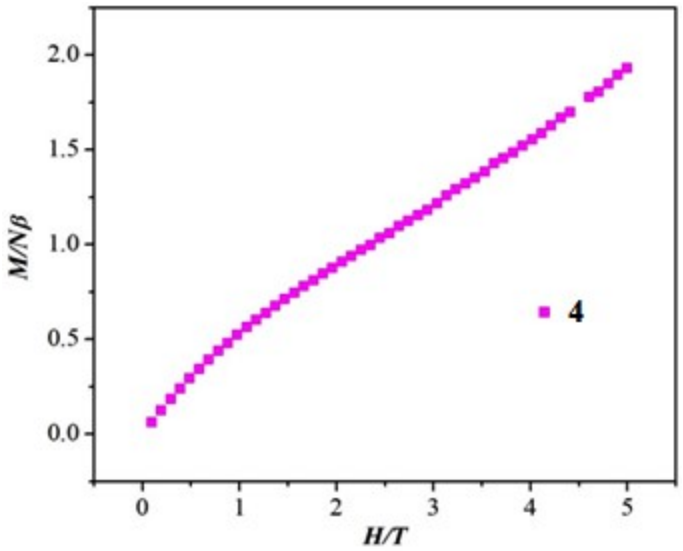


Fig. S9 Isothermal magnetizations at 2 K for complex **4**.

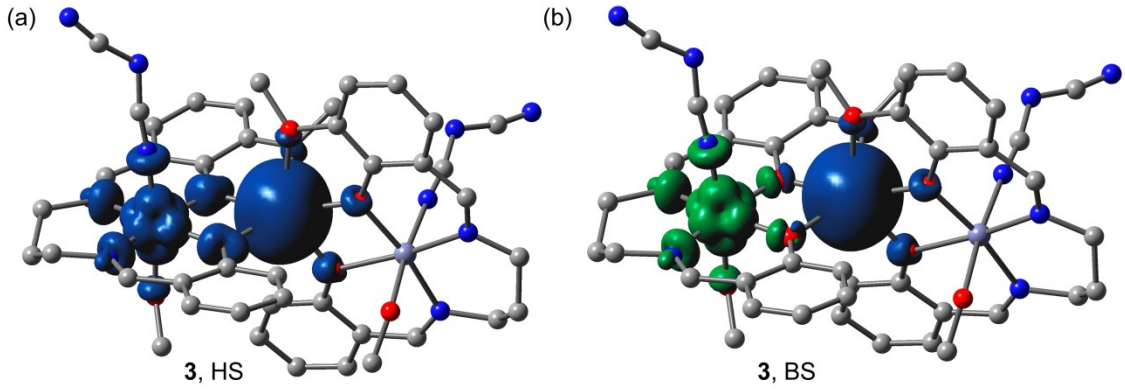
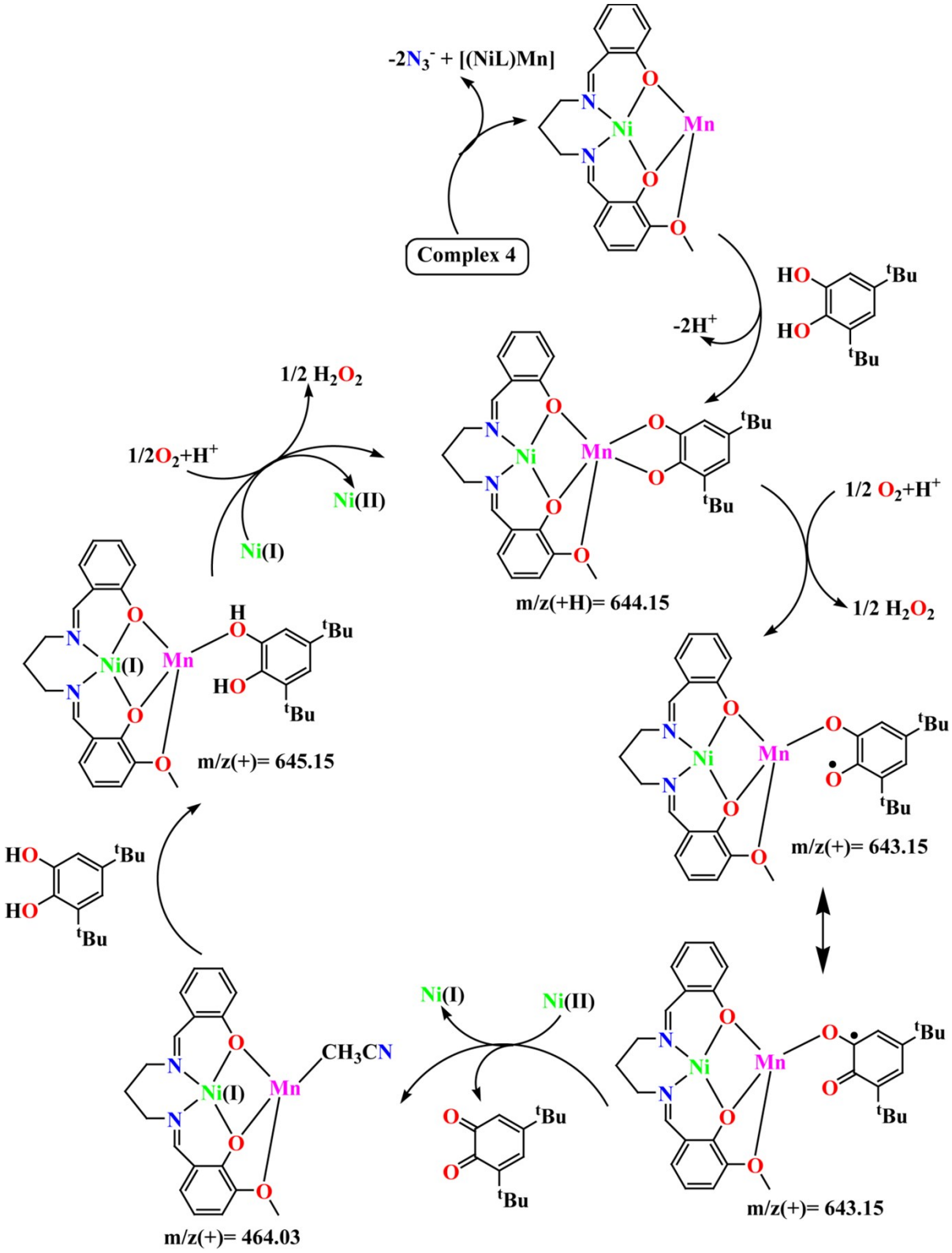


Fig. S10 High spin (a) and low spin (b) density plots of complex **3**.



Scheme S1 Proposed mechanism for catalytic oxidation of 3,5-DTBC to 3,5-DTBQ by complex **4**.

Table S1 Selected bond lengths (Å), bond angles (º) of complexes **2** and **3**.

	Complex **2**	Complex **3**
Ni(1)–O(1)	2.002 (3)	2.008(3)
Ni(1)–O(2)	2.041(3)	2.040(3)
Ni(1)–O(4)	2.194(3)	2.190(3)
Ni(1)–N(1)	2.042(3)	2.040(3)
Ni(1)–N(2)	2.016(4)	2.012(4)
Ni(1)–N(3)	2.083(4)	2.096(4)
Mn(1)–O(1)	2.095(2)	2.087(2)
Mn(1)–O(2)	2.159(3)	2.160(3)
Mn(1)–O(3)	2.397(3)	2.427(3)
O(1)–Ni(1)–O(2)	77.61(10)	77.54(10)
O(1)–Ni(1)–O(4)	89.10(11)	89.34(12)
O(1)–Ni(1)–N(1)	90.61(12)	90.90(12)
O(1)–Ni(1)–N(2)	169.31(12)	170.11(13)
O(1)–Ni(1)–N(3)	94.26(13)	93.44(14)
O(2)–Ni(1)–O(4)	90.51(11)	89.33(11)
O(2)–Ni(1)–N(1)	167.02(13)	166.90(13)
O(2)–Ni(1)–N(2)	92.58(12)	92.63(13)
O(2)–Ni(1)–N(3)	97.11(12)	96.21(14)
O(4)–Ni(1)–N(1)	83.82(13)	84.35(13)
O(4)–Ni(1)–N(2)	86.75(13)	89.51(14)
O(4)–Ni(1)–N(3)	172.18(13)	174.22(14)
N(1)–Ni(1)–N(2)	98.72(14)	98.76(15)
N(1)–Ni(1)–N(3)	89.08(14)	90.54(15)
N(2)–Ni(1)–N(3)	91.11(15)	88.61(15)
O(1)–Mn(1)–O(2)	73.09(10)	73.26(10)
O(1)–Mn(1)–O(3)	69.23(10)	68.79(10)

O(1)–Mn(1)–O(1)[a]	162.95(11)	161.23(11)
O(1)–Mn(1)–O(2)[a]	116.97(10)	118.03(10)
O(1)–Mn(1)–O(3)[a]	97.34(10)	96.32(10)
O(2)–Mn(1)–O(3)	140.62(9)	140.55(10)
O(1)[a]–Mn(1)–O(2)	116.97(10)	118.03(10)
O(2)–Mn(1)–O(2)[a]	113.48(10)	112.22(11)
O(2)–Mn(1)–O(3)[a]	93.80(10)	95.06(10)
O(1)[a]–Mn(1)–O(3)	97.34(10)	96.32(10)
O(2)[a]–Mn(1)–O(3)	93.80(10)	95.06(10)
O(3)–Mn(1)–O(3)[a]	80.18(9)	79.00(9)
O(1)[a]–Mn(1)–O(2)[a]	73.09(10)	73.26(10)
O(1)[a]–Mn(1)–O(3)[a]	69.23(10)	68.79(10)
O(2)[a]–Mn(1)–O(3)[a]	140.62(9)	140.55(10)
Ni(1)–O(1)–Mn(1)	106.49(12)	106.39(12)
Ni(1)–O(2)–Mn(1)	102.81(11)	102.61(12)

[a] = 1-x,y,3/2-z for complex **2**

1/2-x,1/2-y,z for complex **3**

Table S2 Selected bond lengths (Å), bond angles (º) of complex **4**.

	Complex**4**
Ni(1)–O(1)	1.992(2)
Ni(1)–O(2)	2.090(2)
Ni(1)–O(3)	2.181(3)
Ni(1)–N(1)	2.042(3)
Ni(1)–N(2)	1.994(3)
Ni(1)–N(3)[a]	2.155(3)
Mn(1)–O(1)	2.108(2)
Mn(1)–O(2)	2.251(2)
Mn(1)–O(3)	2.331(2)

Mn(1)–N(3)	2.150(3)
Mn(1)–N(6)	2.174(4)
Mn(1)–O(2)[a]	2.317(2)
O(1)–Ni(1)–O(2)	80.12(8)
O(1)–Ni(1)–O(4)	82.99(10)
O(1)–Ni(1)–N(1)	90.20(13)
O(1)–Ni(1)–N(2)	169.74(10)
O(1)–Ni(1)–N(3)[a]	94.87(11)
O(2)–Ni(1)–O(4)	88.83(9)
O(2)–Ni(1)–N(1)	169.66(12)
O(2)–Ni(1)–N(2)	91.38(9)
O(2)–Ni(1)–N(3)[a]	81.95(9)
O(4)–Ni(1)–N(1)	93.61(12)
O(4)–Ni(1)–N(2)	91.16(12)
O(4)–Ni(1)–N(3)[a]	170.76(10)
N(1)–Ni(1)–N(2)	98.60(13)
N(1)–Ni(1)–N(3)[a]	95.38(12)
N(2)–Ni(1)–N(3)[a]	89.58(13)
O(1)–Mn(1)–O(2)	74.08(8)
O(1)–Mn(1)–O(3)	70.66(8)
O(1)–Mn(1)–N(3)	164.73(11)
O(1)–Mn(1)–N(6)	96.33(12)
O(1)–Mn(1)–O(2)[a]	88.57(8)
O(2)–Mn(1)–O(3)	144.65(8)
O(2)–Mn(1)–N(3)	109.83(10)
O(2)–Mn(1)–N(6)	93.50(12)
O(2)–Mn(1)–O(2)[a]	87.87(8)
O(3)–Mn(1)–N(3)	103.65(10)

O(3)–Mn(1)–N(6)	92.71(12)
O(2)[a]–Mn(1)–O(3)	88.87(8)
N(3)–Ni(1)–N(6)	98.13(13)
O(2)[a]–Mn(1)–N(3)	77.00(10)
O(2)[a]–Mn(1)–N(6)	175.11(11)
Ni(1)–O(1)–Mn(1)	106.23(9)
Ni(1)–O(2)–Mn(1)	98.08(8)
Ni(1)[a]–N(3)–Mn(1)	100.80(12)
Mn(1)–N(6)–N(7)	127.1(3)

[a] = 1-x, 1-y, 1-z for complex **4**

Table S3 Comparison table for catecholase activities by previously reported complexes.

Complexes	k_{cat} (h^{-1})	Solvent	References
$[(NiL)_2Mn(NCS)_2]$	104.5	Methanol	53
$[(NiL)_2Mn(NCO)_2]$	77	Methanol	53
$[\{NiL(EtOH)\}_2Mn(NO_2)_2]\cdot 2EtOH$	25.8	Methanol	53
$[(NiL)_2Mn(N_3)(H_2O)](ClO_4)\cdot H_2O$	984	Methanol	31
$[\{(NiL)_2Mn(H_2O)\}_2(\mu_{1,3}N_3)](ClO_4)_3$	2081	Methanol	31
$[(NiL)_2Mn(N_3)](ClO_4)$	768	Methanol	28
$[(NiL)_2Mn_2(N_3)_2(\mu_{1,1}N_3)_2(CH_3OH)_2]$	1985	Methanol	28
$[\{(NiL)_2Mn\}_2(\mu_{1,3}N_3)(H_2O)]\cdot(CH_3OH).(ClO_4)_3$	2309	Methanol	28
$[(NiL)_2Mn_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2(CH_3OH)_2]$	935	Acetonitrile	This work

Table S4 Correlations of magnetic coupling with bridging angle for earlier reported diphenoxido-bridged Ni^{II}–Mn^{II} complexes.

Complex	J_{Ni-Mn}/cm^{-1}	Ni–O–Mn angle/deg	Ref.
$[Mn^{II}(Ni^{II}L)_2]\cdot 2CH_3OH$	+9.30	86.38	52
$[Mn^{II}(Ni^{II}L)_2(OAc)_4(H_2O)_2]$	−0.30	102.31	63
$[(NiL)_2Mn(OCnn)_2(CH_3OH)_2]\cdot CH_3OH$	+1.38	97.24	54
$[(NiL)_2Mn(OPh)_2(CH_3OH)_2][(NiL)_2Mn(O$	+0.50	96.43	54

$Ph)_2]\cdot H_2O$			
$[(NiL)_2Mn(OSal)_2(CH_3OH)_2]\cdot 2[NiL]$	−0.24	98.51	54
$[(NiL^1)^2Mn(OOCPh)_2(H_2O)_2]\cdot CH_3OH$	−0.60	97.35	51
$[(NiL^2)_2Mn(OOCPh)_2(CH_3OH)_2]\cdot CH_3OH$	+2.00	97.34	51
$[(NiL^3)_2Mn(OOCPh)_2(H_2O)_2]\cdot CH_3OH$	+1.10	97.27	51
$[(NiL)_2Mn_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2(CH_3OH)_2]$	–4.95	102.58	28
$[(NiL)_2Mn(NCS)_2(CH_3OH)_2]\cdot CH_3OH$	–4.84	104.65	This work
$[(NiL)_2Mn(N(CN)_2)_2(CH_3OH)_2]\cdot CH_3OH$	–5.23	104.50	This work
$[(NiL)_2Mn_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2(CH_3OH)_2]$	–2.20	102.05	This work

Table S5 Atomic spin densities for the HS and LS configuration for polynuclear complexes **2** and **3**.

Atom	HS	LS
	2	
Ni	1.74	–1.74
Mn	4.91	4.90
O1	0.07	–0.03
O2	0.05	–0.03
	3	
Ni	1.77	–1.75
Mn	4.91	4.91
O1	0.07	–0.03
O2	0.05	–0.03

Table S6 Atomic spin densities at for the HS and LS configuration for the three coupling constants of polynuclear complex **4**.

Atom	HS	LS
	J_1	
Ni1	1.70	–1.67
Mn1	4.86	4.87
O1	0.05	–0.06
O2	0.03	–0.04
	J_2	

Ni1	1.72	–1.75
Mn1	4.84	4.85
O2	0.03	–0.07
N3[a]	0.02	–0.03
	J_3	
Mn1	4.86	–4.84
Mn1[a]	4.86	4.84
O2	0.04	0.00
O2[a]	0.04	0.00

ORCA INPUT FILES:

Complex 2:

```
# gosh multispin
#thio_complex 3, replaceone Ni by Zn
#
!B3LYP def2-TZVP RIjk def2/jk UKS grid4
%pal nprocs 4 end
%maxcore 7500
%scf
        MaxIter 900
        brokensym 5,2
end

* xyz 0 8

 C                  5.06120000    4.44330000   17.64830000
 C                  4.37990000    3.59440000   18.53640000
 C                  3.44900000    2.68350000   18.08210000
 H                  3.00170000    2.13270000   18.68450000
 C                  3.18360000    2.59410000   16.72870000
 H                  2.54740000    1.99140000   16.42110000
 C                  3.85450000    3.38830000   15.84350000
 H                  3.67290000    3.31170000   14.93470000
 C                  4.81970000    4.32660000   16.28440000
 C                  5.51580000    5.08800000   15.26570000
 H                  5.22060000    4.97310000   14.39240000
 C                  7.06410000    6.48940000   14.21280000
 H                  7.23370000    5.76270000   13.59390000
 H                  6.37650000    7.04650000   13.81240000
 C                  8.15920000    7.20880000   14.28180000
 H                  8.01660000    7.84990000   13.56690000
 H                  8.81990000    6.59250000   13.93110000
 C                  8.90950000    7.94290000   15.16400000
 H                  8.73600000    8.88200000   14.99400000
 H                  9.84510000    7.78240000   14.96430000
 C                  9.46270000    8.36140000   17.37750000
 H                 10.05590000    8.94680000   16.96340000
 C                  9.52920000    8.32860000   18.81130000
 C                 10.53380000    9.11640000   19.39840000
 H                 11.05440000    9.65530000   18.84640000
 C                 10.77790000    9.12820000   20.73080000
 H                 11.45160000    9.66160000   21.08820000
 C                  9.99670000    8.32040000   21.54840000
```

H	10.16010000	8.30030000	22.46410000
C	8.98640000	7.54990000	21.02290000
H	8.47610000	7.02190000	21.59270000
C	8.70490000	7.53800000	19.65760000
C	4.39740000	2.74460000	20.79470000
H	3.45190000	2.74550000	20.96140000
H	4.86560000	2.89780000	21.61700000
H	4.65640000	1.89480000	20.43270000
C	6.04970000	9.34620000	17.70530000
H	6.70170000	9.30880000	18.40940000
H	5.21200000	9.64980000	18.06140000
H	6.34850000	9.95340000	17.02540000
C	9.14640000	3.90990000	16.51800000
H	5.19930000	8.06960000	16.64500000
Mn	6.21720000	5.61650000	20.23300000
N	6.49190000	5.90130000	15.42940000
N	8.70330000	7.69940000	16.59430000
N	8.63760000	4.80620000	17.03140000
Ni	7.30610000	6.39500000	17.23530000
O	5.91920000	5.30590000	18.18250000
O	7.69540000	6.80040000	19.19740000
O	4.71950000	3.78310000	19.86020000
O	5.88710000	8.06600000	17.15140000
S	9.86820000	2.63410000	15.81520000
C	7.37310000	4.44330000	22.81770000
C	8.05440000	3.59440000	21.92960000
C	8.98530000	2.68350000	22.38390000
H	9.43260000	2.13270000	21.78150000
C	9.25070000	2.59410000	23.73740000
H	9.88690000	1.99140000	24.04490000
C	8.57980000	3.38830000	24.62250000
H	8.76140000	3.31170000	25.53140000
C	7.61460000	4.32660000	24.18170000
C	6.91850000	5.08800000	25.20040000
H	7.21370000	4.97310000	26.07360000
C	5.37020000	6.48940000	26.25330000
H	5.20060000	5.76270000	26.87220000
H	6.05780000	7.04650000	26.65360000
C	4.27510000	7.20880000	26.18420000
H	4.41770000	7.84990000	26.89910000
H	3.61450000	6.59250000	26.53490000
C	3.52480000	7.94290000	25.30210000
H	3.69830000	8.88200000	25.47200000
H	2.58920000	7.78240000	25.50170000
C	2.97160000	8.36140000	23.08860000
H	2.37840000	8.94680000	23.50270000
C	2.90510000	8.32860000	21.65470000
C	1.90050000	9.11640000	21.06770000
H	1.37990000	9.65530000	21.61970000
C	1.65640000	9.12820000	19.73530000
H	0.98270000	9.66160000	19.37780000
C	2.43760000	8.32040000	18.91760000
H	2.27420000	8.30030000	18.00200000
C	3.44800000	7.54990000	19.44310000
H	3.95820000	7.02190000	18.87340000
C	3.72940000	7.53800000	20.80850000
C	8.03690000	2.74460000	19.67140000
H	8.98240000	2.74550000	19.50460000
H	7.56870000	2.89780000	18.84910000
H	7.77790000	1.89480000	20.03340000
C	6.38460000	9.34620000	22.76080000
H	5.73260000	9.30880000	22.05670000
H	7.22230000	9.64980000	22.40470000
H	6.08580000	9.95340000	23.44060000
C	3.28790000	3.90990000	23.94810000
H	7.23510000	8.06960000	23.82100000
N	5.94240000	5.90130000	25.03660000
N	3.73100000	7.69940000	23.87170000
N	3.79670000	4.80620000	23.43470000
Zn	5.12820000	6.39500000	23.23080000
O	6.51510000	5.30590000	22.28360000

```
O                  4.73890000    6.80040000   21.26870000
 O                 7.71480000    3.78310000   20.60590000
 O                 6.54730000    8.06600000   23.31470000
 S                 2.56610000    2.63410000   24.65080000
*
```

Complex 4:

```
# gosh multispin
#azidaMn-Mn-Zn2, replace 2 Ni by 2 Zn
#
!B3LYP def2-TZVP RIjk def2/jk UKS grid4
%pal nprocs 8 end
%maxcore 10000
%scf
        MaxIter 900
        brokensym 5,5
end

* xyz 0 11
 C                 6.55300000    7.82430000    9.34500000
 C                 7.87230000    8.30600000    9.21050000
 C                 8.71520000    8.41740000   10.27760000
 H                 9.58050000    8.73760000   10.16370000
 C                 8.25770000    8.04310000   11.54710000
 H                 8.82500000    8.10700000   12.28140000
 C                 6.98820000    7.58350000   11.70870000
 H                 6.69480000    7.35650000   12.56130000
 C                 6.10690000    7.44420000   10.62430000
 C                 4.78500000    6.95680000   10.88580000
 H                 4.57230000    6.83160000   11.78250000
 C                 2.55630000    6.23600000   10.62550000
 H                 2.70270000    5.89410000   11.52130000
 H                 1.97380000    7.00850000   10.69690000
 C                 1.86690000    5.18800000    9.81870000
 H                 2.47590000    4.43970000    9.72530000
 H                 1.10560000    4.87450000   10.33210000
 C                 1.38610000    5.54310000    8.48020000
 H                 0.84510000    6.34550000    8.54590000
 H                 0.81380000    4.82960000    8.15600000
 C                 2.29010000    5.28890000    6.33360000
 H                 1.54250000    4.74840000    6.22020000
 C                 3.12310000    5.47350000    5.15920000
 C                 2.78370000    4.67790000    4.03650000
 H                 2.11130000    4.04120000    4.11480000
 C                 3.42500000    4.83110000    2.84360000
 H                 3.19610000    4.29310000    2.12020000
 C                 4.39890000    5.77120000    2.71280000
 H                 4.82140000    5.88520000    1.89210000
 C                 4.76490000    6.55460000    3.78360000
 H                 5.44480000    7.18030000    3.68010000
 C                 4.13460000    6.42580000    5.02350000
 C                 9.43680000    9.30530000    7.67590000
 H                 9.50570000   10.07640000    8.24330000
 H                 9.48880000    9.57830000    6.75690000
 H                10.15560000    8.69930000    7.87060000
 C                 5.04290000    3.68030000    7.78930000
 H                 4.35850000    3.45100000    8.42190000
 H                 5.83860000    3.17870000    7.98280000
 H                 4.74170000    3.47170000    6.90190000
 Mn                6.61270000    7.98250000    6.32910000
N                  3.86410000    6.67160000   10.05810000
 N                 2.45160000    5.77400000    7.49570000
 N                 7.37860000    8.76850000    4.48070000
 N                 7.86010000    8.18220000    3.55540000
 N                 8.32030000    7.63750000    2.66840000
 N                 7.45540000    5.98360000    6.18560000
 N                 8.40000000    5.74330000    5.97710000
 N                 9.53880000    5.33250000    5.67360000
Zn                 4.05850000    6.82690000    8.03090000
```

```
 O                    5.80520000    7.75580000    8.26260000
 O                    4.50030000    7.26230000    6.03560000
 O                    8.19030000    8.65420000    7.90800000
 O                    5.32360000    5.05720000    7.87820000
 H                    6.05700000    5.19150000    7.43900000
 C                    3.73410000    9.58500000    2.99160000
 C                    2.41480000    9.10330000    3.12610000
 C                    1.57190000    8.99190000    2.05900000
 H                    0.70660000    8.67170000    2.17290000
 C                    2.02930000    9.36620000    0.78950000
H                    1.46210000    9.30230000    0.05520000
 C                    3.29890000    9.82580000    0.62790000
 H                    3.59230000   10.05280000   -0.22460000
 C                    4.18020000    9.96510000    1.71230000
 C                    5.50210000   10.45250000    1.45080000
 H                    5.71480000   10.57770000    0.55420000
 C                    7.73070000   11.17330000    1.71110000
 H                    7.58440000   11.51520000    0.81530000
 H                    8.31330000   10.40080000    1.63970000
 C                    8.42020000   12.22130000    2.51790000
 H                    7.81120000   12.96960000    2.61130000
 H                    9.18150000   12.53480000    2.00450000
 C                    8.90100000   11.86620000    3.85640000
 H                    9.44190000   11.06380000    3.79080000
 H                    9.47330000   12.57970000    4.18060000
 C                    7.99700000   12.12040000    6.00300000
 H                    8.74460000   12.66090000    6.11640000
 C                    7.16400000   11.93580000    7.17750000
 C                    7.50330000   12.73140000    8.30010000
 H                    8.17580000   13.36810000    8.22180000
 C                    6.86210000   12.57820000    9.49300000
 H                    7.09100000   13.11620000   10.21640000
 C                    5.88820000   11.63810000    9.62380000
 H                    5.46570000   11.52410000   10.44460000
 C                    5.52210000   10.85470000    8.55300000
 H                    4.84230000   10.22900000    8.65650000
 C                    6.15240000   10.98350000    7.31320000
 C                    0.85030000    8.10400000    4.66080000
 H                    0.78130000    7.33290000    4.09330000
 H                    0.79820000    7.83100000    5.57970000
 H                    0.13150000    8.71000000    4.46600000
 C                    5.24420000   13.72900000    4.54730000
 H                    5.92850000   13.95830000    3.91480000
 H                    4.44850000   14.23060000    4.35380000
 H                    5.54540000   13.93760000    5.43480000
 Mn                   3.67440000    9.42680000    6.00760000
 N                    6.42290000   10.73770000    2.27860000
 N                    7.83550000   11.63530000    4.84090000
 N                    2.90850000    8.64080000    7.85600000
N                    2.42690000    9.22710000    8.78120000
 N                    1.96670000    9.77180000    9.66820000
 N                    2.83170000   11.42570000    6.15100000
 N                    1.88710000   11.66600000    6.35950000
 N                    0.74830000   12.07680000    6.66300000
 Zn                   6.22860000   10.58240000    4.30570000
 O                    4.48190000    9.65350000    4.07400000
 O                    5.78680000   10.14700000    6.30110000
 O                    2.09670000    8.75510000    4.42860000
O                    4.96350000   12.35210000    4.45850000
 H                    4.23000000   12.21780000    4.89760000
*
```

ORCA OUTPUT FILES:

Complex 2

```
                 *****************
                 * O   R   C   A *
                 *****************
```

```
           --- An Ab Initio, DFT and Semiempirical electronic structure package ---

                  ######################################################
                  #                        -***-                       #
                  #          Department of theory and spectroscopy     #
                  #               Directorship: Frank Neese            #
                  #        Max Planck Institute fuer Kohlenforschung   #
                  #                Kaiser Wilhelm Platz 1              #
                  #                 D-45470 Muelheim/Ruhr              #
                  #                      Germany                       #
                  #                                                    #
                  #                 All rights reserved                #
                  #                        -***-                       #
                  ######################################################


                         Program Version 4.1.2  - RELEASE  -
```

[···]

```
-----------------------------------------
BROKEN SYMMETRY MAGNETIC COUPLING ANALYSIS
-----------------------------------------

S(High-Spin)      =   3.5
<S**2>(High-Spin) =  15.7590
<S**2>(BrokenSym) =   5.7514
E(High-Spin)      = -7714.777611 Eh
E(BrokenSym)      = -7714.778007 Eh
E(High-Spin)-E(BrokenSym)= 0.0108 eV     87.027 cm**-1 (ANTIFERROMAGNETIC coupling)

          ---------------------------------------------------------
          | Spin-Hamiltonian Analysis based on H(HDvV)= -2J*SA*SB |
    -------                                                         -----------
    | J(1) =      -7.10 cm**-1    (from -(E[HS]-E[BS])/Smax**2)              |
    | J(2) =      -5.53 cm**-1    (from -(E[HS]-E[BS])/(Smax*(Smax+1))       |
    | J(3) =      -8.70 cm**-1    (from -(E[HS]-E[BS])/(<S**2>HS-<S**2>BS)) |
    -------------------------------------------------------------------------
```


```
  J(1): (a) A.P. Ginsberg J. Am. Chem. Soc. 102 (1980), 111
        (b) L. Noodleman J. Chem. Phys. 74 (1981), 5737
        (c) L. Noodleman E.R. Davidson Chem. Phys. 109 (1986), 131
  J(2)  (d) A. Bencini D. Gatteschi J. Am. Chem. Soc. 108 (1980), 5763
  J(3)  (e) K. Yamaguchi Y. Takahara T. Fueno in: V.H. Smith (Ed.)
            Applied Quantum Chemistry. Reidel, Dordrecht (1986), pp 155
        (f) T.Soda et al. Chem. Phys. Lett., 319, (2000), 223
```


```
-------
TIMINGS
-------

Total SCF time: 1 days 22 hours 41 min 49 sec

Total time                  ....  168109.869 sec
Sum of individual times     ....   32593.462 sec  ( 19.4%)

Fock matrix formation       ....       0.000 sec  (  0.0%)
Diagonalization             ....       0.000 sec  (  0.0%)
Density matrix formation    ....       0.000 sec  (  0.0%)
Population analysis         ....   32593.462 sec  ( 19.4%)
Initial guess               ....       0.000 sec  (  0.0%)
Orbital Transformation      ....       0.000 sec  (  0.0%)
Orbital Orthonormalization  ....       0.000 sec  (  0.0%)
DIIS solution               ....       0.000 sec  (  0.0%)
Grid generation             ....       0.000 sec  (  0.0%)

-------------------------   --------------------
FINAL SINGLE POINT ENERGY     -7714.778007105625
-------------------------   --------------------
```

```
                            ************************************
                            *     ORCA property calculations     *
                            ************************************

                                    ---------------------
                                    Active property flags
                                    ---------------------
   (+) Dipole Moment


------------------------------------------------------------------------------
                        ORCA ELECTRIC PROPERTIES CALCULATION
------------------------------------------------------------------------------

Dipole Moment Calculation                      ... on
Quadrupole Moment Calculation                  ... off
Polarizability Calculation                     ... off
GBWName                                        ... thio_complex2_Zn_BS52.gbw
Electron density file                          ... thio_complex2_Zn_BS52.scfp.tmp
The origin for moment calculation is the CENTER OF MASS  = (11.734695, 11.141024 38.273501)

-------------
DIPOLE MOMENT
-------------
                                X             Y             Z
Electronic contribution:     -3.01033     -19.00040       8.17434
Nuclear contribution   :      2.96791      25.37253      -8.17120
                        -----------------------------------------
Total Dipole Moment    :     -0.04242       6.37213       0.00314
                        -----------------------------------------
Magnitude (a.u.)       :      6.37227
Magnitude (Debye)      :     16.19703



--------------------
Rotational spectrum
--------------------

Rotational constants in cm-1:     0.001947     0.001106     0.001099
Rotational constants in MHz :    58.359760    33.166680    32.959921

 Dipole components along the rotational axes:
x,y,z [a.u.] :     0.028412     0.022929    -6.372169
x,y,z [Debye]:     0.072218     0.058282   -16.196768



Timings for individual modules:

Sum of individual times         ...   168174.647 sec (=2802.911 min)
GTO integral calculation        ...       10.308 sec (=   0.172 min)   0.0 %
SCF iterations                  ...   168164.339 sec (=2802.739 min) 100.0 %
                               ****ORCA TERMINATED NORMALLY****
TOTAL RUN TIME: 1 days 22 hours 42 minutes 56 seconds 982 msec
```

Complex 4

```
                                 *****************
                                 * O   R   C   A *
                                 *****************

           --- An Ab Initio, DFT and Semiempirical electronic structure package ---

                  ######################################################
                  #                        -***-                       #
                  #          Department of theory and spectroscopy     #
```

```
                 #               Directorship: Frank Neese             #
                 #        Max Planck Institute fuer Kohlenforschung    #
                 #                Kaiser Wilhelm Platz 1               #
                 #                 D-45470 Muelheim/Ruhr               #
                 #                      Germany                        #
                 #                                                     #
                 #                  All rights reserved                #
                 #                        -***-                        #
                 #######################################################

[···]

                          Program Version 4.2.1 -  RELEASE  -
----------------------------------------
BROKEN SYMMETRY MAGNETIC COUPLING ANALYSIS
----------------------------------------

S(High-Spin)      =   5.0
<S**2>(High-Spin) =  30.0157
<S**2>(BrokenSym) =   5.0124
E(High-Spin)      = -8811.595969 Eh
E(BrokenSym)      = -8811.596205 Eh
E(High-Spin)-E(BrokenSym)= 0.0064 eV     51.818 cm**-1 (ANTIFERROMAGNETIC coupling)

          ---------------------------------------------------------
          | Spin-Hamiltonian Analysis based on H(HDvV)= -2J*SA*SB |
    -------                                                         -----------
    | J(1) =      -2.07 cm**-1    (from -(E[HS]-E[BS])/Smax**2)              |
    | J(2) =      -1.73 cm**-1    (from -(E[HS]-E[BS])/(Smax*(Smax+1))       |
    | J(3) =      -2.07 cm**-1    (from -(E[HS]-E[BS])/(<S**2>HS-<S**2>BS)) |
    ---------------------------------------------------------------------------

  J(1): (a) A.P. Ginsberg J. Am. Chem. Soc. 102 (1980), 111
        (b) L. Noodleman J. Chem. Phys. 74 (1981), 5737
        (c) L. Noodleman E.R. Davidson Chem. Phys. 109 (1986), 131
  J(2)  (d) A. Bencini D. Gatteschi J. Am. Chem. Soc. 108 (1980), 5763
  J(3)  (e) K. Yamaguchi Y. Takahara T. Fueno in: V.H. Smith (Ed.)
            Applied Quantum Chemistry. Reidel, Dordrecht (1986), pp 155
        (f) T.Soda et al. Chem. Phys. Lett., 319, (2000), 223

-------
TIMINGS
-------

Total SCF time: 1 days 21 hours 11 min 40 sec

Total time                  ....  162700.879 sec
Sum of individual times     ....   42620.788 sec  ( 26.2%)

Fock matrix formation       ....       0.000 sec  (  0.0%)
Diagonalization             ....       0.000 sec  (  0.0%)
Density matrix formation    ....       0.000 sec  (  0.0%)
Population analysis         ....   42620.788 sec  ( 26.2%)
Initial guess               ....       0.000 sec  (  0.0%)
Orbital Transformation      ....       0.000 sec  (  0.0%)
Orbital Orthonormalization  ....       0.000 sec  (  0.0%)
DIIS solution               ....       0.000 sec  (  0.0%)
Grid generation             ....       0.000 sec  (  0.0%)

-------------------------   --------------------
FINAL SINGLE POINT ENERGY     -8811.596205104523
-------------------------   --------------------


                            ************************************
                            *     ORCA property calculations     *
                            ************************************

                                    ---------------------
                                    Active property flags
                                    ---------------------
```

(+) Dipole Moment

```
-------------------------------------------------------------------------------
                        ORCA ELECTRIC PROPERTIES CALCULATION
-------------------------------------------------------------------------------

Dipole Moment Calculation                       ... on
Quadrupole Moment Calculation                   ... off
Polarizability Calculation                      ... off
GBWName                                         ... azidaMn2Zn2.gbw
Electron density file                           ... azidaMn2Zn2.scfp
The origin for moment calculation is the CENTER OF MASS  = ( 9.719880, 16.449405 11.656425)

-------------
DIPOLE MOMENT
-------------
                                X             Y             Z
Electronic contribution:      0.00043       0.00002      -0.00015
Nuclear contribution   :     -0.00022      -0.00000      -0.00021
                        -----------------------------------------
Total Dipole Moment    :      0.00021       0.00002      -0.00036
                        -----------------------------------------
Magnitude (a.u.)       :      0.00042
Magnitude (Debye)      :      0.00106



--------------------
Rotational spectrum
--------------------

Rotational constants in cm-1:     0.001608     0.001321     0.001120
Rotational constants in MHz :    48.214959    39.609306    33.570329

 Dipole components along the rotational axes:
x,y,z [a.u.] :    -0.000340     0.000020    -0.000238
x,y,z [Debye]:    -0.000864     0.000052    -0.000606



Timings for individual modules:

Sum of individual times         ...   162784.947 sec (=2713.082 min)
GTO integral calculation        ...       20.290 sec (=   0.338 min)   0.0 %
SCF iterations                  ...   162764.657 sec (=2712.744 min) 100.0 %
                             ****ORCA TERMINATED NORMALLY****
TOTAL RUN TIME: 1 days 21 hours 13 minutes 8 seconds 817 msec
```