Supplementary Information

Effects of the Anion Substitution between I⁻ and NCS⁻ coordinated to Co²⁺-centered Tetrahedra in the Organic-Inorganic Hybrid Halides

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Figure S1. Powder XRD patterns with repeated scanning in air of the (a) $(CH_3NH_3)_2Co(NCS)_4$, (b) $(CH_3NH_3)_3CoI_4(NCS)$ and (c) $(CH_3NH_3)_2CoI_4$ and their simulation patterns of target compounds. * indicates the diffraction from impurities. For $(CH_3NH_3)_2Co(NCS)_4$, each XRD patterns obtained by three repeated scan matches completely, while for $(CH_3NH_3)_3CoI_4(NCS)$ and $(CH_3NH_3)_2CoI_4$, the impurity peaks gradually increased with repeated measurement. For $(CH_3NH_3)_2Co(NCS)_4$, the integrated pattern of these three patterns is taken in Figure 1a. For $(CH_3NH_3)_3CoI_4(NCS)$ and $(CH_3NH_3)_2CoI_4$, the patterns obtained by the first scan are shown in Figure 1b, c.

Empirical formula	$C_8Co_2N_8S_8$
Formula weight	582.50
Temperature (K)	100.15
Crystal system	cubic
Space group	I43m
<i>a</i> (Å)	9.6359(1)
<i>b</i> (Å)	9.6359(1)
<i>c</i> (Å)	9.6359(1)
α (°)	90
eta (°)	90
γ (°)	90
Unit-cell volume (Å ³)	894.699(16)
Ζ	1
$ ho_{ m calc}~({ m g~cm^{-3}})$	1.081
$\mu (\mathrm{mm}^{-1})$	0.308
$F(0\ 0\ 0)$	286.6
Crystal size (mm ³)	$0.09 \times 0.09 \times 0.07$
Radiation	synchrotron ($\lambda = 0.4132$ Å)
2θ range for data collection (°)	3.48 to 42.84
Index ranges	$-17 \le h \le 16, -16 \le k \le 16, -16 \le l \le 17$
Reflections collected	22921
Independent reflections	510 [$R_{int} = 0.0719, R_{sigma} = 0.0234$]
Data / restraints / parameters	510 / 0 / 14
Goodness-of-fit on F^2	0.96
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0517, wR_2 = 0.1132$
Final R indexes [all data]	$R_1 = 0.0630, wR_2 = 0.1210$
Largest diff. peak / hole (e Å ⁻³)	0.54 / -0.48
Flack parameter	0.00(4)

Table S1. Crystallographic data obtained by single crystal X-ray structure analysis of (CH₃NH₃)₂Co(NCS)₄. Estimated standard deviations are shown in parentheses.

Table S2. Fractional atomic coordinates and equivalent isotropic displacement parameters for $(CH_3NH_3)_2Co(NCS)_4$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor. Estimated standard deviations are shown in parentheses.

Atom	x	у	Ζ	$U_{\rm eq}$ (Å ²)
Co01	0.5	0.5	0.5	0.0401(4)
S002	0.2225(2)	0.2225(2)	0.2225(2)	0.216(3)
N003	0.3830(3)	0.3830(3)	0.3830(3)	0.0644(8)
C2	0.3117(4)	0.3117(4)	0.3117(4)	0.0859(16)

Table S3. Anisotropic displacement parameters for $(CH_3NH_3)_2Co(NCS)_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$. Estimated standard deviations are shown in parentheses.

Atom	U_{11} (Å ²)	U_{22} (Å ²)	U_{33} (Å ²)	U_{23} (Å ²)	U_{13} (Å ²)	U_{12} (Å ²)
Co01	0.0626(19)	0.0626(19)	0.0626(19)	0	0	0
S002	0.216(3)	0.216(3)	0.216(3)	-0.0825(14)	-0.0825(14)	-0.0825(14)
N003	0.0644(8)	0.0644(8)	0.0644(8)	-0.0013(9)	-0.0013(9)	-0.0013 (9)
C2	0.0859(16)	0.0859(16)	0.0859(16)	-0.007(2)	-0.007(2)	-0.007(2)

Empirical formula	C4H18C0I4N4S
Formula weight	720.81
Temperature (K)	299.98
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a (Å)	10.4690(9)
<i>b</i> (Å)	11.5048(9)
<i>c</i> (Å)	15.7129(12)
α (°)	90
β (°)	90
γ (°)	90
Unit-cell volume (Å ³)	1892.5(3)
Ζ	4
$ ho_{ m calc}~(m g~cm^{-3})$	2.530
$\mu (\mathrm{mm}^{-1})$	7.524
<i>F</i> (0 0 0)	1300.0
Crystal habit	rectangular prism
Radiation	Mo $K\alpha$ ($\lambda = 0.71073$ Å)
2θ range for data collection	4.676 ° to 49.528 °
Index ranges	$-12 \le h \le 12, -13 \le k \le 13, -18 \le l \le 18$
Reflections collected	19600
Independent reflections	$3206 [R_{int} = 0.0543, R_{sigma} = 0.0359]$
Data / restraints / parameters	3206 / 0 / 133
Goodness-of-fit on F^2	1.119
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0442, wR_2 = 0.1016$
Final R indexes [all data]	$R_1 = 0.0532, wR_2 = 0.1056$
Largest diff. peak / hole (e Å ⁻³)	0.88 / -0.86
Flack parameter	-0.01(4)

Table S4. Crystallographic data obtained by single crystal X-ray structure analysis for (CH₃NH₃)₃CoI₄(NCS). Estimated standard deviations are shown in parentheses.

Table S5. Fractional atomic coordinates and equivalent isotropic displacement parameters for $(CH_3NH_3)_3CoI_4(NCS)$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor. Estimated standard deviations are shown in parentheses.

Atom	x	у	Ζ	$U_{\rm eq}({ m \AA}^2)$
I1	0.50207(13)	0.55259(12)	0.42721(8)	0.0535(3)
I2	0.60158(13)	0.27851(12)	0.84104(9)	0.0580(4)
I3	0.78202(13)	0.52164(13)	0.61924(10)	0.0605(4)
I4	0.61345(15)	0.21938(12)	0.51459(10)	0.0640(4)
Col	0.5702(2)	0.4333(2)	0.55899(15)	0.0421(6)
S1	0.2450(5)	0.4436(6)	0.7666(4)	0.0677(16)
N3	0.3066(16)	0.2977(16)	0.9760(11)	0.062(5)
N1	0.4327(16)	0.4345(14)	0.6432(10)	0.054(4)
C1	0.3540(16)	0.4393(18)	0.6939(12)	0.045(5)
N4	0.5646(16)	0.5845(16)	0.8069(11)	0.062(5)
N2	0.1398(18)	0.7182(18)	0.8187(14)	0.081(6)
C3	0.3610(30)	0.3920(20)	1.0243(17)	0.082(8)
C4	0.6790(20)	0.6240(20)	0.8483(18)	0.079(8)
C2	0.0280(20)	0.7340(30)	0.7722(18)	0.099(10)

Table S6. Anisotropic Displacement Parameters (Å²) for (CH₃NH₃)₃CoI₄(NCS). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$. Estimated standard deviations are shown in parentheses.

Atom	U_{11} (Å ²)	U_{22} (Å ²)	U_{33} (Å ²)	U_{23} (Å ²)	U_{13} (Å ²)	U_{12} (Å ²)
I1	0.0583(7)	0.0549(8)	0.0474(7)	0.0032(6)	-0.0093(7)	0.0057(7)
I2	0.0603(8)	0.0489(8)	0.0650(9)	0.0028(7)	-0.0071(7)	0.0020(7)
I3	0.0525(7)	0.0596(9)	0.0693(9)	0.0052(7)	-0.0088(7)	-0.0059(6)
I4	0.0862(10)	0.0405(7)	0.0653(9)	-0.0025(7)	0.0150(8)	-0.0008(7)
Co1	0.0462(14)	0.0414(13)	0.0388(14)	-0.0014(12)	0.0039(10)	-0.0014(11)
S 1	0.063(4)	0.070(4)	0.070(4)	0.003(3)	0.025(3)	-0.003(3)
N3	0.061(11)	0.060(11)	0.063(12)	-0.002(9)	-0.008(9)	0.010(9)
N1	0.067(11)	0.047(10)	0.047(10)	-0.007(8)	0.014(8)	0.001(8)
C1	0.037(9)	0.047(11)	0.050(11)	-0.005(9)	0.007(8)	0.008(8)
N4	0.056(10)	0.072(13)	0.058(11)	0.005(10)	-0.015(8)	0.011(9)
N2	0.086(15)	0.057(12)	0.100(17)	-0.009(12)	-0.007(12)	-0.014(11)
C3	0.100(20)	0.051(14)	0.091(19)	-0.011(14)	0.025(16)	-0.017(13)
C4	0.068(15)	0.068(16)	0.100(20)	-0.021(15)	-0.020(14)	0.019(12)
C2	0.068(19)	0.130(30)	0.090(20)	0.030(20)	-0.04(15)	0.012(17)



Figure S2. Pictures of (a) $(CH_3NH_3)_2Co(NCS)_4$, (b) $(CH_3NH_3)_3CoI_4(NCS)$, and (c) $(CH_3NH_3)_2CoI_4$ powder samples.



Figure S3. Normalized Kubelka-Munk diffuse reflectance spectra of $(CH_3NH_3)_2Co(NCS)_4$, $(CH_3NH_3)_3CoI_4(NCS)$, and $(CH_3NH_3)_2CoI_4$. The absorption bands are attributed to the *d-d* transitions of the Co²⁺ ion. The bands shift to higher energy with the substitution of I⁻ for NCS⁻. Substitution to species with stronger ligand fields increases crystal field splitting, shifting the bands to higher energy. $(CH_3NH_3)_3CoI_4(NCS)$ showed not only a unique absorption band in the energy region between those of the other two samples but also the same absorption band as that of $(CH_3NH_3)_2CoI_4$ in the smaller energy region. It is due to degradation during the measurement in the air, which is consistent with the powder XRD data (Figure S1b).



Figure S4. Le Bail analysis profile of the X-ray diffraction pattern of the $(CH_3NH_3)_3Co(NCS)_4$ powder. The R_{wp} value of the fitting was 1.619 %. The black circles indicate the experimental Cu K α XRD data, the red solid line shows the simulation pattern calculated by the Le Bail fitting, the blue solid line is the difference between the experiment and calculated patterns, and the green ticks indicate the peak position of Bragg diffraction of $(CH_3NH_3)_3Co(NCS)_4$.



Figure S5. Temperature-dependent synchrotron X-ray powder diffraction patterns of $(CH_3NH_3)_2Co(NCS)_4$. ($\lambda = 0.7798318$ Å)



Figure S6. Rietveld analysis profiles of the X-ray diffraction pattern of the powder samples of (a) $(CH_3NH_3)_3CoI_4(NCS)$ and (b) $(CH_3NH_3)_3CoI_4$. The R_{wp} value of the fitting was 3.75 % and 3.81 %, respectively. The black circles indicate the experimental Cu K α XRD data, the red solid line shows the simulation pattern calculated by the Rietveld fitting, the blue solid line is the difference between the experiment and calculated patterns, and the green and yellow ticks indicate the peak position of Bragg diffraction of products and impurities shown in the legend.



Figure S7. Hypothetical crystal structure of $X_3Co(NCS)_4$ used for generation of the simulation pattern in Figure 2 a. Note that the number of electrons of hypothetical X ion is 2/3 that of methylammonium ion, which follows with the four methylammoniums disorder the interstitial voids that can accommodate six cations in a single lattice.



Figure S8. Electronic band structure and density of states (DOS) calculated for a non-magnetic state of $(CH_3NH_3)_2Co(NCS)_4$, $(CH_3NH_3)_3CoI_4(NCS)$, and $(CH_3NH_3)_2CoI_4$. The bands located near the Fermi correspond to the Co 3*d* states and are used for the wannierization. The wannierized bands are highlighted in red. The Fermi level is at zero energy.



Figure S9. Crystal structure of (CH₃NH₃)₂Co(NCS)₄ with fixed methylammonium ions (Co, blue; C, brown; N, gray; S, yellow; I, purple; H, pink).



Figure S10. (a) Energy levels of the Co²⁺ ion in the tetrahedral crystal field. Parameters of the one-electron part of the electronic model are $\Delta = 0.4 \text{ eV}$, $\lambda = 0.06 \text{ eV}$, and the Slater parameters are $F^0 = 2.65 \text{ eV}$, $F^2 = 4.62 \text{ eV}$, and $F^4 = 3.59 \text{ eV}$. (b) Spin and orbital contributions to the *g* factor as a function of the crystal-field splitting and spin-orbit coupling. The inset shows the spin contribution. The grey area highlights the range of the crystal-field splitting obtained from electronic structure calculations for (CH₃NH₃)₂Co(NCS)₄, (CH₃NH₃)₃CoI₄(NCS), (CH₃NH₃)₂CoI₄, and single [CoX₄]²⁻ tetrahedra (X = I and NCS).

I. First-principles calculations.

Spin-nonpolarized electronic structures of $(CH_3NH_3)_2Co(NCS)_4$, $(CH_3NH_3)_3CoI_4(NCS)$, and $(CH_3NH_3)_2CoI_4$ are shown in Figure S8. All three compounds feature a set of partially occupied bands near the Fermi level corresponding to the Co 3*d* states, indicating a Stoner-type instability, which further leads to an insulating state when including the on-site Coulomb interaction in the Co 3*d* shell and considering a magnetic state. The Co 3*d* states are well separated from the rest of the electronic spectrum and are weakly dispersive, suggesting that the magnetic coupling between neighbouring Co ions is weak.

Analysis of the magnetic properties in all three compounds can be carried out by constructing the electronic Hubbard models for the Co 3*d* states using the results of electronic structure calculations. Given the low symmetry and large size of the unit cells, constructing such models for $(CH_3NH_3)_3CoI_4(NCS)$ and $(CH_3NH_3)_2CoI_4$ becomes computationally demanding, and our further analysis is restricted to single $[CoX_4]^{2-}$ tetrahedra with X = I and NCS.

II. Electronic model.

Assuming that the Co X_4 tetrahedra are weakly coupled, we perform a quantitative analysis by considering a single Co²⁺ ion (3 d^7) coordinated in a perfect tetrahedral environment which can be described by the following electronic model:

$$\mathcal{H} = \mathcal{H}_{\rm CF} + \mathcal{H}_{\rm SOC} + \mathcal{H}_U.$$

With $c_{\alpha}^{\dagger\sigma}$ the creation operator of an electron with spin σ at orbital α (running over *yz*, *zx*, *xy*, *x*²*y*², and *z*² orbitals), the first term accounts for the crystal-field splitting between the low-lying *e* (*x*²-*y*² and *z*²) and high-lying *t*₂ (*yz*, *zx*, and *xy*) states:

$$\mathcal{H}_{\rm CF} = \Delta \sum_{\alpha \in t_2} n_{\alpha}$$

where $n_{\alpha}^{\sigma} = c_{\alpha}^{\dagger \sigma} c_{\alpha}^{\sigma}$ is the density operator, and $n_{\alpha} = n_{\alpha}^{\dagger} + n_{\alpha}^{\downarrow}$. The second term is spin-orbit coupling adopted in a spherically symmetric form:

$$\mathcal{H}_{\mathrm{SOC}} = \lambda \boldsymbol{S} \cdot \boldsymbol{L},$$

where λ is the SOC constant, L is the orbital angular momentum operator in the basis of d orbitals, and S is the spin angular momentum operator (defined in terms of the Pauli matrices). Finally, the on-site Coulomb interaction is given as:

$$\mathcal{H}_{U} = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} U_{\alpha\beta\gamma\delta} c_{\alpha}^{\dagger\sigma} c_{\gamma}^{\dagger\sigma'} c_{\beta}^{\sigma} c_{\delta}^{\sigma'}.$$

For the sake of simplicity, the matrix of Coulomb parameters is also adopted in a spherically symmetric form which can be parametrised by the Slater parameters F^k in the basis of spherical harmonics:

$$U_{m_1m_2m_3m_4}^{\text{sph}} = \sum_{k=0}^{2l} \alpha_k \ (m_1, m_2, m_3, m_4) F^k$$

where α_k are the Racah-Wigner coefficients, and $m_1, m_2, m_3, m_4 \in [-l, l]$ with l = 2 (*d* orbitals). Parameters $U_{\alpha\beta\gamma\delta}$ are obtained by transforming $U_{m_1m_2m_3m_4}^{\text{sph}}$ to the basis of cubic harmonics.

The electronic model is diagonalized in the basis of d^7 states:

$$\mathcal{H} = \sum_n \varepsilon_n |\alpha_n\rangle \langle \alpha_n|.$$

An exemplary electronic spectrum is shown in Figure S10a. In the tetrahedral crystal field, the ground state is given by the four-fold degenerate ${}^{4}A_{2}$ state.

Realistic model parameters for single $[CoX_4]^{2-}$ tetrahedra with X = I and NCS are obtained from first principles using the basis of Wannier functions. To this end, we take the bond lengths from the experimental crystal structures of $(CH_3NH_3)_2Co(NCS)_4$ and $(CH_3NH_3)_2CoI_4$ (for the $[CoI_4]^{2-}$ tetrahedron, we take the average bond length of 2.604 Å) and consider a single tetrahedron in a cubic box with a side length of 40 Å. By carrying out spin-nonpolarized electronic structure calculations, the crystal-field splitting and spin-orbit coupling parameters are further obtained using the Wannier functions by projecting the states located near the Fermi level onto the Co 3*d* atomic orbitals that allows taking into account hybridization with the ligand states. The resulting one-electron part of the electronic model (in meV) is for $[Co(NCS)_4]^{2-}$:

$$\mathcal{H}_{\rm CF} + \mathcal{H}_{\rm SOC} = \begin{pmatrix} 370.0\sigma_0 & 22.0i\sigma_z & -22.0i\sigma_y & -18.6i\sigma_x & -32.2i\sigma_x \\ -22.0i\sigma_z & 370.0\sigma_0 & 22.0i\sigma_x & -18.6i\sigma_y & 32.2i\sigma_y \\ 22.0i\sigma_y & -22.0i\sigma_x & 370.0\sigma_0 & 37.3i\sigma_z & 0 \\ 18.6i\sigma_x & 18.6i\sigma_y & -37.3i\sigma_z & 0 & 0 \\ 32.2i\sigma_x & -32.2i\sigma_y & 0 & 0 & 0 \end{pmatrix}$$

and for $[CoI_4]^2$:

$$\mathcal{H}_{\rm CF} + \mathcal{H}_{\rm SOC} = \begin{pmatrix} 292.7\sigma_0 & -57.8i\sigma_z & 57.8i\sigma_y & -31.6i\sigma_x & -54.4i\sigma_x \\ 57.8i\sigma_z & 292.7\sigma_0 & -57.8i\sigma_x & -31.6i\sigma_y & 54.4i\sigma_y \\ -57.8i\sigma_y & 57.8i\sigma_x & 292.7\sigma_0 & 62.6i\sigma_z & 0 \\ 31.6i\sigma_x & 31.6i\sigma_y & -62.6i\sigma_z & 0 & 0 \\ 54.4i\sigma_x & -54.4i\sigma_y & 0 & 0 & 0 \end{pmatrix}$$

where the orbital indices are given in the order yz, zx, xy, x^2-y^2 , and z^2 , and the spin indices are represented by the Pauli and unity matrices, σ_x , σ_y , σ_z , and σ_0 , respectively. Note that the realistic model parameters do not have an exact spherically symmetric form. One can see that the crystalfield splitting (diagonal elements) is larger in $[Co(NCS)_4]^{2-}$ ($\Delta = 370.0 \text{ meV}$) compared to $[CoI_4]^{2-}$ ($\Delta = 292.7 \text{ meV}$) due to shorter Co-N bondlengths. Moreover, the spin-orbit coupling term (nondiagonal elements) is greatly enhanced in the $[CoI_4]^{2-}$ complex owing to the presence of heavier I⁻ ions and the hybridization of the Co 3*d* and I 5*p* states.

In order to take into account the screening of Coulomb interactions in real systems, the Coulomb parameters are calculated for $(CH_3NH_3)_2Co(SCN)_4$ without $(CH_3NH_3)^+$ units, which has

the tetrahedral (T_d) symmetry. The full matrix of Coulomb interactions is calculated using constrained random phase approximation in the basis of Wannier functions. The Slater parameters obtained by fitting the calculated Coulomb matrix (which is not spherically symmetric due to the crystal field) are $F^0 = 2.65 \text{ eV}$, $F^2 = 4.62 \text{ eV}$, and $F^4 = 3.59 \text{ eV}$, giving the average Coulomb and Hund's coupling parameters $U = F^0 = 2.65 \text{ eV}$ and $J_H = (F^2 + F^4)/14 = 0.59 \text{ eV}$, respectively. Given that the Co 3*d* states reveal similar features in all three compounds, one can except similar screening effects and the same range for Coulomb parameters in (CH₃NH₃)₃CoI₄(NCS) and (CH₃NH₃)₂CoI₄. The calculated Slater parameters are further used to reconstruct the matrix of Coulomb parameters in a spherically symmetric form as outlined above.

III. *g* factor.

In order to calculate the g factor, we include the Zeeman term to the model above:

$$\mathcal{H}_{\mathbf{Z}} = \mu_B \boldsymbol{B} \cdot (\boldsymbol{L} + 2\boldsymbol{S}),$$

where μ_B is the Bohr's magneton, and **B** is the magnetic field. The fourfold degenerate ground state split by the magnetic field can further be mapped onto the spin states $|\tilde{S}, \tilde{S}_z\rangle$, with $\tilde{S}_z \in [-\tilde{S}, \tilde{S}]$ and $\tilde{S} = 3/2$, which are written in terms of the electronic states using the Clebsch-Gordan coefficients as:

$$\left|\frac{3}{2}, \frac{3}{2}\right\rangle = |\uparrow\uparrow\uparrow\rangle,$$

$$\left|\frac{3}{2}, \frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}(|\uparrow\uparrow\downarrow\rangle + |\uparrow\downarrow\uparrow\rangle + |\downarrow\uparrow\uparrow\rangle),$$

$$\left|\frac{3}{2}, -\frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}(|\downarrow\downarrow\uparrow\rangle + |\downarrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\rangle),$$

$$\left|\frac{3}{2}, -\frac{3}{2}\right\rangle = |\downarrow\downarrow\downarrow\rangle,$$

where the electronic basis states are given as:

$$|\sigma\sigma'\sigma''\rangle = c_{x^2-y^2}^{\dagger\uparrow}c_{x^2-y^2}^{\dagger\downarrow}c_{z^2}^{\dagger\uparrow}c_{z^2}^{\dagger\downarrow}c_{yz}^{\sigma\prime}c_{xz}^{\sigma\prime\prime}c_{xy}^{\sigma\prime\prime}|0\rangle$$

with $\sigma, \sigma', \sigma'' = \uparrow, \downarrow$. The effective low-energy Hamiltonian is obtained as:

$$\mathcal{H}_{\mathrm{S}} = \sum_{n=1}^{4} \varepsilon_n |\bar{\varphi}_n\rangle \langle \bar{\varphi}_n|,$$

with *n* running over the ⁴A₂ states, where the $|\bar{\varphi}_n\rangle$ is the orthonormalized set of states $|\varphi_n\rangle$ obtained by projectung the corresponding electronic states onto the $|\tilde{S}, \tilde{S}_z\rangle$ states:

$$|\varphi_n\rangle = \sum_{\tilde{S}_z} |\tilde{S}, \tilde{S}_z\rangle \langle \tilde{S}, \tilde{S}_z |\alpha_n\rangle.$$

Using numerical differentiation with respect to the magnetic field (we use $\mu_B |\mathbf{B}| \sim 0.0001 \text{ eV}$) and comparing the resulting matrix elements, the effective spin Hamiltonian can be recast as:

$$\mathcal{H}_{S} = \tilde{\boldsymbol{S}}^{T} \boldsymbol{\widetilde{A}} \, \tilde{\boldsymbol{S}} + \boldsymbol{\mu}_{B} \boldsymbol{B}^{T} \, \boldsymbol{\widetilde{g}} \, \tilde{\boldsymbol{S}}$$

with \tilde{S} the spin-3/2 vector, where the first term is the on-site anisotropy (\tilde{A}), and the second term gives the *g* tensor (\tilde{g}). In the absence of structural distortions, the anisotropy term vanishes, and the *g* tensor can be replaced by a scalar *g* factor.

Upon considering separately the coupling of the magnetic field to the spin and orbital angular momentum operators, one can calculate the spin and orbital contributions to the *g* factor. The results obtained for the spherically symmetric model are summarized in Figure S10b. One can see that there is a substantial orbital contribution to the *g* factor that vanishes in the limit $\lambda \ll \Delta$, indicating that the orbital degrees of freedom are quenched by the crystal field. Importantly, the *g* factor has a noticeable orbital contribution in the region of realistic parameters ($\Delta \sim 0.3$ -0.5 eV as highlighted by the grey area).

Using realistic model parameters given above, the calculated g factor is 2.26 and 2.58 for $[Co(NCS)_4]^{2-}$ and $[CoI_4]^{2-}$, respectively.