

Supporting Information for *Magnetic circular dichroism spectra of transition metal complexes calculated from restricted active space wavefunctions*

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Table S1: Calculated vs. experimental bond lengths (in Å).

	TD-KST/CAM-B3LYP	Expt
$\text{PdCl}_4^{2-}$	2.33	2.30 <sup>1</sup>
$\text{PdBr}_4^{2-}$	2.47	–
$\text{AuCl}_4^-$	2.30	2.27 <sup>2</sup>
$\text{AuBr}_4^-$	2.45	2.43 <sup>3</sup>
$\text{CuCl}_4^{2-}$	2.27	2.26 <sup>4</sup>
$\text{CuBr}_4^{2-}$	2.41	2.41 <sup>5</sup>
$\text{MnO}_4^-$	1.58	1.63 <sup>6</sup>
$\text{Fe}(\text{CN})_6^{3-}$	1.92	1.95 <sup>7</sup>

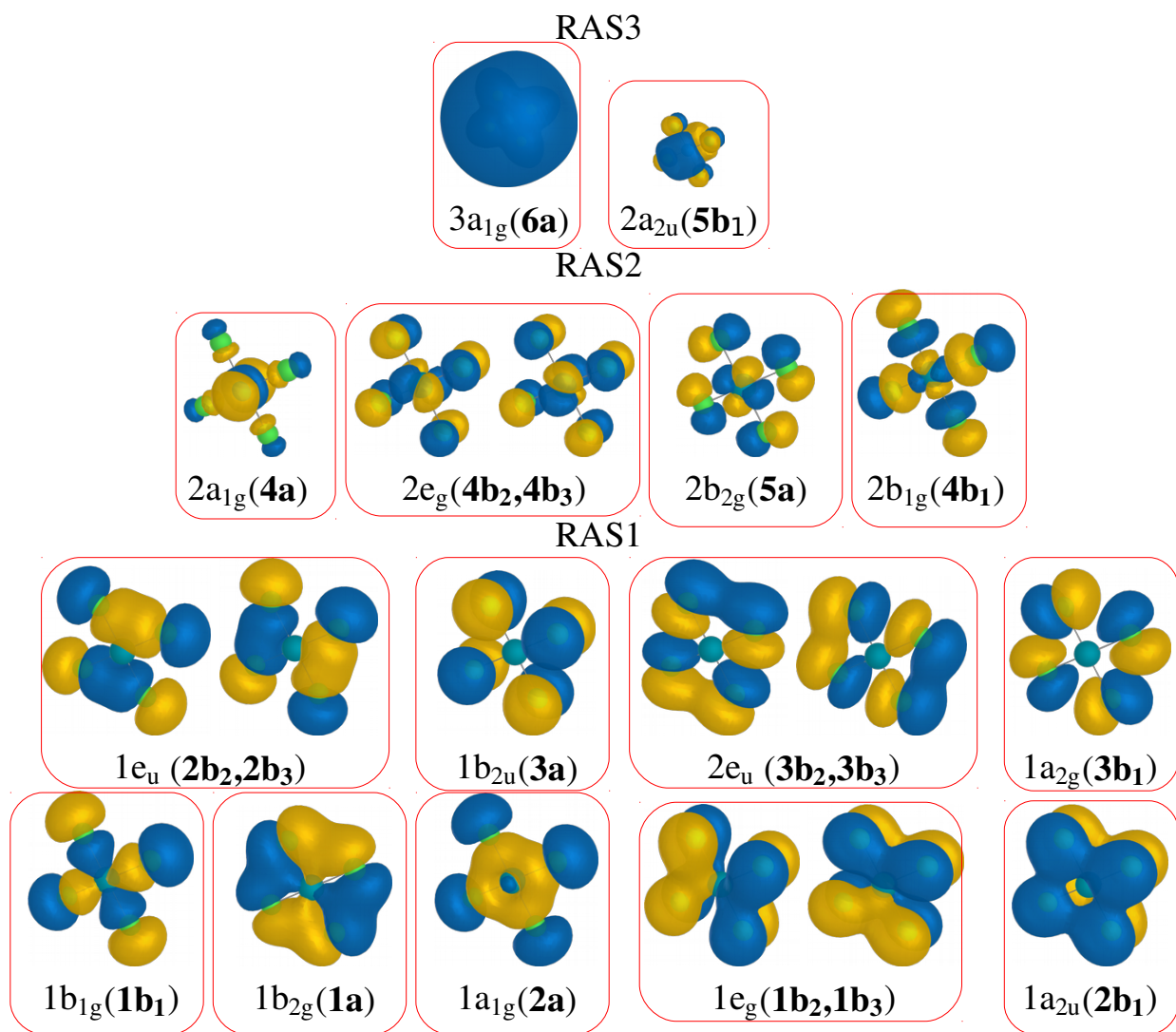


Figure S1:  $\text{PdCl}_4^{2-}$  active space orbitals visualized as isosurfaces of  $\pm 0.03$  except for the  $4a_1$  ( $\pm 0.005$ ) and  $4b_2$  ( $\pm 0.02$ ) RAS3 orbitals. Symmetry labels are from the  $D_{4h}$  ( $D_2$ ) point group.

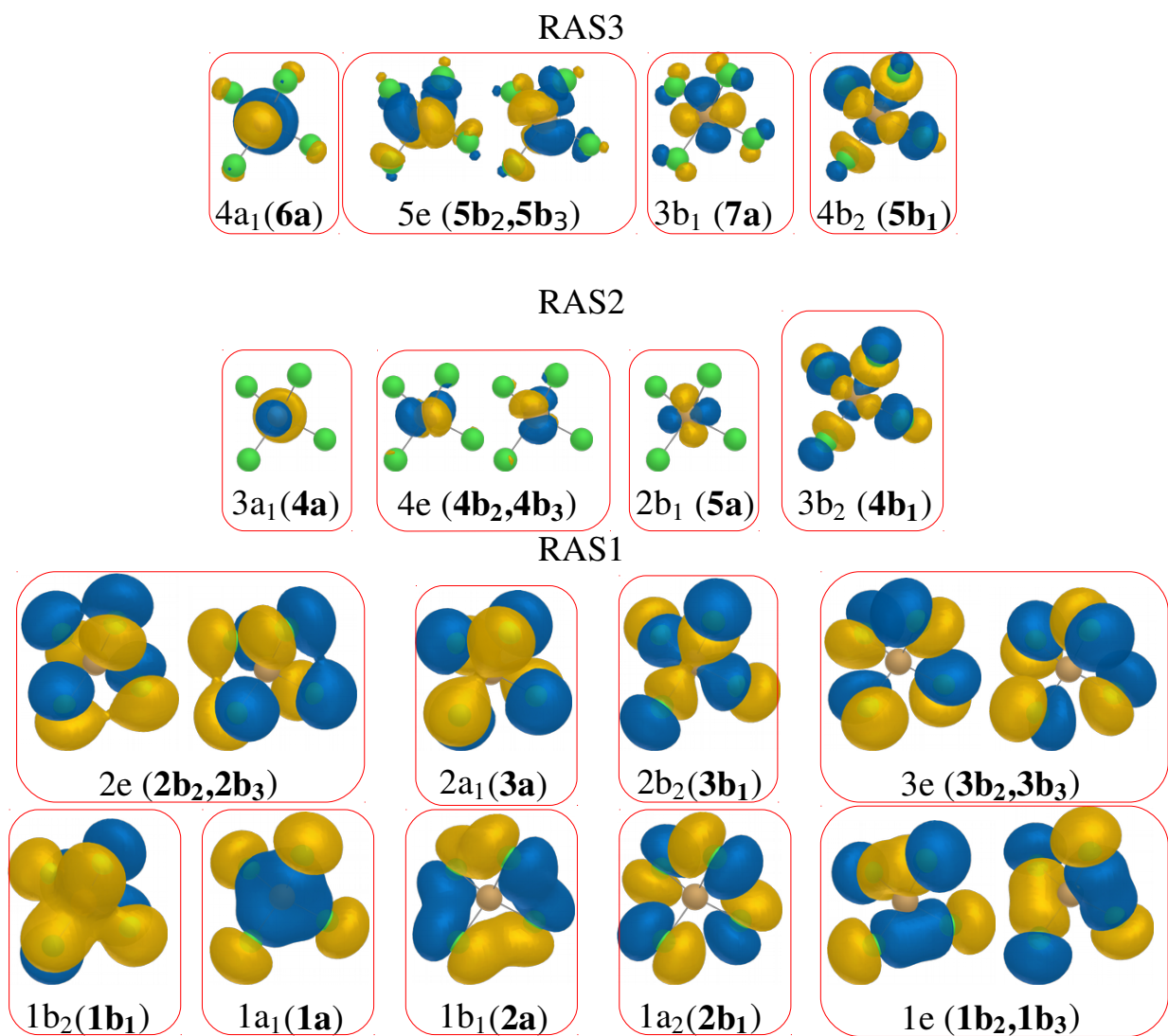


Figure S2:  $\text{CuCl}_4^{2-}$  active space orbitals visualized as isosurfaces ( $\pm 0.03$ ). Symmetry labels are from the  $D_{2d}$  ( $D_2$ ) point group.

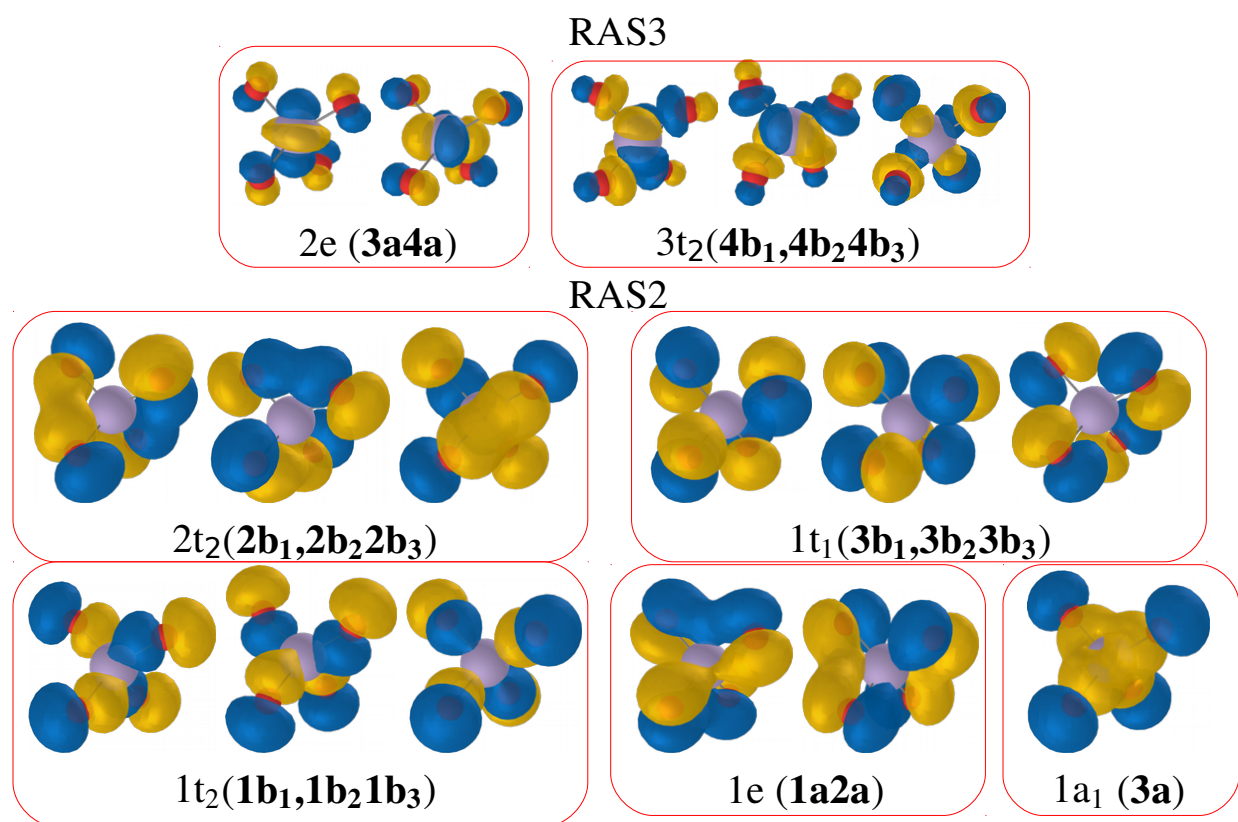


Figure S3:  $\text{MnO}_4^-$  active space orbitals visualized as isosurfaces ( $\pm 0.08$ ). Symmetry labels are from the  $T_d$  ( $D_2$ ) point group.

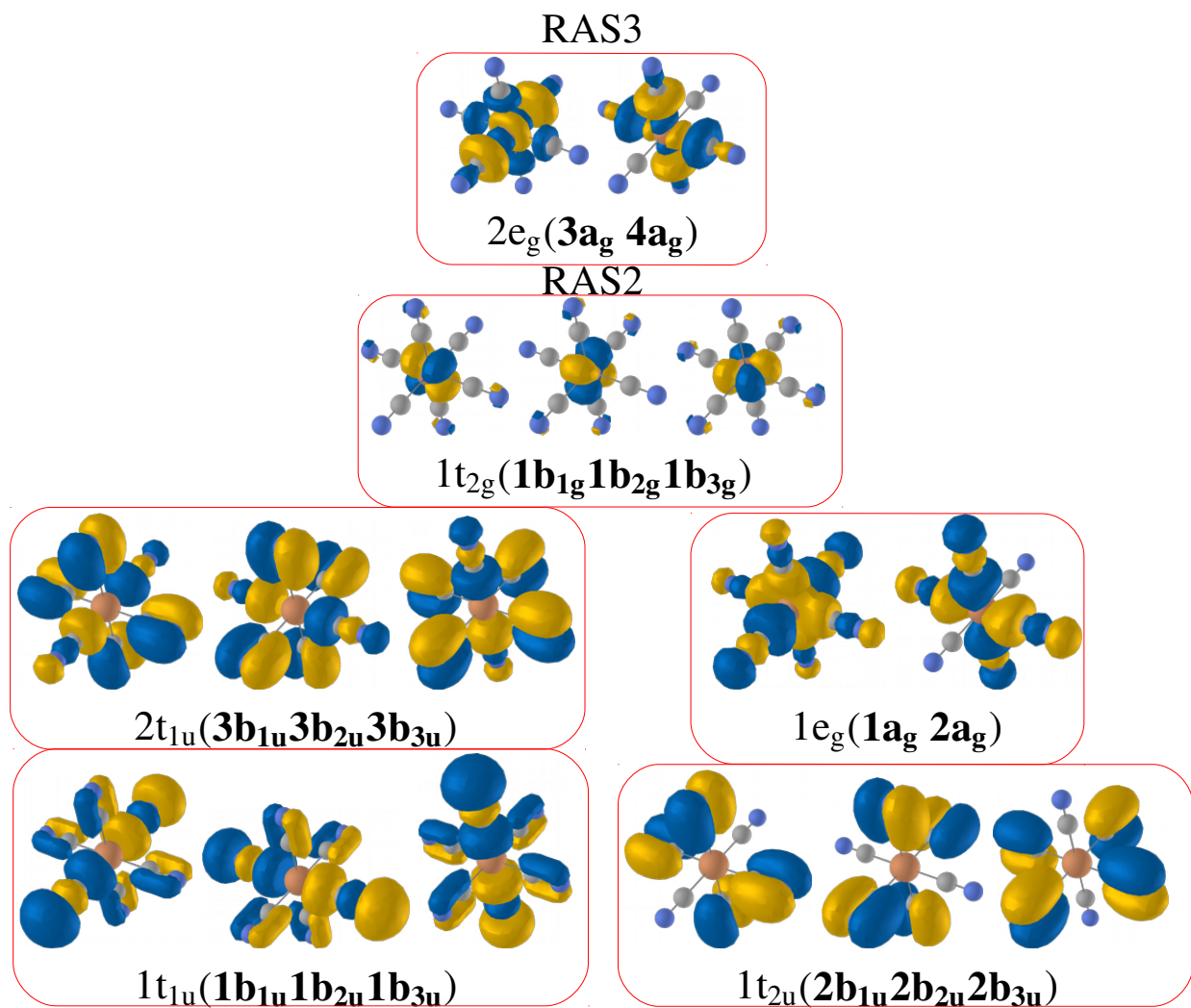


Figure S4:  $\text{Fe}(\text{CN})_6^{3-}$  active space orbitals visualized as isosurfaces ( $\pm 0.04$ ). Symmetry labels are from the  $O_h$  ( $D_{2h}$ ) point group.

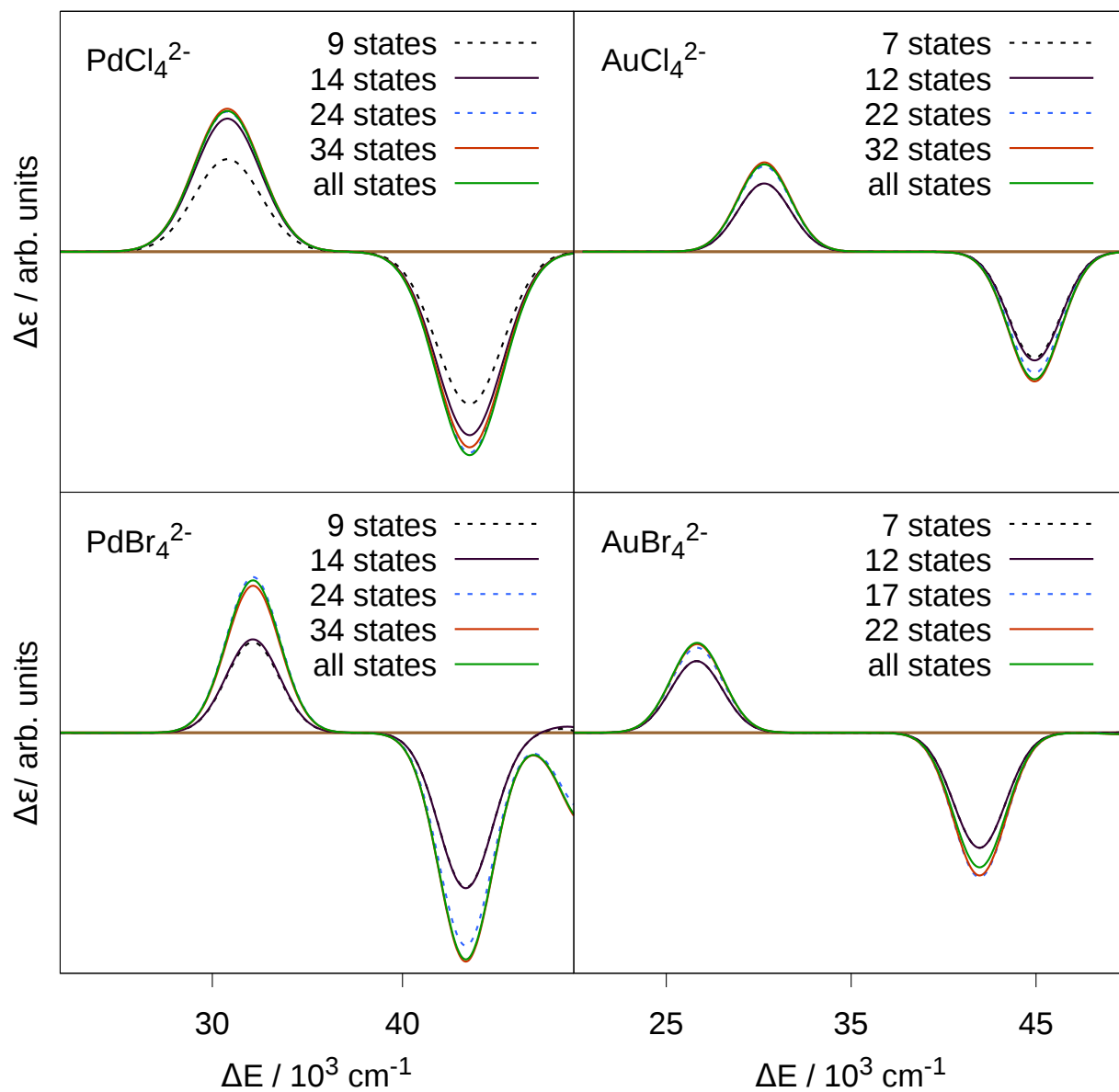


Figure S5: Calculated  $B$ -term spectra, for the various  $d^8$  complexes, with an increasing number of states for the SOS of Equation 4 (see the main article). The spectra were produced with a Gaussian broadening of  $2000 \text{ cm}^{-1}$  for the individual transitions. The solid black curves correspond to the experimental spectra.<sup>8</sup>

Table S2: Calculated excitation energies and oscillator strengths ( $f$ ), for various  $d^8$  complexes, with TD-KST.<sup>a</sup>

	State	$\Delta E$ (cm <sup>-1</sup> )	$f$
PdCl <sub>4</sub> <sup>2-</sup>	<sup>1</sup> E <sub>u</sub> (2e <sub>u</sub> )	35471	0.492
	<sup>1</sup> A <sub>2u</sub> (1b <sub>2u</sub> )	36584	0.001403
	<sup>1</sup> E <sub>u</sub> (1e <sub>u</sub> )	45100	1.376
PdBr <sub>4</sub> <sup>2-</sup>	<sup>1</sup> E <sub>u</sub> (2e <sub>u</sub> )	29408	0.592
	<sup>1</sup> A <sub>2u</sub> (1b <sub>2u</sub> )	30932	0.00269
	<sup>1</sup> E <sub>u</sub> (1e <sub>u</sub> )	39558	1.593
AuCl <sub>4</sub> <sup>-</sup>	<sup>1</sup> A <sub>2u</sub> (1b <sub>2u</sub> )	30304	0.000693
	<sup>1</sup> E <sub>u</sub> (2e <sub>u</sub> )	30586	0.103
	<sup>1</sup> E <sub>u</sub> (1e <sub>u</sub> )	45090	1.048
AuBr <sub>4</sub> <sup>-</sup>	<sup>1</sup> E <sub>u</sub> (1e <sub>u</sub> )	24805	0.389
	<sup>1</sup> A <sub>2u</sub> (1b <sub>2u</sub> )	25465	0.00143
	<sup>1</sup> E <sub>u</sub> (2e <sub>u</sub> )	37044	1.938

<sup>a</sup>The main excited orbital is noted between parentheses; the acceptor orbital is always 2b<sub>1g</sub>.

Table S3: Change in RAS-SCF orbital natural occupations involved in the first three intense transitions of MnO<sub>4</sub><sup>-</sup>.

$\Delta E$ (cm <sup>-1</sup> )	Transition
21799	(1t <sub>1</sub> ) <sup>5.73</sup> (2e) <sup>0.464</sup> → (1t <sub>1</sub> ) <sup>5.01</sup> (2e) <sup>1.27</sup>
31153	(1t <sub>1</sub> ) <sup>5.73</sup> (2t <sub>2</sub> ) <sup>5.73</sup> (2e) <sup>0.464</sup> → (1t <sub>1</sub> ) <sup>5.32</sup> (2t <sub>2</sub> ) <sup>5.29</sup> (2e) <sup>1.28</sup>
36447	(1t <sub>1</sub> ) <sup>5.73</sup> (3t <sub>2</sub> ) <sup>0.50</sup> → (1t <sub>1</sub> ) <sup>4.98</sup> (3t <sub>2</sub> ) <sup>1.27</sup>

Table S4: Excitation energies and oscillator strengths ( $f$ ) calculated with TD-KST for the first three intense transitions of MnO<sub>4</sub><sup>-</sup>.

Transition	$\Delta E$ (cm <sup>-1</sup> )	$f$
1t <sub>1</sub> → 2e	25694	0.0909
1t <sub>1</sub> , 2t <sub>2</sub> → 2e	36195	0.0268
1t <sub>1</sub> , 2t <sub>2</sub> → 2e, 3t <sub>2</sub>	39737	0.110

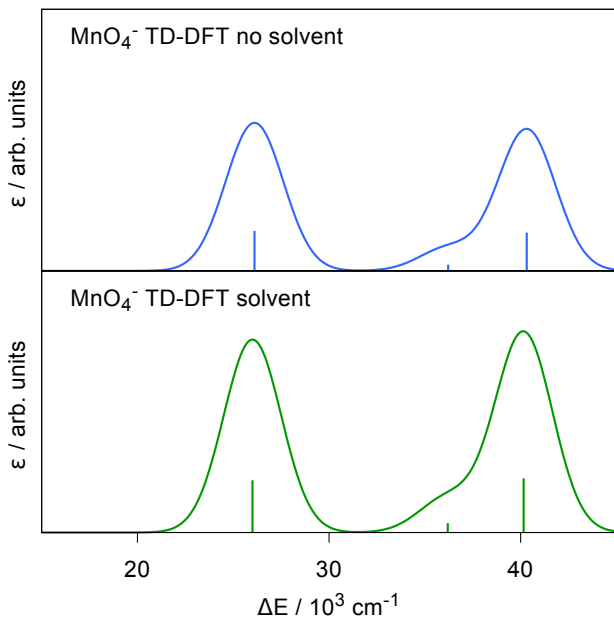


Figure S6: Calculated absorption spectrum of  $\text{MnO}_4^-$  with TD-KST in the gas-phase (top) and in water solvent (bottom). The spectra were produced with a Gaussian broadening for the individual transitions of  $1500\text{ cm}^{-1}$ .

Table S5: Calculated low-energy SR states for  $d^9$  complexes. Assignments are made in the  $D_{2d}$  symmetry point group.<sup>a</sup>

		RAS-CI	PT2//CI
		$\Delta E$ ( $\text{cm}^{-1}$ )	$\Delta E$ ( $\text{cm}^{-1}$ )
$\text{CuCl}_4^{2-}$	$1^2\text{B}_2$	0	0
	$1^2\text{E}$ (3e)	61658	26933
	$2^2\text{E}$ (2e)	66694	33228
	$1^2\text{B}_1$ (2b <sub>1</sub> )	70510	35423
	$3^2\text{E}$ (1e)	70947	36259
	$1^2\text{A}_1$ (2a <sub>1</sub> )	74758	43807
$\text{CuBr}_4^{2-}$	$1^2\text{B}_2$	0	0
	$1^2\text{A}_2$ (1a <sub>2</sub> )	51527	13289
	$1^2\text{E}$ (3e)	52049	20390
	$2^2\text{B}_2$ (2b <sub>2</sub> )	55317	22993
	$2^2\text{E}$ (2e)	56797	26430
	$3^2\text{B}_2$ (1b <sub>2</sub> )	60045	25453
	$1^2\text{B}_1$ (1b <sub>1</sub> )	62338	29716
	$3^2\text{E}$ (1e)	61454	29726
	$1^2\text{A}_1$ (1a <sub>1</sub> )	66593	39126

<sup>a</sup>The main excited orbital is given in parentheses; the acceptor orbital is always  $3b_2$ .



Table S6: Calculated SO states for  $d^9$  complexes. The SO states are developed in terms of the SR states listed in Table S5.

	$\Delta E$ (cm $^{-1}$ )	RAS-CI+SO	$\Delta E$ (cm $^{-1}$ )	PT2//CI+SO
CuCl $_4^{2-}$	0	99% 1 $^2B_2$	0	99% 1 $^2B_2$
	61585	85% 1 $^2E$ + 15% 1 $^2A_2$	26942	99% 1 $^2E$
	61877	100% 1 $^2E$	27146	100% 1 $^2E$
	62041	85% 1 $^2A_2$ + 15% 1 $^2E$	33321	98% 2 $^2E$
	66811	99% 2 $^2E$	33330	100% 2 $^2E$
	66864	94% 2 $^2E$	36352	93% 3 $^2E$
	71043	89% 3 $^2E$ + 11% 1 $^2B_1$	36470	100% 3 $^2E$
	71166	100% 3 $^2E$	43925	100% 1 $^2A_1$
	74886	100 1 $^2A_1$		
CuBr $_4^{2-}$	0	99% 1 $^2B_2$	0	99% 1 $^2B_2$
	51278	78% 1 $^2E$ + 21% 1 $A_2$	20016	99% 1 $^2E$
	52339	96% 1 $^2E$	20394	85% 1 $^2E$ + 15% 2 $^2B_2$
	52755	75% 1 $A_2$ + 20% 1 $^2E$	23382	81% 2 $^2B_2$ + 12% 1 $^2E$
	56969	80% 2 $^2E$ + 12% 2 $^2B_2$	26732	74% 2 $^1E$ + 13% 3 $^2B_2$
	60175	79% 3 $^2B_2$	29171	56% 3 $^2E$ + 41% 1 $^2B_1$
	61254	73% 3 $^2E$ + 13% 3 $^2B_2$ + 10% 1 $^2B_1$	30527	93% 3 $^2E$
	62295	92% 3 $^2E$	30674	55% 1 $^2B_1$ + 36% 3 $^2E$
	62987	80% 1 $^2B_1$ + 14% 3 $^2E$	39321	99% 1 $^2A_1$
	66841	99% 1 $^2A_1$		

Table S7: Spin-orbit excitation energies and oscillator strengths ( $f$ ) calculated with TD-KST+SO for Cu $^{2+}$  complexes.

	State	$\Delta E$ (cm $^{-1}$ )	$f$
CuCl $_4^{2-}$	12A	24326	0.0440
	13A	24367	0.0414
	24A	34040	0.126
	26A	34439	0.125
	33A	43036	0.0950
CuBr $_4^{2-}$	10A	16690	0.0144
	12A	18332	0.0358
	14A	19161	0.0332
	16A	23621	0.0121
	23A	26922	0.0609
	24A	28050	0.0877
	27A	29760	0.122
	32A	37891	0.121

Table S8: Excitation energies calculated with MC-pDFT-SR for  $\text{Fe}(\text{CN})_6^{3-}$ .

State	$\Delta E$ ( $\text{cm}^{-1}$ )	Excitation
$T_{2g}$	0	
$T_{1u}$	20098	$(2t_{1u})^{6.00}(1t_{2g})^{4.98} \rightarrow (2t_{1u})^{5.00}(1t_{2g})^{6.00}$
$T_{2u}$	29437	$(1t_{2u})^{6.00}(1t_{2g})^{4.98} \rightarrow (1t_{2u})^{5.00}(1t_{2g})^{6.00}$
$T_{1u}$	32978	$(1t_{1u})^{6.00}(1t_{2g})^{4.98} \rightarrow (1t_{1u})^{5.00}(1t_{2g})^{6.00}$

Table S9: Spin-orbit excitation energies (in  $\text{cm}^{-1}$ ) and oscillator strengths ( $f$ ) calculated with TD-KST+SO for  $\text{Fe}(\text{CN})_6^{3-}$ .

State	$\Delta E$	$f$
16A	31983	0.00285
17A	32051	0.00487
19A	32691	0.0359
21A	32942	0.0321
41A	41464	0.00481
42A	41599	0.00204
43A	41621	0.00247
44A	41995	0.0483
56A	42285	0.0578
51A	47447	0.00140
52A	47504	0.00389
55A	48033	0.0182
58A	48142	0.0292

Table S10: TD-KST/CAM-B3LYP optimized structures.

$\text{PdCl}_4^{2-}$				$\text{AuCl}_4^-$			
Pd	0.000000000	0.000000000	0.000000000	Pd	0.000000000	0.000000000	0.000000000
Cl	1.649946700	1.649946700	0.000000000	Br	1.74514519	1.74514519	0.000000000
Cl	-1.649946700	-1.649946700	0.000000000	Br	-1.74514519	-1.74514519	0.000000000
Cl	-1.649946700	1.649946700	0.000000000	Br	-1.74514519	1.74514519	0.000000000
Cl	1.649946700	-1.649946700	0.000000000	Br	1.74514519	-1.74514519	0.000000000
$\text{PdBr}_4^{2-}$				$\text{AuBr}_4^-$			
Au	0.000000000	0.000000000	0.000000000	Au	0.000000000	0.000000000	0.000000000
Cl	1.628937850	1.628937850	0.000000000	Br	1.73135590	1.73135590	0.000000000
Cl	-1.628937850	-1.628937850	0.000000000	Br	-1.73135590	-1.73135590	0.000000000
Cl	-1.628937850	1.628937850	0.000000000	Br	-1.73135590	1.73135590	0.000000000
Cl	1.628937850	-1.628937850	0.000000000	Br	1.73135590	-1.73135590	0.000000000
$\text{CuCl}_4^{2-}$				$\text{CuBr}_4^{2-}$			
Cu	0.000000000	0.000000000	0.000000000	Cu	0.000000000	0.000000000	0.000000000
Cl	1.485418000	1.485418000	0.859124000	Br	1.56044100	1.56044100	0.964758000
Cl	-1.485418000	-1.485418000	0.859124000	Br	-1.56044100	-1.56044100	0.964758000
Cl	-1.485418000	1.485418000	-0.859124000	Br	-1.56044100	1.56044100	-0.964758000
Cl	1.485418000	-1.485418000	-0.859124000	Br	1.56044100	-1.56044100	-0.964758000
$\text{MnO}_4^-$				$\text{Fe}(\text{CN})_6^{3-}$			
Mn	0.000000000	0.000000000	0.000000000	Fe	0.000000000	0.000000000	0.000000000
O	0.911737000	0.911737000	0.911737000	C	0.000000000	0.000000000	1.932242000
O	0.911737000	-0.911737000	-0.911737000	C	0.000000000	1.93224200	0.000000000
O	-0.911737000	-0.911737000	0.911737000	C	1.93224200	0.000000000	0.000000000
O	-0.911737000	0.911737000	-0.911737000	C	0.000000000	0.000000000	-1.932242000
				C	0.000000000	-1.93224200	0.000000000
				C	-1.93224200	0.000000000	0.000000000
				N	0.000000000	0.000000000	3.087170000
				N	0.000000000	3.08717000	0.000000000
				N	3.08717000	0.000000000	0.000000000
				N	0.000000000	0.000000000	-3.087170000
				N	0.000000000	-3.08717000	0.000000000
				N	-3.08717000	0.000000000	0.000000000

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