

\hat{H}_{LF} expressed in terms of spherical harmonics functions $Y_{k,q}$

$$\hat{H}_{LF} = \sum_{k=2,4} \sum_{q=-k}^k B_q^k C_q^k \text{ with } C_q^k = \sqrt{\frac{4\pi}{2k+1}} Y_{k,q}$$

Eq. S1

B_q^k are in general complex numbers, called Wybourne parameters^[1]. Depending on the symmetry of the system, many B_q^k might vanish. In the particular case of C_{3v} symmetry, only B_0^2 , B_0^4 and $B_3^4 = \sqrt{3} B_{-3}^4$ parameters are non-zero. B_0^4 is a diagonal matrix term, meanwhile B_3^4 represents the mixing between one-electron states with $|m_l|=1$ and $|m_l|=2$. B_0^2 represents the axiality of the system, being zero for a tetrahedral ML_4 system and positive (negative) for a compressed (stretched) tetrahedron along an M-L direction.

[1] B. G. Wybourne, *Spectroscopic Properties of Rare Earths*, Wiley Interscience, New York, 1965, p;

Spin Hamiltonian for non-degenerate ground state including fourth order splitting parameters ^[2]

$$\hat{H}_{mod} = \left[D\hat{S}_Z^2 + E(\hat{S}_X^2 - \hat{S}_Y^2) + \sum_{n,k>4} B_k^n \cdot \hat{O}_k^n \right]$$

Eq. S2

[2] R. Maurice, C. de Graaf and N. Guihéry, *J. Chem. Phys* **2010**, 133.

Table S1. Selected bond lengths (Å) and angles (°) for the resulting DFT optimized structures of investigated complexes. Experimental values are given in parenthesis.

Complex	R(M-Cl)	R(M-N)	Cl-M-N
[VTpCl] ⁺	2.159	1.980	121.5
[CrTpCl] ⁺	2.166	1.947	125.0
[CoTpCl]	2.167	2.014	122.8
[NiTpCl]	2.160	1.992	124.9
[VTp ^{CH3} Cl] ⁺	2.174	1.972	120.3
[CrTp ^{CH3} Cl] ⁺	2.187	1.948	124.1
[CoTp ^{CH3} Cl]	2.189	2.010	122.2
[NiTp ^{CH3} Cl]	2.187(2.195)	1.987(1.961)	124.1(123.05)

Table S2. Racah parameters B and C (cm⁻¹), Ligand Field parameters B_q^k (cm⁻¹), and spin-orbit coupling constants (cm⁻¹)

Complex	CF	B	C	B_0^2	B_0^4	B_3^4	ζ
[VTpCl] ⁺	C_{3v}	416	2490	2627	-8293	-18552	171
[CrTpCl] ⁺	C_{3v}	478	2522	3181	-15207	-19205	218
[CoTpCl]	C_{3v}	598	2891	3615	-7096	-12701	533
[NiTpCl]	C_{3v}	577	2495	3832	-10398	-13667	462
[VTp ^{CH3} Cl] ⁺	C_{3v}	371	2442	753	-6514	-18003	171
[CrTp ^{CH3} Cl] ⁺	C_{3v}	455	2484	872	-13774	-18427	218
[CoTp ^{CH3} Cl]	C_{3v}	584	2836	1904	-6759	-13004	533
[NiTp ^{CH3} Cl]	C_{3v}	572/585 ^a	2535/2536 ^a	1850/ 1817 ^a	-9429/ -8973 ^a	-13669/ -13626 ^a	462
[MnTpCl] ⁺	C_{3v}	529	2543	1938	-10557	-15944	275
[MnTpCl] ⁺	C_s	505	2477	1728	-11226	-15964	272
[MnTp ^{CH3} Cl] ⁺	C_{3v}	507	2525	-508	-8872	-15380	271
[MnTp ^{CH3} Cl] ⁺	C_s	492	2438	-441	-3440	-11759	270
[MnTp ^{t-but} Cl] ⁺	C_{3v}	501	2559	-1480	-4642	-13882	273
[MnTp ^{t-but} Cl] ⁺	C_s	499	2503	-1035	-4165	-11476	237
[FeTpCl]	C_{3v}	618	3059	4549	-7865	-11965	346
[FeTpCl]	C_s	624	3062	4867	-8500	-11695	347
[FeTp ^{CH3} Cl]	C_{3v}	599	3001	3218	-7702	-12330	343
[FeTp ^{CH3} Cl]	C_s	603	3019	1735	-3667	-9059	343
[FeTp ^{t-but} Cl]	C_{3v}	605	3003	1746	-4345	-11265	344
[FeTp ^{t-but} Cl]	C_s	626	2978	1685	-2023	-8391	333

^a LF-DFT results obtained at experimental geometries

Table S3. Calculated excitation energies for d-d excited states (cm^{-1}) and the most important contributions of excited states to MAE (cm^{-1}) for $[\text{VTpCl}]^+$ and $[\text{NiTpCl}]$. The ground electronic state is 3A_2 .

State	$[\text{VTpCl}]^+$		$[\text{NiTpCl}]$	
	Energy	Contribution	Energy	Contribution
3E	3537	3.2	7572	27.2
1E	7806	0.0	9349	0.0
3A_1	10176	-3.4	8697	-20.8
1A_1	11093	1.8	15662	0.7
1E	11301	-1.2	16580	-10.8
3E	11445	1.2	12686	0.0
1A_1	18292	0.4	17996	8.8
3E	17731	0.0	19181	0.00

Table S4. Calculated excitation energies for d-d excited states and the most important contributions of excited states to MAE (cm⁻¹) for [CrTpCl]⁺ and [CoTpCl]. The ground electronic state is ⁴A₂.

State	[CrTpCl] ⁺		[CoTpCl]	
	Energy	Contribution	Energy	Contribution
⁴ E	10966	3.8	2240	69.4
² E	10891	-0.2	7734	-18.0
⁴ A ₁	11898	-3.3	6731	-42.3
² A ₁	16170	3.0	12055	0.0
² E	16873	-2.2	12814	-1.4
⁴ E	16093	0.0	7857	6.2
² A ₁	20731	0.0	13867	0.0
² E	21767	-1.4	14179	-5.8

Table S5. Calculated fourth order splitting parameters (10^{-3}) for Mn^{3+} and Fe^{2+} complexes in C_s symmetry (cm^{-1})

Complex	B_4^0	B_4^2	B_4^4
$[\text{MnTpCl}]^+$	0.60	0.70	0.10
$[\text{MnTp}^{\text{CH}_3}\text{Cl}]^+$	-0.60	0.90	-0.30
$[\text{MnTp}^{\text{t-but, CH}_3}\text{Cl}]^+$	0.00	-0.30	-4.60
$[\text{FeTpCl}]$	28.30	-19.30	-4.80
$[\text{FeTp}^{\text{CH}_3}\text{Cl}]$	35.90	-31.70	-7.60
$[\text{FeTp}^{\text{t-but, CH}_3}\text{Cl}]$	13.10	-17.20	-2.00