

Supplementary Materials

Reaching the maximal unquenched orbital angular momentum $L = 3$ in mononuclear transition-metal complexes: where, when, and how?

Vladimir S. Mironov ^{1,2,*}

¹ Shubnikov Institute of Crystallography of Federal Scientific Research Centre
"Crystallography and Photonics" of Russian Academy of Sciences, Leninskiy Prospekt 59,
119333, Moscow, Russia

² Institute of Problems of Chemical Physics, IPCP RAS, Chernogolovka 142432, Russia.

* Correspondence: mirsa@list.ru

THEORETICAL CALCULATIONS

Ligand-field (LF) and angular-overlap model (AOM) calculations

Ligand-field (LF) calculations for the $3d^2$, $3d^3$, $3d^7$ and $3d^8$ complexes are performed in terms of a model Hamiltonian

$$H = \sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \zeta_{3d} \sum_i \mathbf{L}_i \mathbf{S}_i + V_{LF}, \quad (\text{S1})$$

in which the first term represents Coulomb repulsion between 3d electron (where i and j numerate 3d electrons of the metal ion in the complex), the second term is the spin-orbit coupling (SOC) of 3d electrons and V_{LF} is a ligand-field Hamiltonian. The Coulomb repulsion energy is treated in terms of Racah parameters B and C . The one-electron operator V_{LF} of the LF potential is specified by a symmetric 5×5 matrix with real matrix elements $\langle m | V_{LF} | n \rangle$ on the basis set of d-orbitals xy , x^2-y^2 , z^2 , xz , yz . In the case of axially symmetric 3d-complexes, this matrix is diagonal and its matrix elements are quantified by two independent energy parameters E and Δ , where $E + \Delta$ is the energy of the upper 3d orbital and $\Delta = \pm(E(xy, x^2-y^2) - E(xz, yz))$ is the energy difference between the (xy, x^2-y^2) and (xz, yz) doubly generate orbitals (see the inset in Figures 2, 3a, 5 and 6). LF calculations are performed with fixed energy $E(z^2) = 10000 \text{ cm}^{-1}$ ($3d^2$ and $3d^7$ ions) and $E(xz, yz) = 5000 \text{ cm}^{-1}$ ($3d^3$ and $3d^8$ ions) and variable Δ . The employed sets of atomic parameters (B , C , ζ_{3d}) are $B = 600$, $C = 2900$, $\zeta_{3d} = 150 \text{ cm}^{-1}$ for $3d^2$ ions, $B = 650$, $C = 3000$, $\zeta_{3d} = 250 \text{ cm}^{-1}$ for $3d^3$ ions, $B = 750$, $C = 3800$ and $\zeta_{3d} = 480 \text{ cm}^{-1}$ for $3d^7$ ions and $B = 800$, $C = 3200$ and $\zeta_{3d} = 600 \text{ cm}^{-1}$ for $3d^8$ ions. LF calculations are performed with the full basis set of $3d^N$ configurations involving 45 ($3d^2$, $3d^8$) and 120 ($3d^3$, $3d^7$) $|LM_L S M_S\rangle$ microstates. This LF computational approach was implemented in a computer code written by V.S. Mironov and then used to analyze the magnetic properties of transition metal complexes (see e.g., [49–51]).

LF calculations for the trigonal-prismatic coordination are performed with the use of the angular overlap model (AOM) outlined in ref. [46,47]. In this approach, the matrix elements $\langle m|V_{LF}|n\rangle$ are expressed as linear combination of two AOM parameters e_σ and e_π of donor atoms involved in the coordination polyhedron. The angular dependence of these contributions to the LF term V_{LF} is analytically expressed through the spherical angles θ and φ ; in the high-symmetry trigonal prismatic coordination, V_{LF} depends only on the polar angle θ . The AOM parameters were set to $e_\sigma = 9000 \text{ cm}^{-1}$ for Cr^{3+} ion and $e_\sigma = 5000 \text{ cm}^{-1}$ for Ni^{2+} ion, with fixed ratio $e_\pi/e_\sigma = 0.25$. These values correspond to the typical total LF splitting energy for octahedral 3d complexes $10Dq = 3e_\sigma - 4e_\pi = 2e_\sigma$, with is around 18000 cm^{-1} for the trivalent Cr^{3+} ion and 10000 cm^{-1} for the divalent Ni^{2+} ion. For the specific donor atoms (O, N) these values can also be estimated from the Jorgensen's equation [48]. Results of the LF/AOM calculations for trigonal-prismatic Cr^{3+} and Ni^{2+} complexes are presented graphically in Figures 4 and 7.