Electronic Supplementary Information

Synthesis, molecular and electronic structure of an incomplete cuboidal Re_3S_4 cluster with an unusual quadruplet ground state

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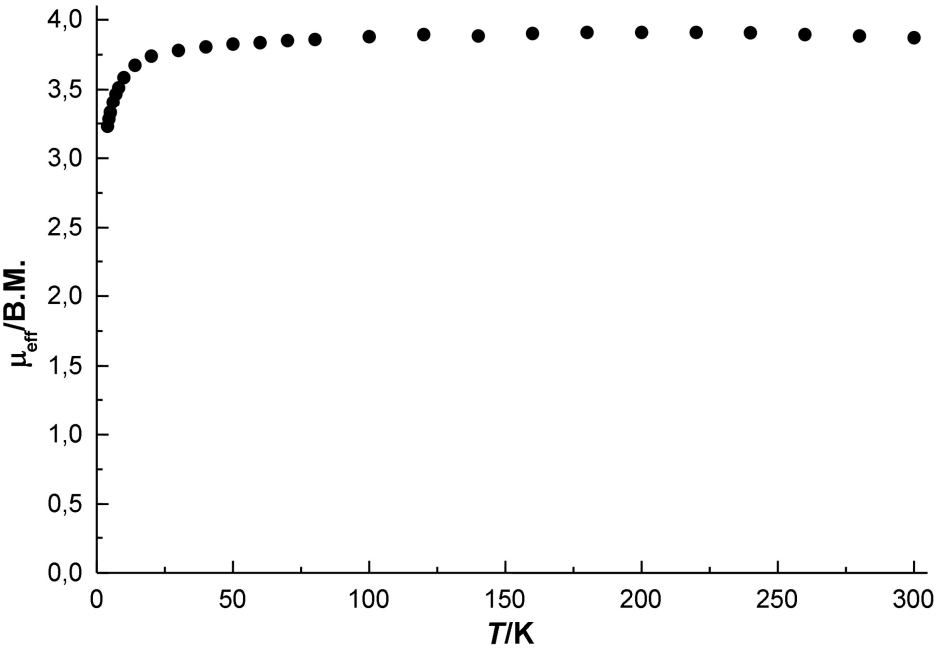

Fig. S1. μ_{eff} *vs. T* plot for complex [**1**]Br·3MeCN.

Computational Details

All calculations were performed with the Gaussian09 package[1] at the B3LYP level[2] using the unrestricted formalism. Rhenium was represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set[2] (SDD keyword in Gaussian 09). The 6-31G(d) basis set was used for all the other atoms (C , H, Br, P, S).[3]

Table S1. UDFT data of cluster $\mathbf{1}^{+}$ in quartet (Q) and doublet (D) states. Absolute energies (in a.u.), $\langle \hat{S}^2 \rangle$ values, lowest frequency (cm^{-1}), zero-point energy correction (in a.u.), absolute enthalpies and free energies (in a.u.).

	E(UDFT)	$\langle \hat{S}^2 \rangle_{UDFT}$	Low. freq	ZPE	H	G
$\mathbf{1}^{+}D$	-11833.42296	1.78	47.6	0.30509	-11833.08119	-11833.18635
$\mathbf{1}^{+}Q$	-11833.42778	3.76	48.4	0.30543	-11833.08588	-11833.19106

While $\mathbf{1}^{+}Q$ presents a $\langle \hat{S}^2 \rangle_{UDFT}$ value of 3.76 close to the pure quartet state (3.75), the $\langle \hat{S}^2 \rangle_{UDFT}$ value for the calculated $\mathbf{1}^{+}D$ (1.79) deviates severely from the pure doublet state (0.75) due to spin contamination. Then, spin purification techniques must be employed in order to obtain precise energy gaps. Assuming that the main contamination of the doublet results from the quartet, the energy is corrected using the following equations:

$$E(UDFT, \mathbf{1}^{+}D) = xE(\mathbf{1}^{+}D) + (1-x)E(\mathbf{1}^{+}Q) \quad (1)$$

$$E(\mathbf{1}^{+}D) = \frac{1}{x}E(UDFT, \mathbf{1}^{+}D) - \frac{(1-x)}{x}E(\mathbf{1}^{+}Q) \quad (2)$$

Where x is determined from the expectation values $\langle \hat{S}^2 \rangle$ calculated from KS orbitals :

$$\langle \hat{S}^2 \rangle_{UDFT,\mathbf{1}^{+}D} = x\langle \hat{S}^2 \rangle_{\mathbf{1}^{+}D} + (1-x)\langle \hat{S}^2 \rangle_{\mathbf{1}^{+}Q} \quad (3)$$

$$x = \frac{\langle S^2 \rangle_{UDFT,\mathbf{1}^{+}D} - \langle S^2 \rangle_{\mathbf{1}^{+}Q}}{\langle S^2 \rangle_{\mathbf{1}^{+}D} - \langle S^2 \rangle_{\mathbf{1}^{+}Q}} \quad (4)$$

Replacing the values from table S1, x = 0.656 and E($\mathbf{1}^{+}\mathbf{D}$) = -11833.42043

Table S2.
Cartesian coordinates (in Å) of **1^{+}Q**
Charge +1, Multiplicity 4.
Energy: -11833.42778

Re	-0.753163	-1.439096	0.209677
Re	1.622800	0.067252	0.209716
Re	-0.869833	1.371705	0.209387
S	0.000061	-0.000178	-1.548118
S	-1.981421	-0.126012	1.704678
S	1.099597	-1.652776	1.705101
S	0.881267	1.778852	1.704802
P	-1.645595	-3.346211	1.518551
P	3.720679	0.248532	1.518570
P	-2.075834	3.097522	1.518403
P	-2.850160	-1.921582	-1.052673
P	3.089481	-1.507552	-1.052090
P	-0.238652	3.429582	-1.051690
Br	0.065193	-3.475712	-1.294598
Br	2.977731	1.793664	-1.294716
Br	-3.042074	1.681645	-1.295399
C	4.996704	-0.967972	0.914611
H	4.817020	-1.899827	1.463452
H	5.999893	-0.618842	1.178874
C	-3.473481	-3.617378	-0.599885
C	4.869796	-1.198734	-0.600122
C	-1.396102	4.816934	-0.599339
H	5.194490	-0.316164	-1.158412
H	5.486154	-2.047352	-0.913873
H	-4.516425	-3.726979	-0.914060
H	-2.871295	-4.340527	-1.157095
C	-3.337847	-3.841258	0.915124
H	-4.054054	-3.217913	1.463168
H	-3.538723	-4.884005	1.180542
H	-2.322720	4.656985	-1.157779
H	-0.969381	5.775134	-0.912787
C	-1.659652	4.811028	0.915363
H	-0.762847	5.120887	1.464524
H	-2.463471	5.505351	1.179778
H	-1.835635	3.165926	2.904317
H	-2.801907	-1.930263	-2.458007
H	3.072569	-1.461819	-2.457422
H	3.660078	0.005191	2.904304
H	-0.269554	3.392824	-2.457057
H	-1.825255	-3.172015	2.904378
H	-0.867111	-4.515444	1.478820
H	4.342544	1.508062	1.479283
H	1.037240	3.965776	-0.802430
H	-3.952823	-1.084855	-0.804604
H	2.916442	-2.880812	-0.803612
H	-3.477582	3.006968	1.478164

Table S3.
Cartesian coordinates (in Å) of **1^{+}D**
Charge +1, Multiplicity 2.
Energy: -11833.42296

Re	1.544197	-0.511969	0.206142
Re	-0.332599	1.591087	0.205173
Re	-1.209609	-1.086268	0.207147
S	0.001716	-0.002672	-1.552050
S	0.459291	-1.941156	1.696255
S	1.437781	1.369758	1.706043
S	-1.919370	0.572751	1.697270
P	3.568777	-1.065347	1.523893
P	-0.866811	3.621099	1.522260
P	-2.711367	-2.553660	1.524496
P	2.378258	-2.490613	-1.056868
P	0.976257	3.305044	-1.048863
P	-3.345721	-0.804887	-1.052375
Br	3.418177	0.643988	-1.284492
Br	-2.255782	2.639940	-1.301891
Br	-1.157970	-3.280294	-1.292962
C	0.129471	5.081457	0.933591
H	1.077163	5.048715	1.483660
H	-0.376887	6.013187	1.205026
C	4.151255	-2.823617	-0.592429
C	0.379842	5.006758	-0.581515
C	-4.526616	-2.167661	-0.585685
H	-0.543202	5.188030	-1.139413
H	1.116676	5.756182	-0.888050
H	4.433666	-3.834348	-0.904139
H	4.767395	-2.110782	-1.147652
C	4.342696	-2.650931	0.923339
H	3.845950	-3.461179	1.469772
H	5.403365	-2.674613	1.192715
H	-4.222353	-3.060030	-1.140004
H	-5.542285	-1.902594	-0.896580
C	-4.472015	-2.417549	0.930297
H	-4.916746	-1.577559	1.476509
H	-5.028923	-3.319644	1.202726
H	-2.808809	-2.327056	2.910754
H	2.388711	-2.433540	-2.461834
H	0.929031	3.291471	-2.454250
H	-0.627686	3.590941	2.909350
H	-3.306922	-0.842953	-2.457611
H	3.422260	-1.272079	2.909084
H	4.590256	-0.101181	1.487234
H	-2.210693	4.028678	1.473122
H	-4.078404	0.370376	-0.810744
H	1.733396	-3.717905	-0.820638
H	2.359621	3.355770	-0.802573
H	-2.397967	-3.922998	1.481994

Table S4. Selected bond lengths in [**1**]Br obtained by x-ray and for **1**$^{+}$**Q** and **1**$^{+}$**D** obtained from DFT gas-phase geometry optimizations.

	[**1**]Br·3MeCN	**1**$^{+}$**Q**	**1**$^{+}$**D**
Average distance (Å)[a]	x-ray	DFT	DFT
M–M	2.780	2.813	2.818
M–(μ_3-S)	2.344	2.393	2.393
M–(μ-S)[b]	2.327	2.390	2.400
M–(μ-S)[c]	2.283	2.338	2.331
M–Hal	2.586	2.660	2.659
M–P[d]	2.536	2.495	2.495
M–P[e]	2.511	2.479	2.478

[a] Standard deviations for averaged values are given in square brackets. . [b] Distance *trans* to the M–P bond [c] Distance *trans* to the M–Hal bond. [c] Distance *trans* to the M–Hal bond. [d] Distance trans to the M–(μ-S) bond [e] Distance trans to the M–(μ_3-S) bond

Table S5. Molecular orbital overlap population (MOOP) for the SOMOs of **1**$^{+}$**Q** calculated using UDFT.

MOOP	Re-Re
181	0.006
182	-0.024
183	-0.011

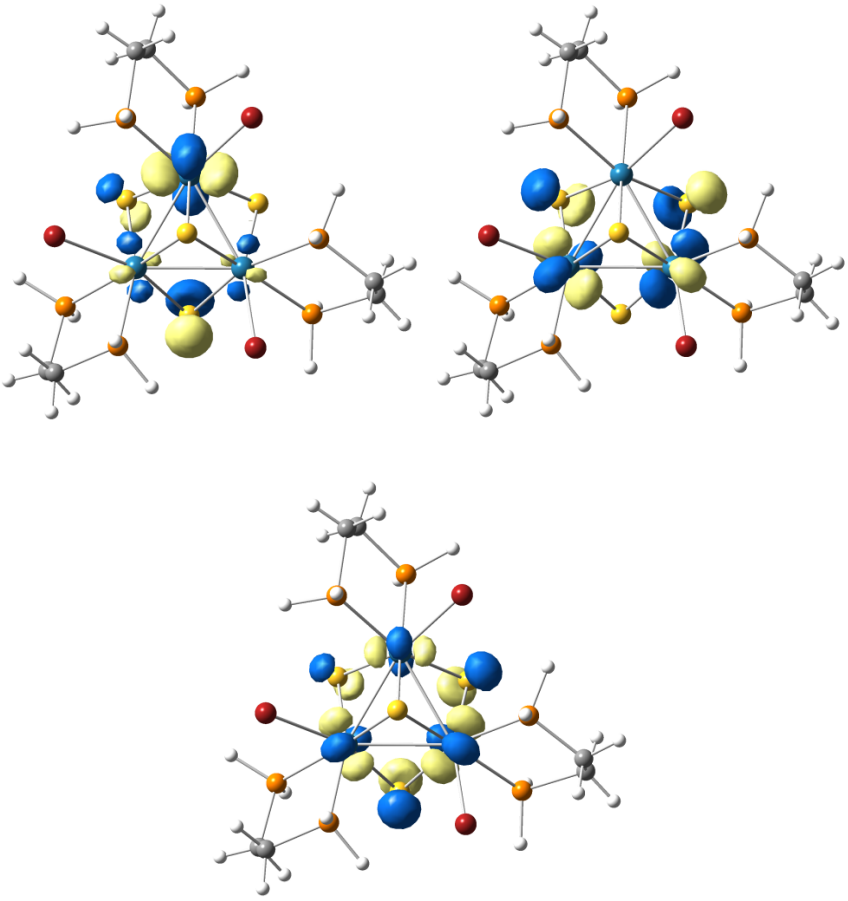

Fig. S2. Graphical representation of SOMOs of **1**$^{+}$**Q** complex calculated using UDFT methods. Isocontour values of 0.07.

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