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Reactivity of cobalt(II)-dichalcogenide complexes: correlation between redox conversion and ligand-field strength

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Citation

Marvelous, C. (2022, July 5). *Reactivity of cobalt(II)-dichalcogenide complexes: correlation between redox conversion and ligand-field strength*. Retrieved from <https://hdl.handle.net/1887/3421554>

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Appendix I

Supplementary Information for Chapter 2

Synthesis of Compound $[\text{Co}(\text{L}^1\text{S})(\text{phen})](\text{SbF}_6)_2$

The compound $[\text{Co}(\text{L}^1\text{S})(\text{phen})](\text{SbF}_6)_2$ was prepared in a similar manner as compound **[3]** $(\text{SbF}_6)_2$, using 1,10-phenanthroline (phen) instead of bpy. A red powder was obtained in 85% yield. IR (neat, cm^{-1}): 1608s, 1518m, 1485w, 1426s, 1376w, 1344w, 1298w, 1247w, 1225w, 1149w, 1105m, 1091m, 1058m, 1022m, 979w, 955w, 909w, 869w, 847s, 769s, 726s, 649vs, 569m, 526m, 448m, 421s. ESI-MS in acetonitrile calcd. for $[\text{Co}(\text{L}^1\text{S})(\text{phen})](\text{SbF}_6)^+ m/z$ 732.0, found m/z 732.0; calcd. for $[\text{Co}(\text{L}^1\text{S})(\text{phen})]^{2+} m/z$ 248.55, found m/z 248.6; calcd. for $[\text{Co}(\text{phen})_3]^{2+} m/z$ 299.6, found m/z 299.9. Elemental analysis (%) for $[\text{Co}(\text{L}^1\text{S})(\text{phen})](\text{SbF}_6)_2$, calcd. C, 32.23; H, 2.50; N, 7.23; found C, 33.03; H, 2.48; N, 7.18. Single crystals were obtained by vapor diffusion of dry and deoxygenated diethyl ether into the dry and deoxygenated acetonitrile solution of compound $[\text{Co}(\text{L}^1\text{S})(\text{phen})](\text{SbF}_6)_2$.

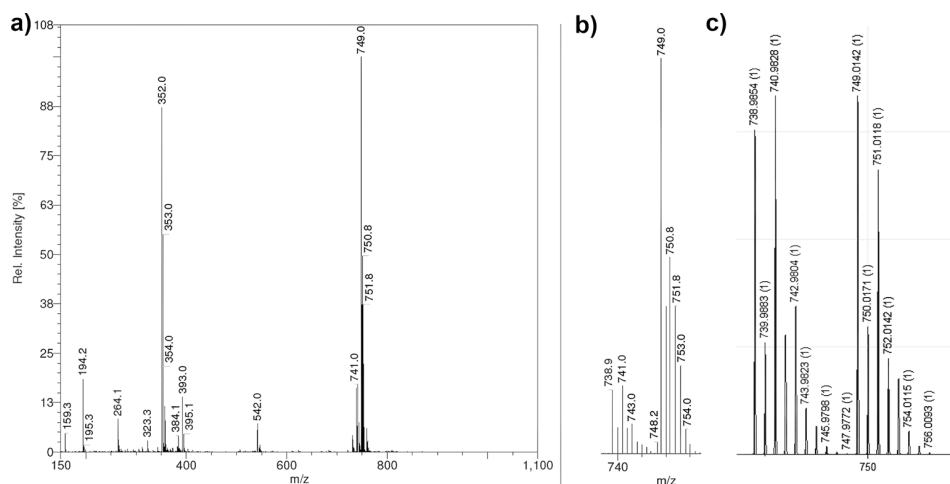


Figure AI.1. ESI-MS spectrum of a) **[1Cl]** dissolved in acetonitrile; b) the experimental isotopic distribution of the main signals; c) simulated isotopic distribution of the main signals. ESI-MS found (calcd.) for $[\text{1Cl} - 2\text{Cl}^-]^{2+} m/z$ 352.0 (352.0), for $[\text{1Cl} - \text{Cl}^-]^+ m/z$ 741.0 (741.0), and for $[\text{1Cl} - 2\text{Cl}^- + \text{HCOO}^-]^+ m/z$ 749.0 (749.0).

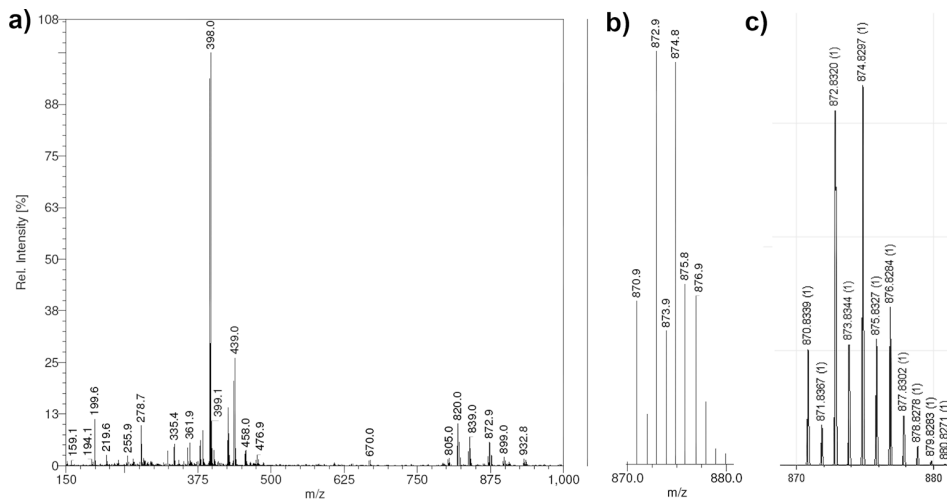


Figure AI.2. ESI-MS spectrum of a) [**1_{Br}**] dissolved in acetonitrile; b) the experimental isotopic distribution; c) simulated isotopic distribution. ESI-MS found (calcd.) for [**1_{Br}** – 2Br[–]]²⁺ *m/z* 398.0 (397.9), for [**1_{Br}** – 2Br[–] + HCOO[–]]⁺ *m/z* 839.0 (838.9), and for [**1_{Br}** – Br[–]]⁺ *m/z* 872.9 (872.8).

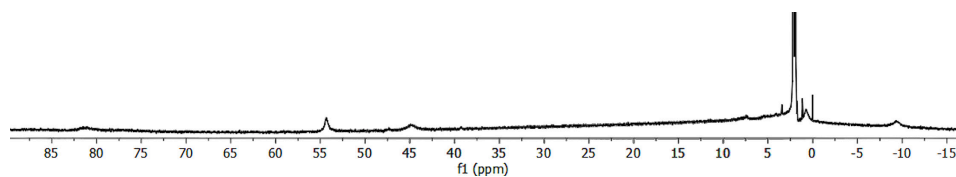


Figure AI.3. ¹H-NMR spectrum of compound [**1_{Cl1}**] dissolved in CD₃CN.

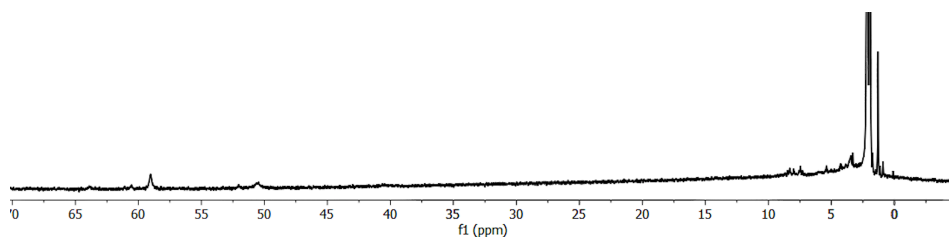


Figure AI.4. ¹H-NMR spectrum of compound [**1_{Br}**] dissolved in CD₃CN.

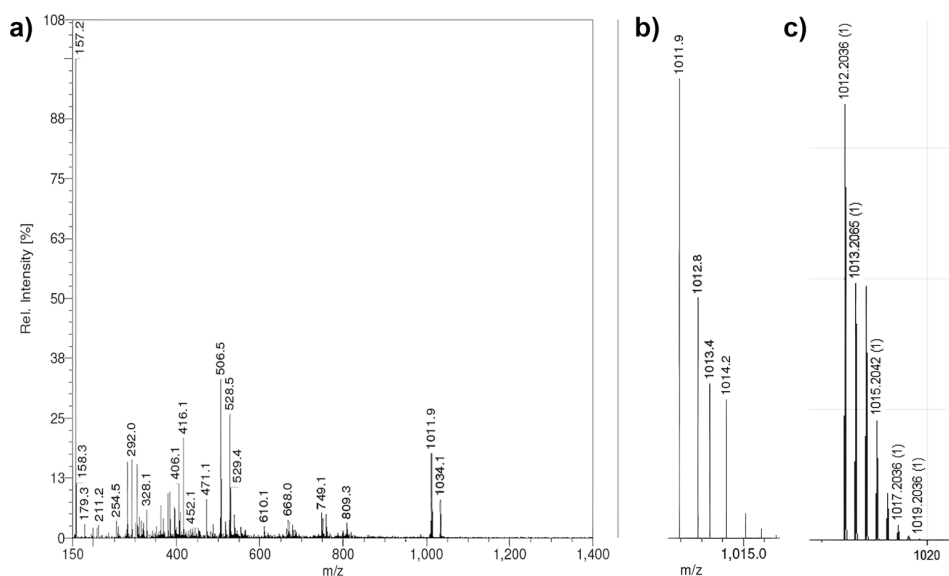


Figure AI.5. ESI-MS spectrum of a) $[2\text{Cl}](\text{BPh}_4)_2$ dissolved in methanol; b) the experimental isotopic distribution; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[2\text{Cl} - \text{Cl}^- + \text{OMe}]^{2+}$ m/z 506.5 (506.1), for partially reduced species $[2\text{Cl} - \text{Cl}^- + \text{OMe}]^+$ m/z 1011.9 (1012.2).

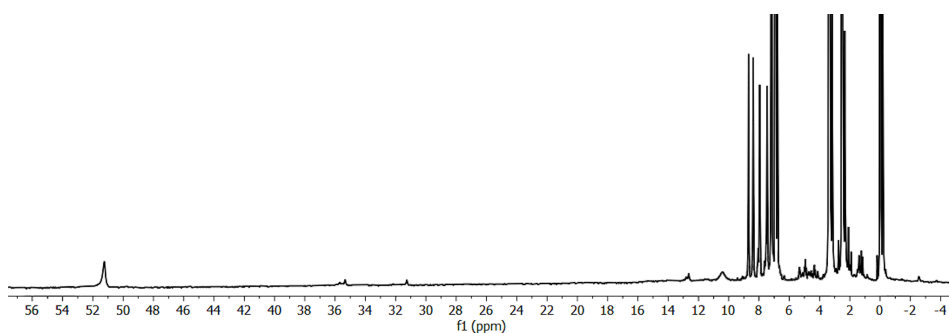


Figure AI.6. ^1H -NMR spectrum of compound $[2\text{Cl}](\text{BPh}_4)_2$ dissolved in DMSO-d_6 . The diamagnetic region contains peaks that corresponds to the ligand L^1SSL^1 and bipyridine, indicating dissociation of the ligand upon dissolution of the compound.

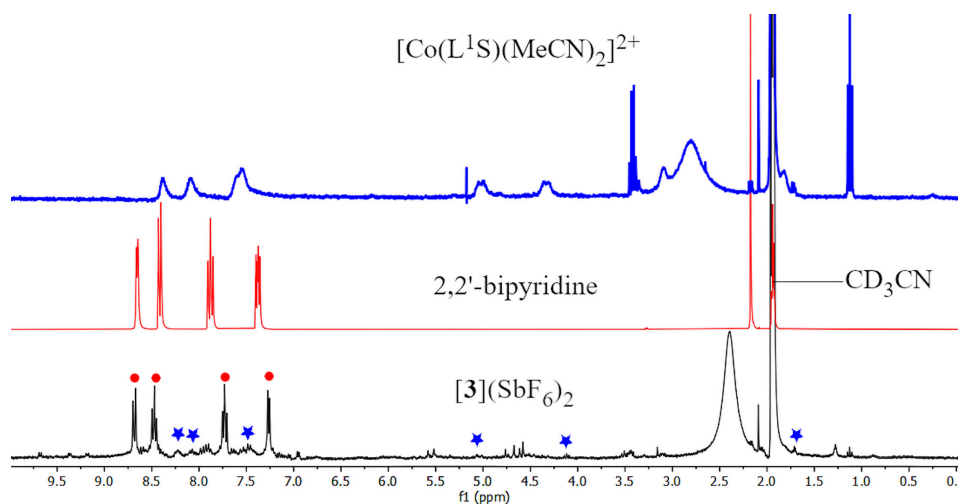


Figure AI.7. ^1H -NMR spectrum of compound $[3](\text{SbF}_6)_2$ (black trace) dissolved in CD_3CN . ^1H -NMR spectrum of $[\text{Co}(\text{L}^1\text{S})(\text{MeCN})_2]^{2+}$ (blue trace) and 2,2'-bipyridine (red trace) dissolved in CD_3CN are provided. The red dots and blue stars indicated the presence of 2,2'-bipyridine and $[\text{Co}(\text{L}^1\text{S})(\text{MeCN})_2]^{2+}$, respectively.

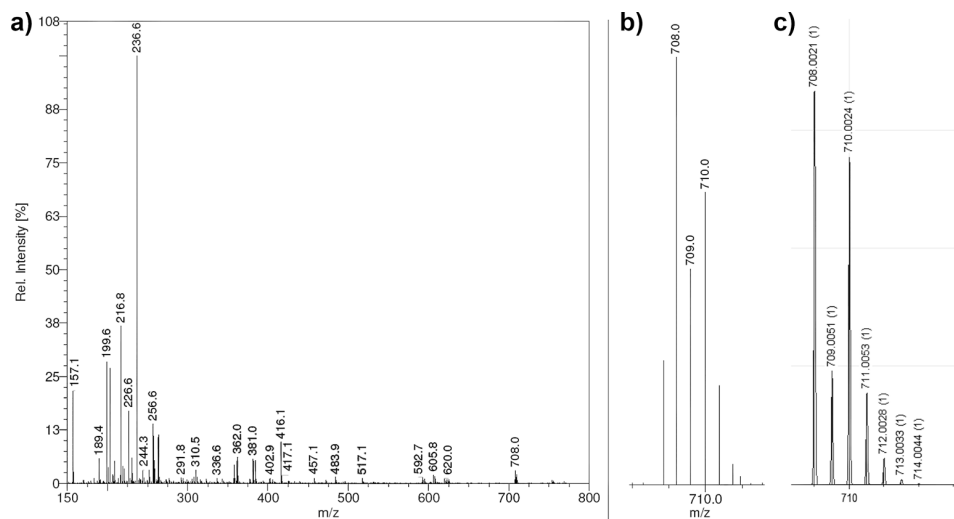


Figure AI.8. ESI-MS spectrum of a) $[3](\text{SbF}_6)_2$ dissolved in acetonitrile; b) the experimental isotopic distribution; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[3]^{2+}$ m/z 236.6 (236.55), for $[3](\text{SbF}_6)^+$ m/z 708.0 (708.0). Species $[\text{Co}(\text{L}^1\text{S})(\text{MeCN})_2]^{2+}$ (m/z 199.6 (199.55)) and $[2,2'\text{-bipyridine} + \text{H}]^+$ (m/z 157.1 (157.0)) are present.

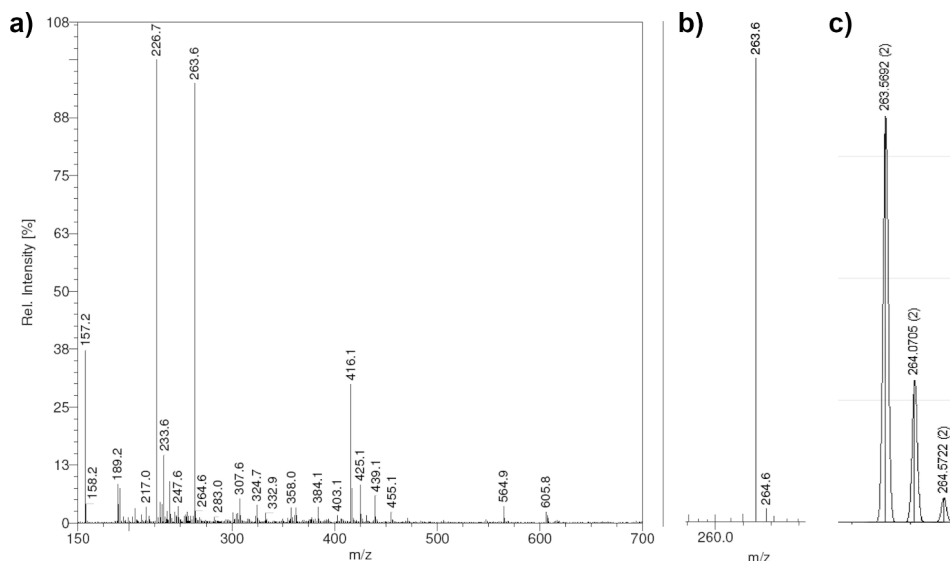


Figure AL9. ESI-MS spectrum of a) the isolated brown-reddish powder from the reaction between $[2\text{Cl}](\text{BPh}_4)_2$ with AgSbF_6 , the powder was dissolved in acetonitrile; b) the experimental isotopic distribution; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[(\text{Co}(\text{bpy})_3)_2]^+$ m/z 263.6 (263.6).

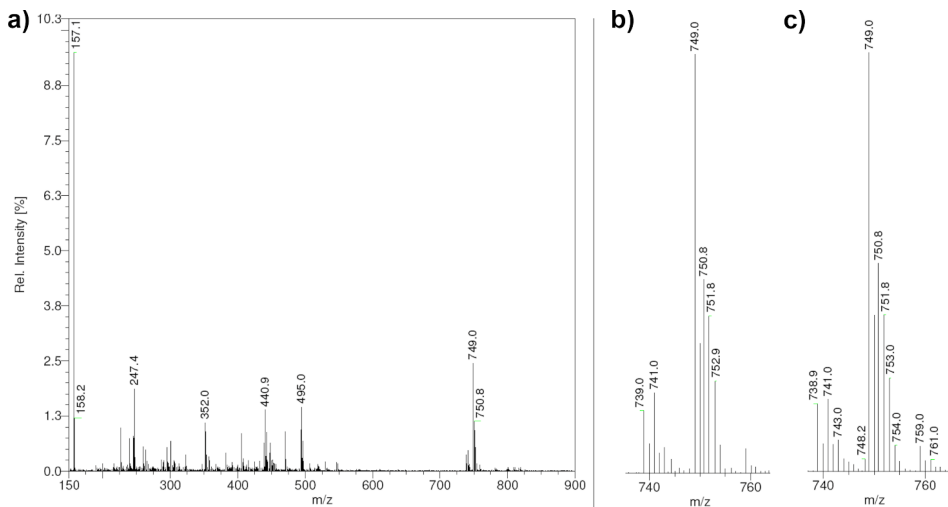


Figure AL10. ESI-MS spectrum of a) the isolated purple powder from the reaction between $[3](\text{SbF}_6)_2$ with NEt_4Cl , the powder was dissolved in acetonitrile; b) the experimental isotopic distribution; c) the experimental isotopic distribution for compound $[1\text{Cl}]$. ESI-MS found (calcd.) for $[1\text{Cl} - 2\text{Cl}]^{2+}$ m/z 352.0 (352.0), for $[1\text{Cl} - \text{Cl}]^+$ m/z 741.0 (741.0), and for $[1\text{Cl} - 2\text{Cl} + \text{HCOO}]^+$ m/z 749.0 (749.0).

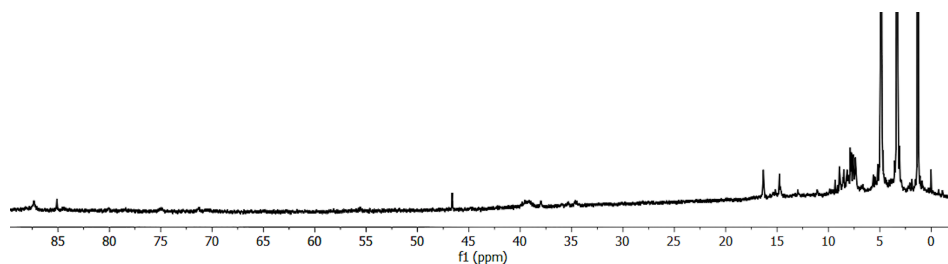


Figure AI.11. ^1H -NMR spectrum of the isolated purple powder from the reaction between $[\mathbf{3}](\text{SbF}_6)_2$ with NEt_4Cl , the powder was dissolved in CD_3CN .

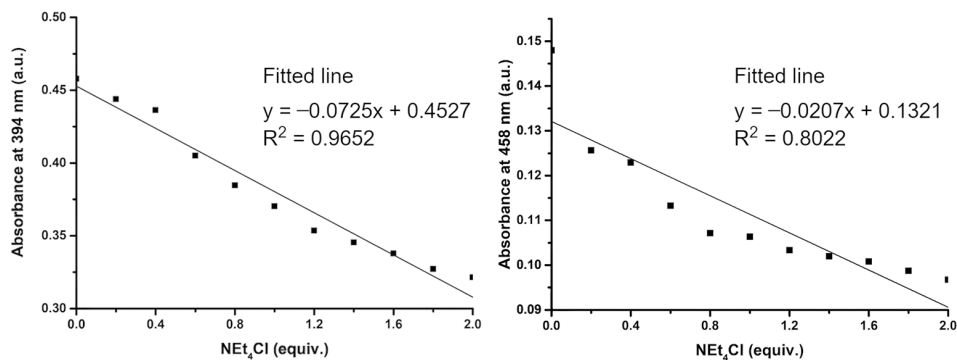


Figure AI.12. Changes of absorbance at 394 nm and 458 nm as a function of the amount of added NEt_4Cl to 5 mM solution of $[\mathbf{3}](\text{SbF}_6)_2$. Linear fitting details are provided.

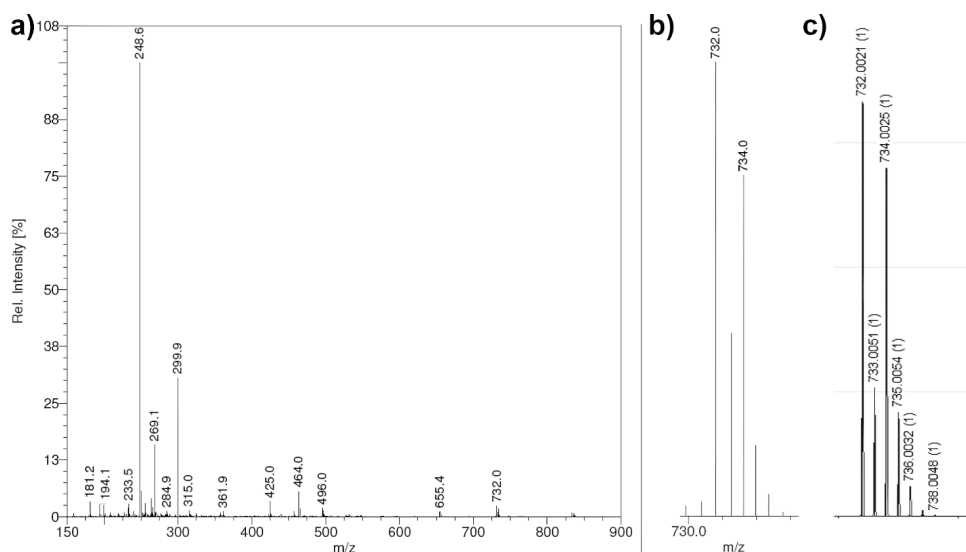


Figure AI.13. ESI-MS spectrum of a) $[\text{Co}(\text{L}^1\text{S})(\text{phen})](\text{SbF}_6)_2$, the powder was dissolved in acetonitrile; b) the experimental isotopic distribution; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[\text{Co}(\text{L}^1\text{S})(\text{phen})]^{2+}$ m/z 248.6 (248.55) and for $[\text{Co}(\text{L}^1\text{S})(\text{phen})](\text{SbF}_6)^+$ m/z 732.0 (732.0). The species $[\text{Co}(\text{phen})_3]^{2+}$ is also found (calcd.) at m/z 299.9 (299.6).

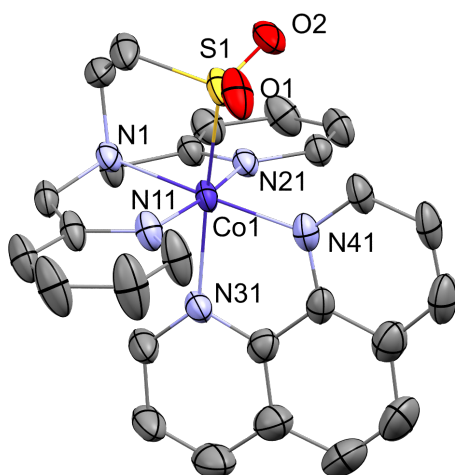


Figure AI.14. Displacements ellipsoid plot (50% probability level) of the oxidized compound $[\text{Co}(\text{L}^1\text{SO}_2)(\text{phen})](\text{SbF}_6)_2$ at 110(2) K. Hydrogen atoms, non-coordinated anions, and lattice solvent molecules are omitted for clarity.

Table AI.1. Selected bond distances and bond angles in [Co(L¹SO₂)(phen)](SbF₆)₂.

Atoms	distance (Å)	Atoms	Bond angles (°)
Co1–N1	1.976(4)	S1–Co1–N1	86.78(11)
Co1–N11	1.921(4)	S1–Co1–N11	88.59(13)
Co1–N21	1.929(4)	S1–Co1–N21	95.64(11)
Co1–N31	2.084(4)	S1–Co1–N31	172.01(12)
Co1–N41	1.969(4)	S1–Co1–N41	92.32(12)
Co1–S1	2.1866(13)	N31–Co1–N41	82.36(16)
S1–O1	1.460(4)	N31–Co1–N1	98.77(15)
S1–O2	1.456(4)	N21–Co1–N1	84.00(16)

Table AI.2. Crystallographic Data for the crystal structures in the present work.

	[1Br]	[2Cl](BPh ₄) ₂	[Co(L ¹ SO ₂)(phen)](SbF ₆) ₂
Chemical formula	C ₂₈ H ₃₂ Br ₄ Co ₂ N ₆ S ₂ , CH ₄ O	C ₄₈ H ₄₈ Cl ₂ Co ₂ N ₁₀ S ₂ , 2(C ₂₄ H ₂₀ B), 2(C ₃ H ₆ O), 0.42(O)	C ₂₆ H ₂₄ CoN ₅ O ₂ S, 2(F ₆ Sb), 0.566(C ₄ H ₁₀ O), 1.434(C ₂ H ₃ N)
<i>M_r</i>	986.26	1779.17	1101.82
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Cell lengths (<i>a</i> , <i>b</i> , <i>c</i>) (Å)	15.7651(7), 11.9665(5), 19.6343(8)	19.0139(7), 20.1121(7), 27.0156(13)	21.5627 (5), 13.6523 (4), 14.0315 (4)
Cell angles (α, β, γ) (°)	90, 103.345(4), 90	90, 108.171(4), 90	90, 103.059 (3), 90
Cell volume (Å ³)	3604.1 (3)	9815.8 (7)	4023.8 (2)
<i>Z</i>	4	4	4
μ (mm ⁻¹)	5.50	0.49	1.89
Crystal size (mm)	0.11 × 0.08 × 0.02	0.26 × 0.19 × 0.10	0.29 × 0.09 × 0.05
Temperature (K)	110(2)	110(2)	110(2)
Diffractionmeter	SuperNova, Dual, Cu at zero, Atlas detector	SuperNova, Dual, Cu at zero, Atlas detector	SuperNova, Dual, Cu at zero, Atlas detector
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
<i>T_{min}</i> , <i>T_{max}</i>	0.734, 0.982	0.520, 1.000	0.439, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	28658, 6355, 4720	38544, 11261, 8613	50549, 7091, 5615
<i>R_{int}</i>	0.065	0.038	0.049
(sin θ/λ) _{max} (Å ⁻¹)	0.595	0.650	0.595
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.047, 0.114, 1.05	0.043, 0.105, 1.02	0.039, 0.102, 1.04
No. of reflections	6355	11261	7091
No. of parameters	398	652	661
No. of restraints		309	404
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.94, -0.82	0.56, -0.31	0.79, -0.77

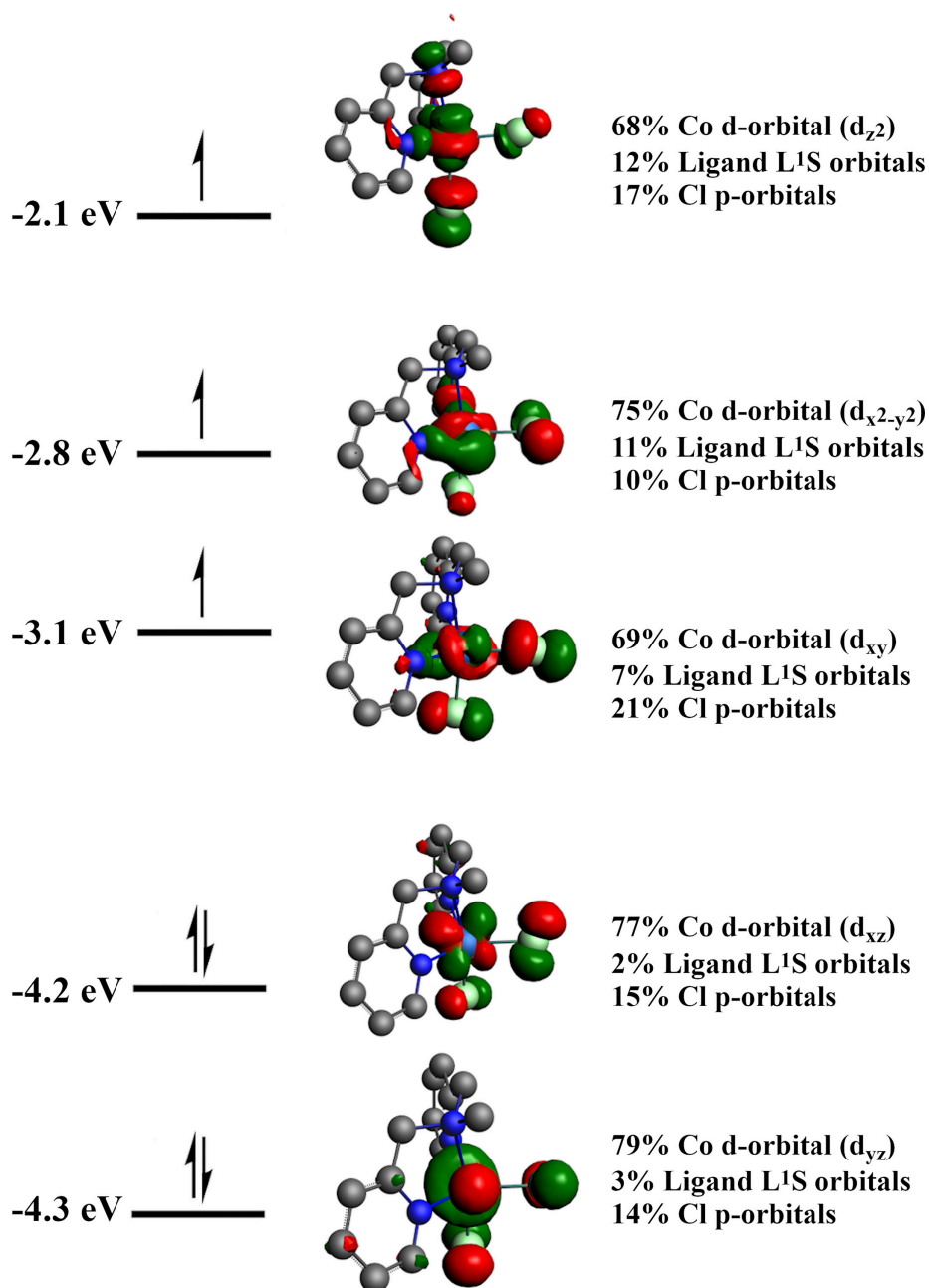


Figure AI.15. Several frontier orbitals of [1*] associated with Co *d*-orbitals along with their energies, orbital visualization, and orbital composition.

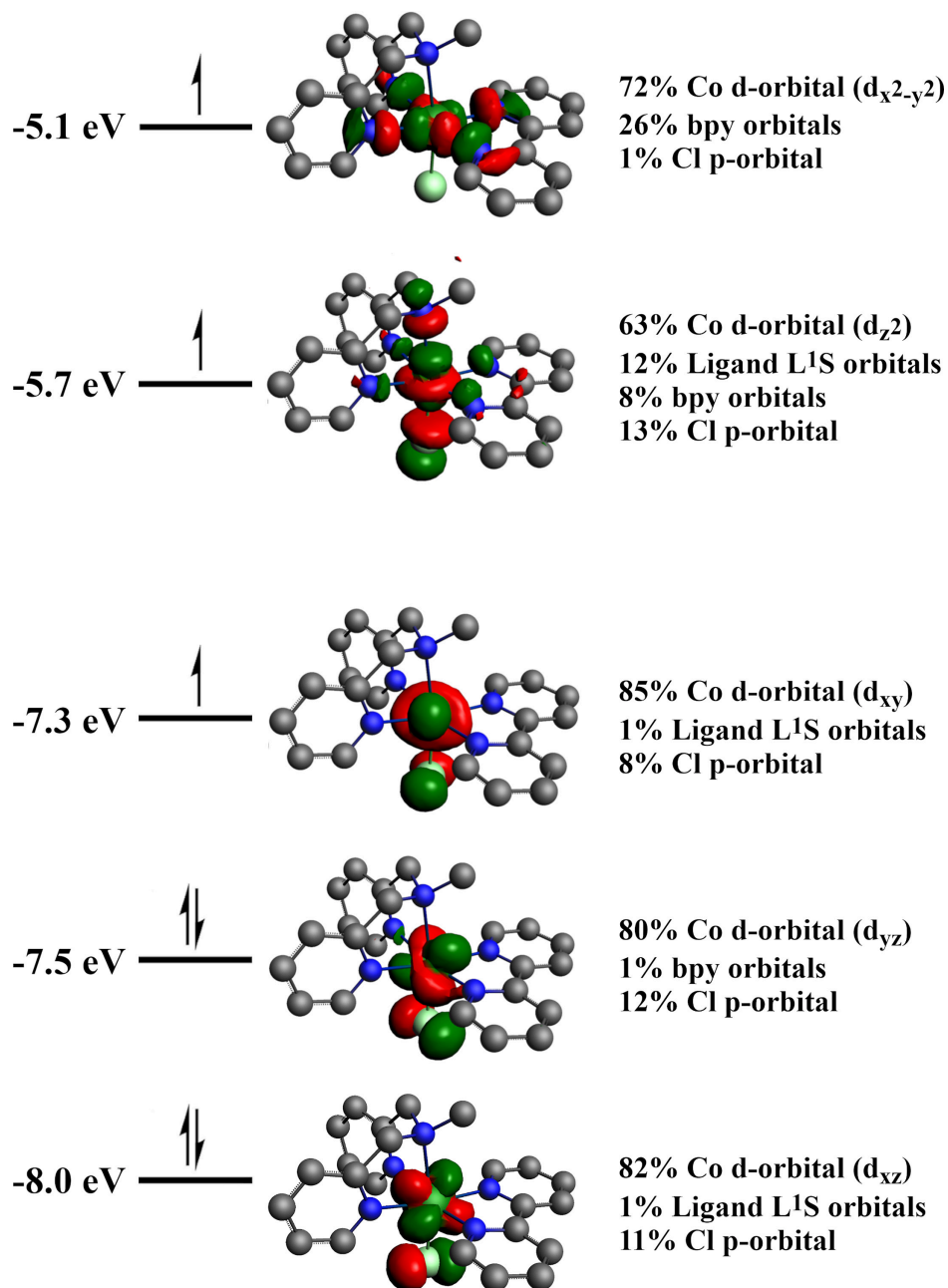


Figure AI.16. Several frontier orbitals of $[2^*]^+_{\text{fac}}$ associated with Co d -orbitals along with their energies, orbital visualization, and orbital composition.

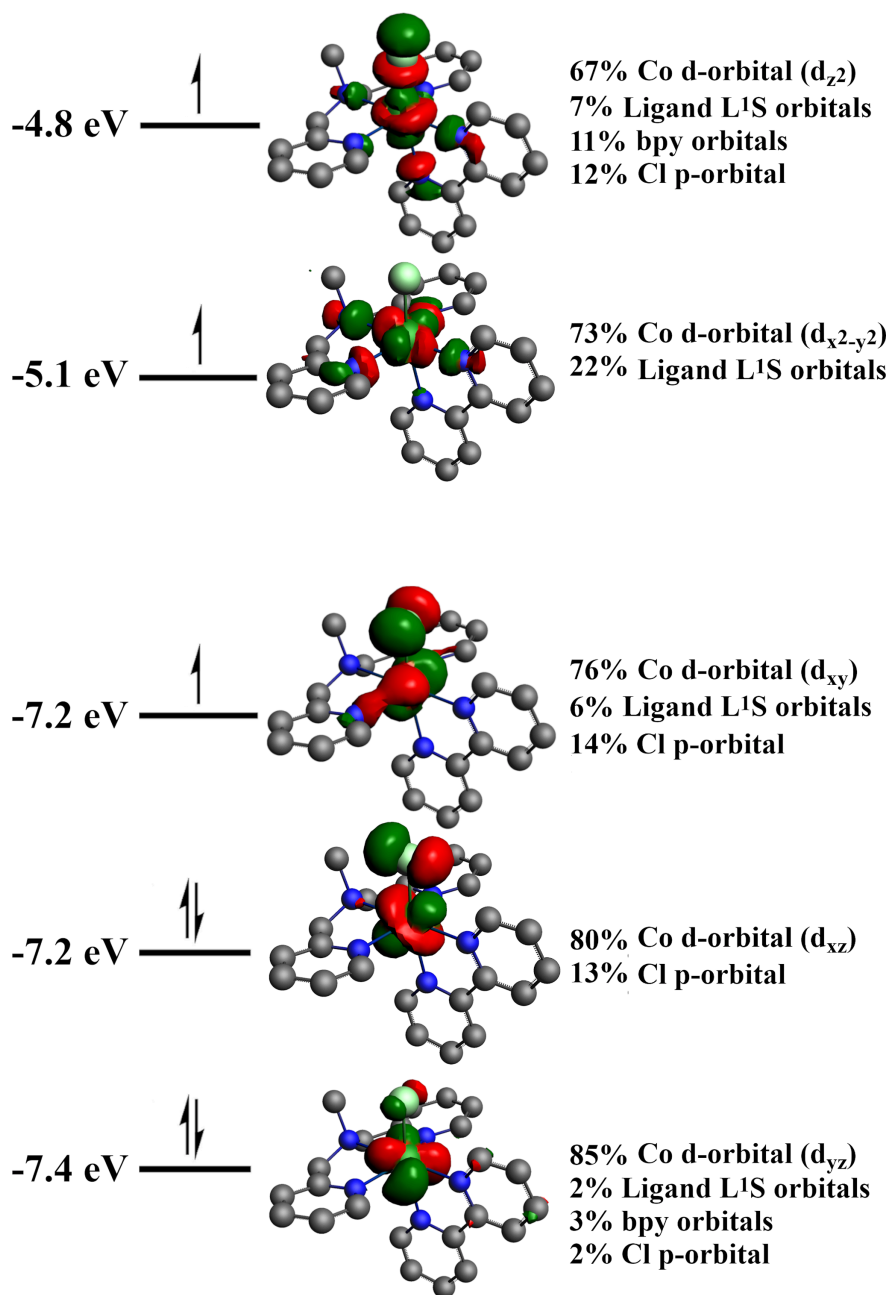


Figure AI.17. Several frontier orbitals of $[2^*]^+_{\text{mer}}$ associated with Co d -orbitals along with their energies, orbital visualization, and orbital composition.

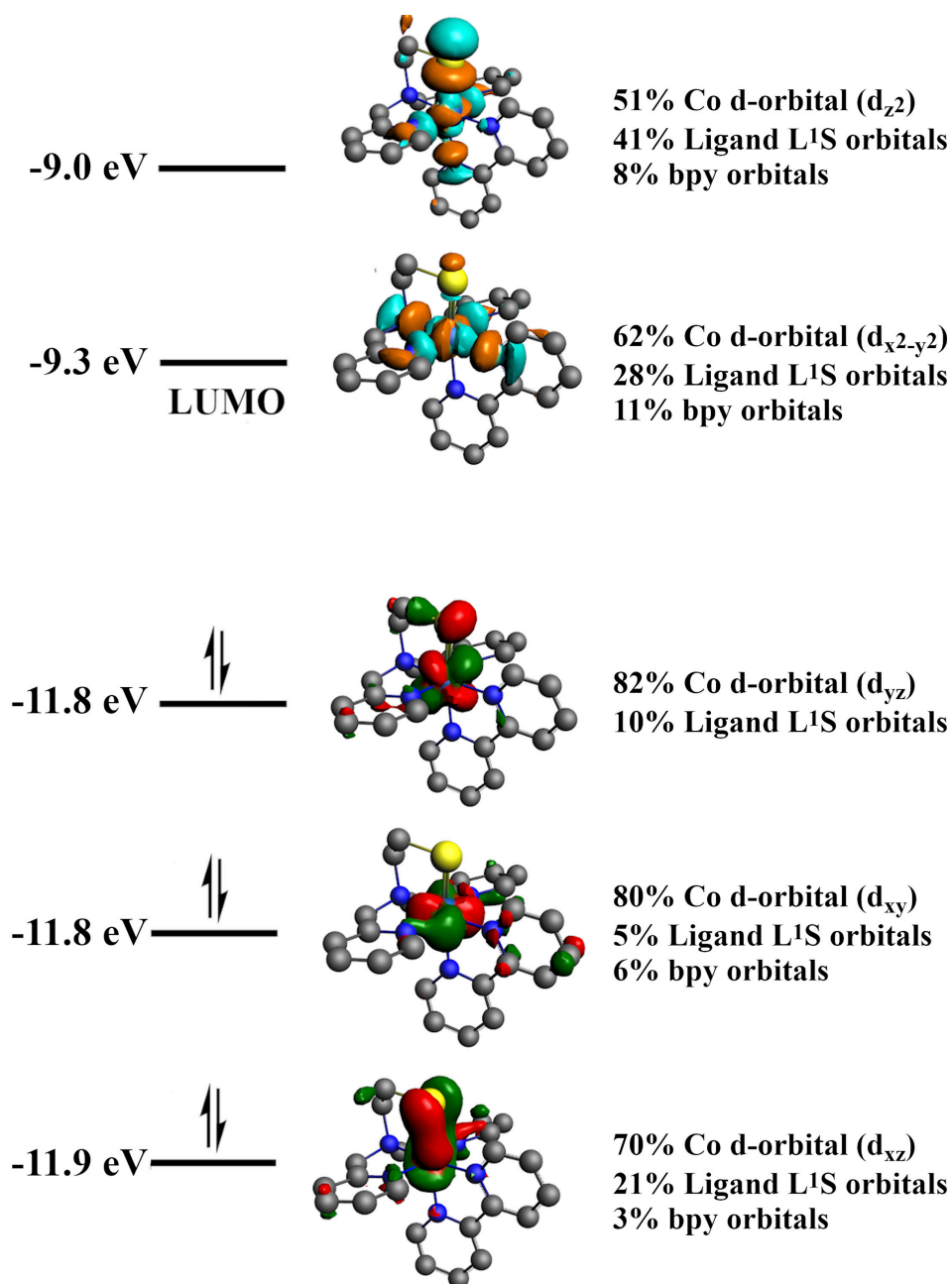


Figure AI.18. Several frontier orbitals of $[3]^{2+}_{\text{mer}}$ associated with Co d -orbitals along with their energies, orbital visualization, and orbital composition.

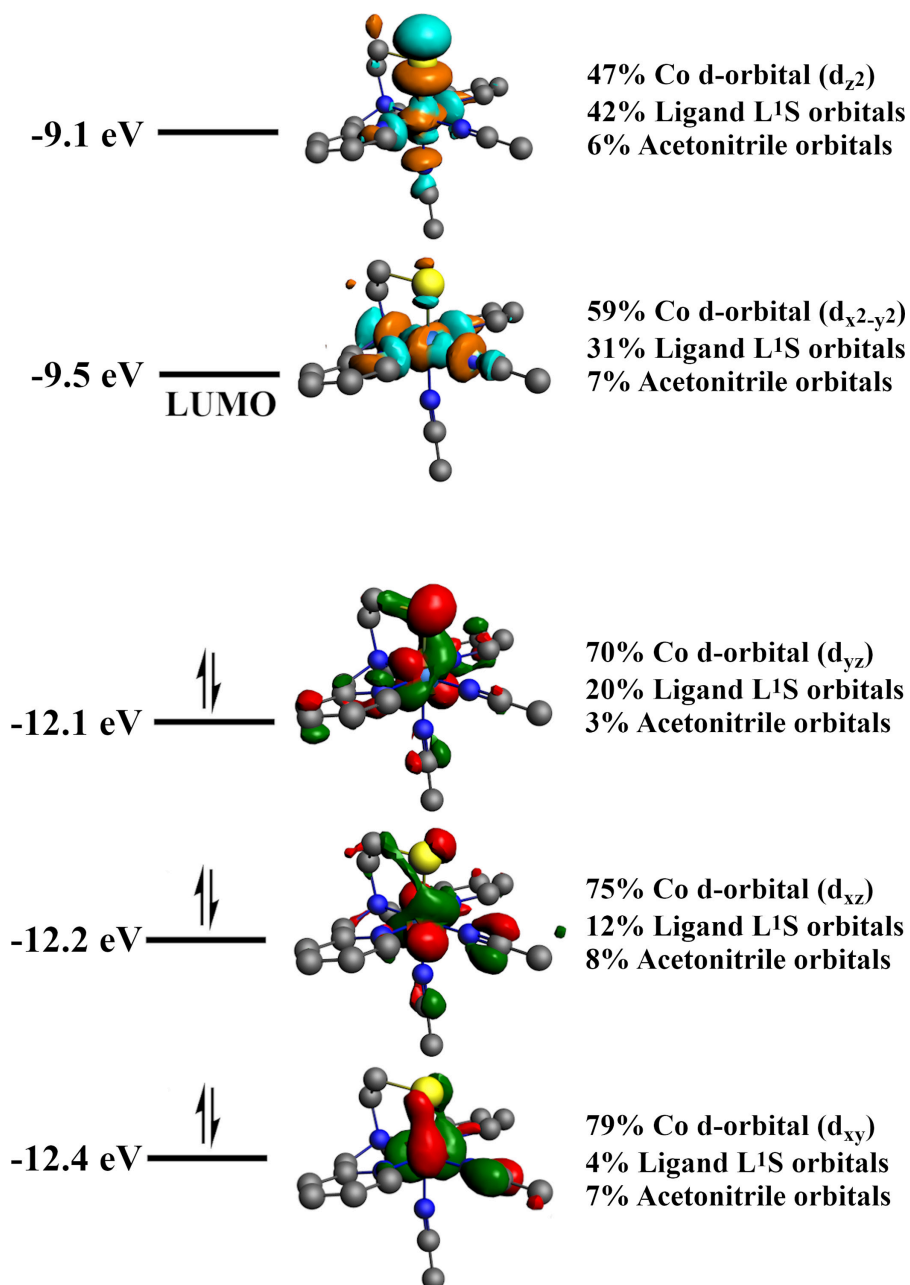


Figure AI.19. Several frontier orbitals of $[4]^{2+}$ associated with Co d -orbitals along with their energies, orbital visualization, and orbital composition.

Appendix II

Supplementary Information for Chapter 3

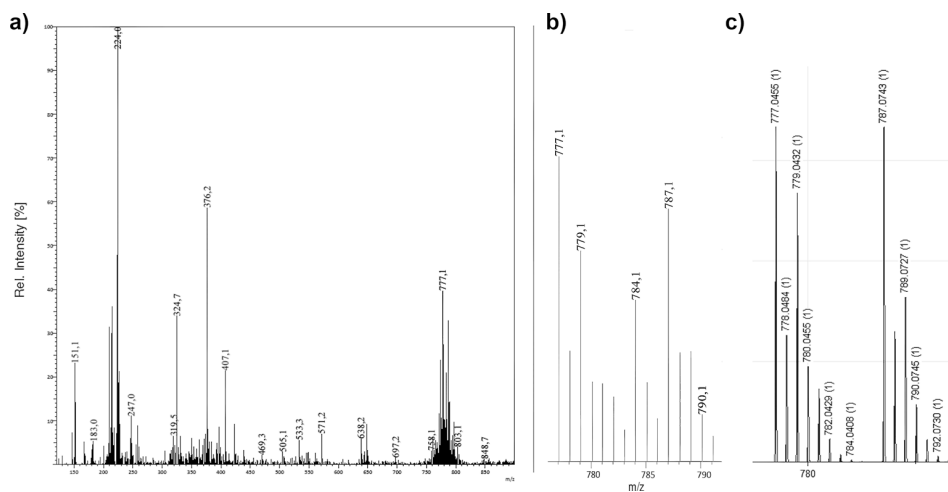


Figure AII.1. ESI-MS spectrum of compound [2ss] dissolved in methanol. ESI-MS found (calcd.) for $[2ss - 4Cl^- + 2HCOO^-]^{2+}$ m/z 376.2 (376.04), for $[2ss - 2Cl^- + HCOO^-]^+$ m/z 777.1 (777.05), and for $[2ss - 3Cl^- + 2HCOO^-]^+$ m/z 787.1 (787.07).

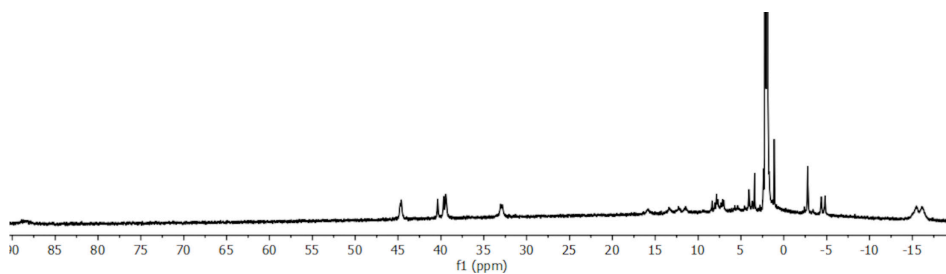


Figure AII.2. 1H -NMR spectrum of compound [2ss] dissolved in CD_3CN .

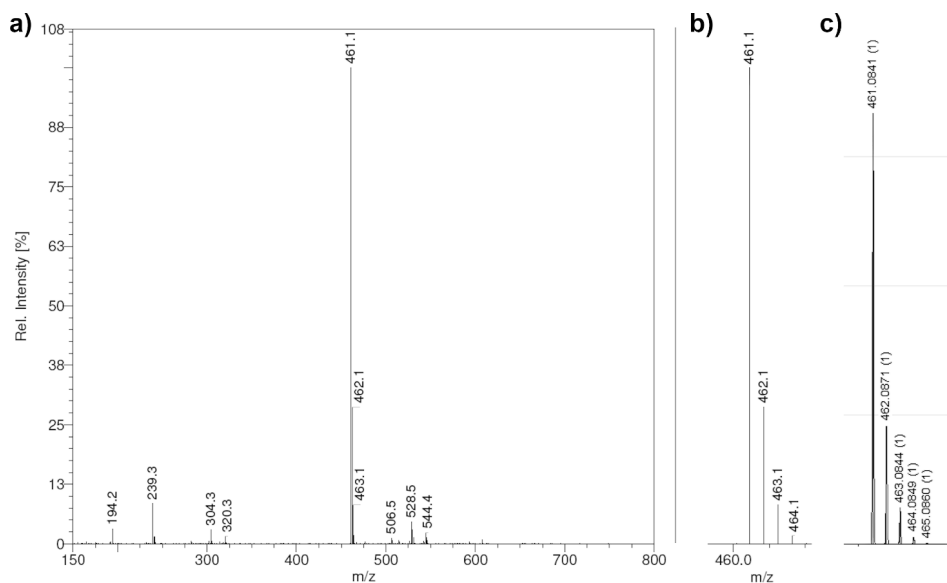


Figure AII.3. ESI-MS spectrum of a) $[1s]Cl$ dissolved in methanol; b) the experimental isotopic distribution of the main signal; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[1s]^+$ m/z 461.1 (461.08).

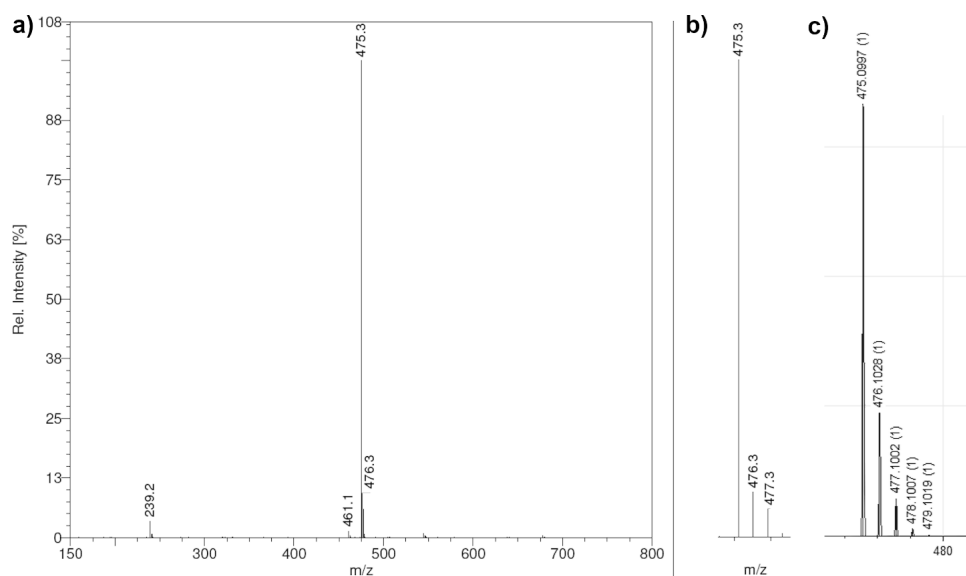


Figure AII.4. ESI-MS spectrum of a) $[2s]Cl$ dissolved in acetonitrile; b) the experimental isotopic distribution of the main signal; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[2s]^+$ m/z 475.3 (475.1).

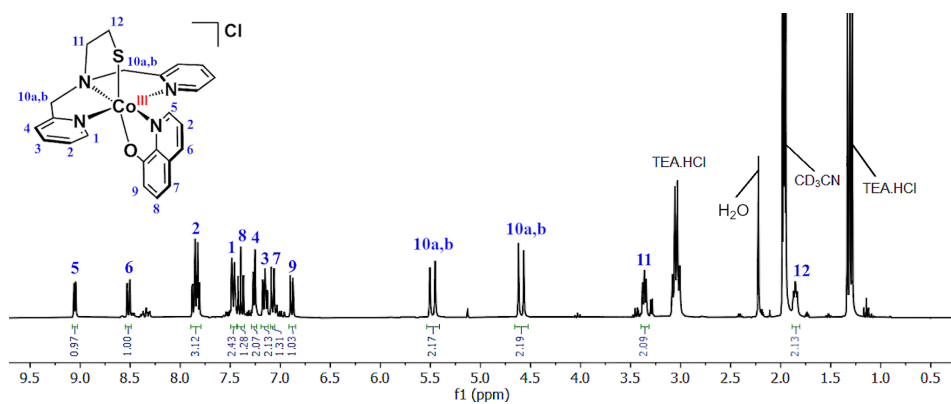


Figure AII.5. ^1H -NMR spectrum of $[\mathbf{1s}]\text{Cl}$ dissolved in CD_3CN .

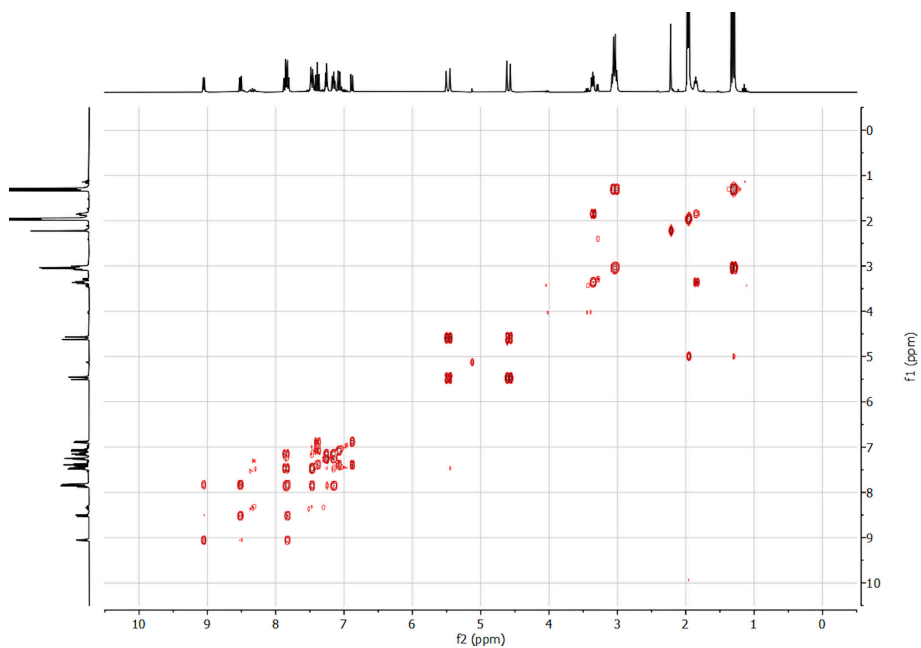


Figure AII.6. ^1H - ^1H -COSY NMR spectrum of $[\mathbf{1s}]\text{Cl}$ dissolved in CD_3CN .

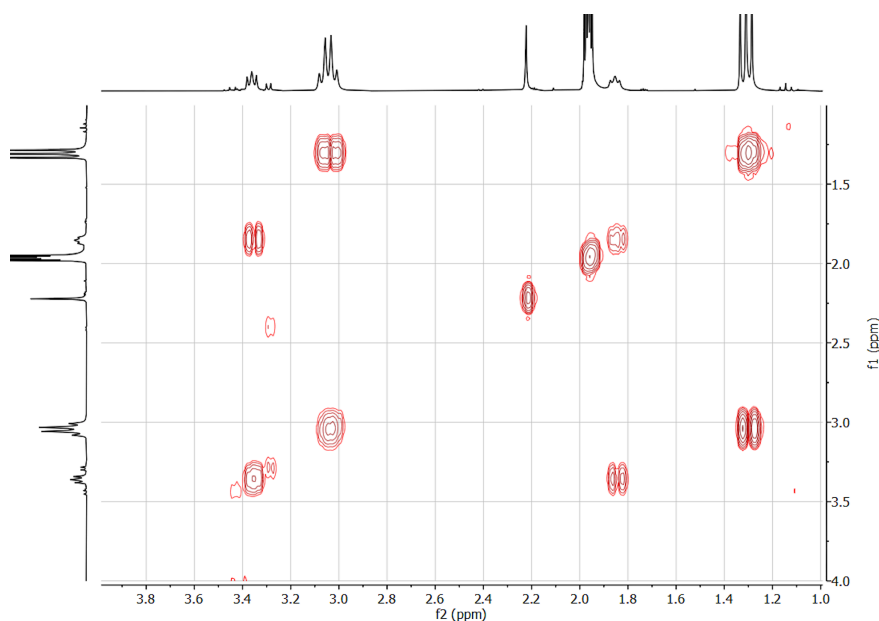


Figure AII.7. ^1H - ^1H -COSY NMR spectrum of $[1\text{s}]\text{Cl}$ dissolved in CD_3CN . The spectrum shows the correlation of protons in $\text{N-CH}_2\text{-CH}_2\text{-S}$ (3.2–3.5 ppm and 1.84–1.87 ppm).

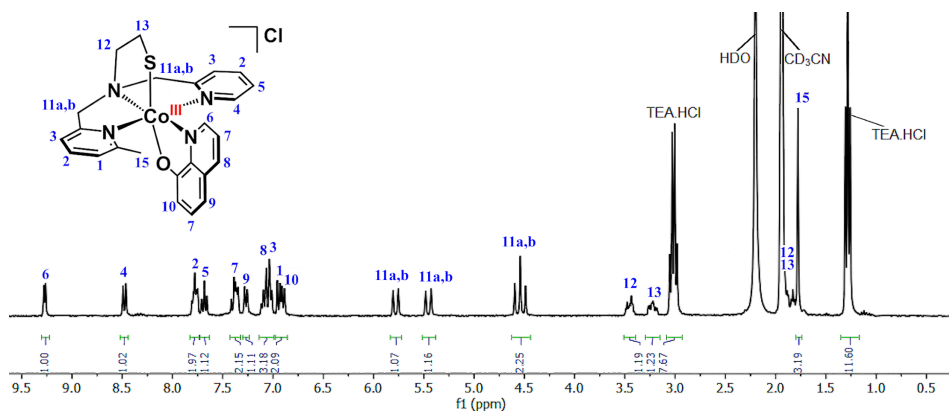


Figure AII.8. ^1H -NMR spectrum of $[2\text{s}]\text{Cl}$ dissolved in CD_3CN .

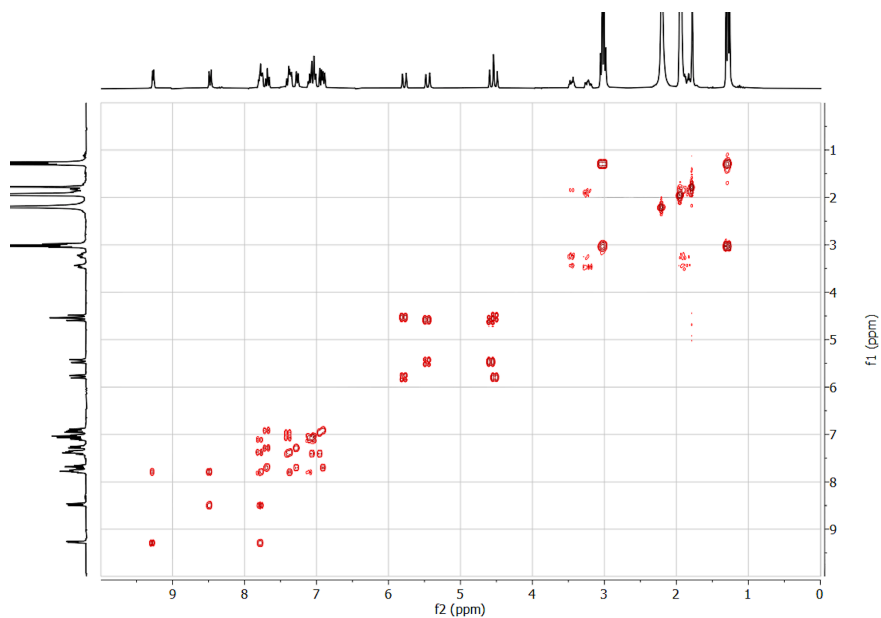


Figure AII.9. ^1H - ^1H -COSY NMR spectrum of $[2s]\text{Cl}$ dissolved in CD_3CN .

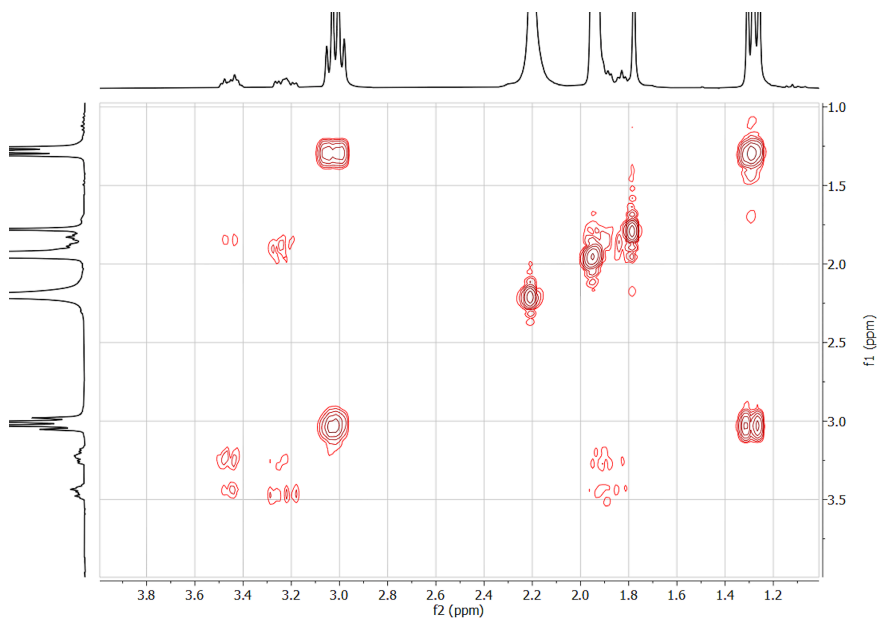


Figure AII.10. ^1H - ^1H -COSY NMR spectrum of $[2s]\text{Cl}$ dissolved in CD_3CN . The spectrum shows the correlation of protons in $\text{N-CH}_2\text{-CH}_2\text{-S}$ (3.18–3.50 ppm) with the solvent peak (1.9 ppm), indicating that the solvent peak obscures the proton peak of interest.

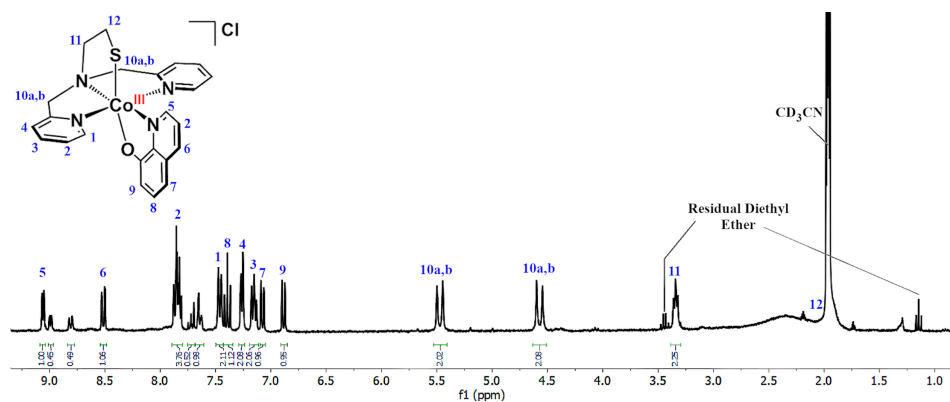


Figure AII.11. ^1H -NMR spectrum of $[1s]\text{Cl}$ dissolved in CD_3CN . The synthesis was done in absence of triethylamine. Impurities (as unlabeled peaks) are present mostly in the aromatic region.

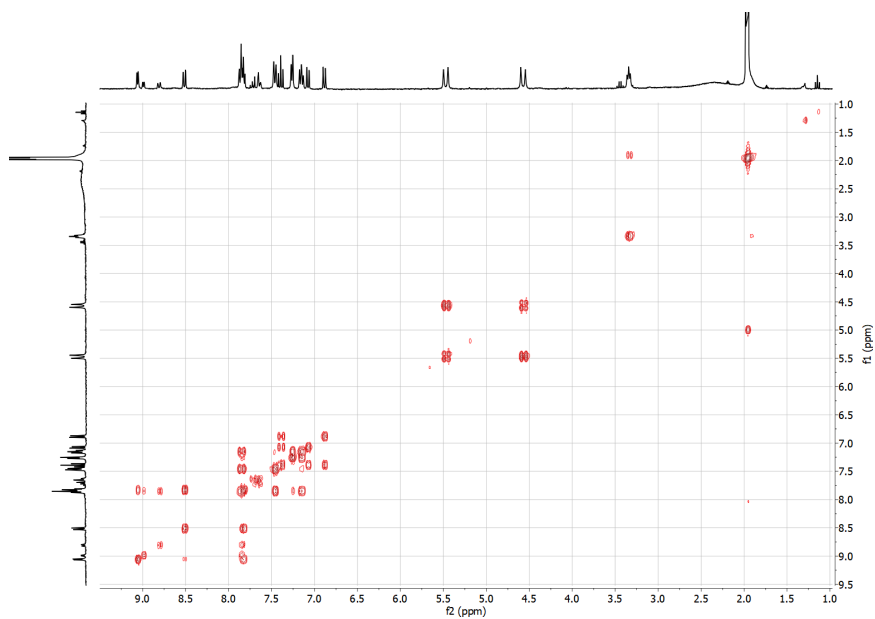


Figure AII.12. ^1H - ^1H -COSY NMR spectrum of $[1s]\text{Cl}$ dissolved in CD_3CN . The synthesis was done in absence of triethylamine.

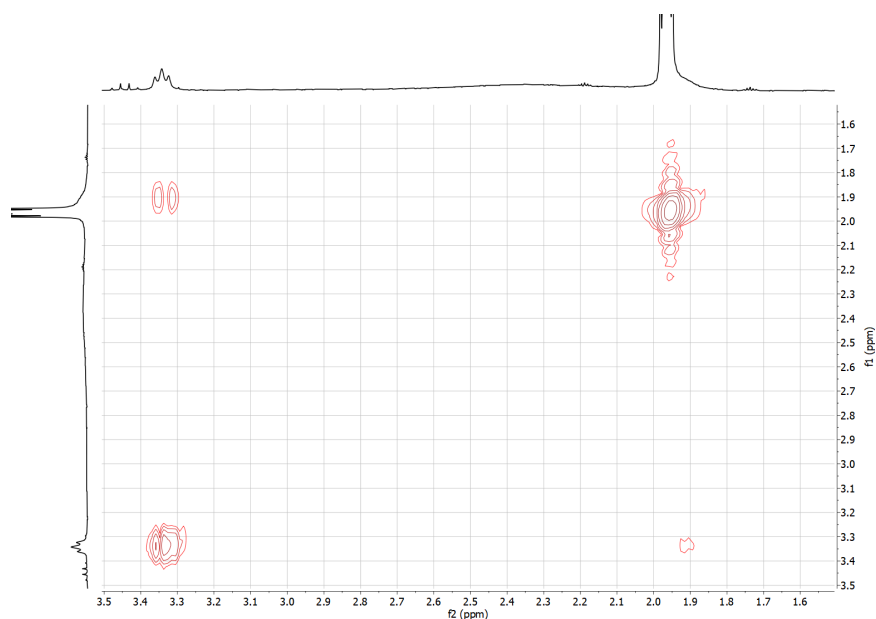


Figure AII.13. ^1H - ^1H -COSY NMR spectrum of $[\mathbf{1s}]\text{Cl}$ dissolved in CD_3CN . The synthesis was done in absence of triethylamine. The spectrum shows the correlation of protons in $\text{N-CH}_2\text{-CH}_2\text{-S}$ (3.2–3.4 ppm and 1.84–1.87 ppm).

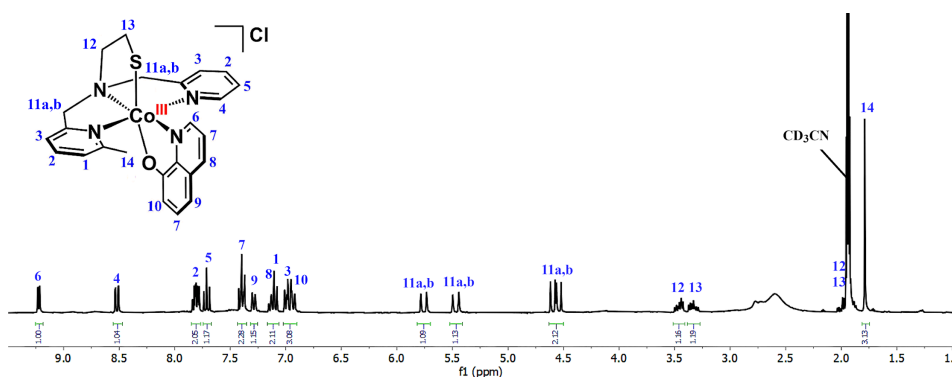


Figure AII.14. ^1H -NMR spectrum of $[\mathbf{2s}]\text{Cl}$ dissolved in CD_3CN . The synthesis was done in absence of triethylamine.

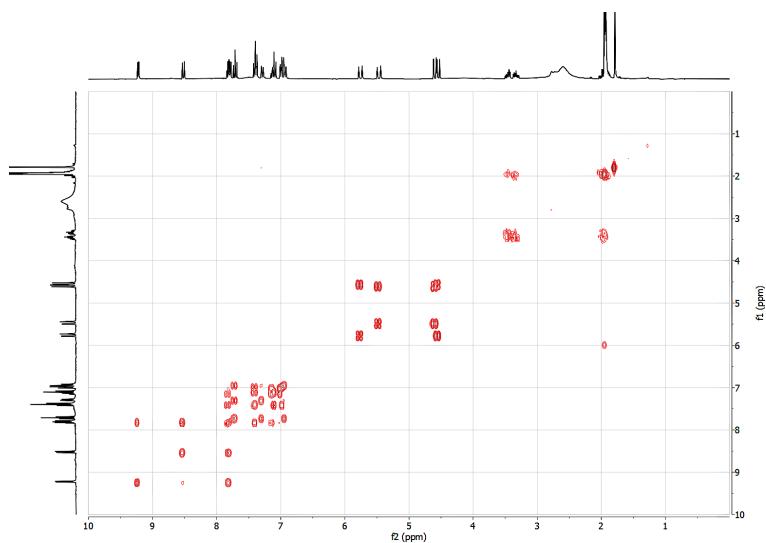


Figure AII.15. ^1H - ^1H -COSY NMR spectrum of $[2_s]\text{Cl}$ dissolved in CD_3CN . The synthesis was done in absence of triethylamine.

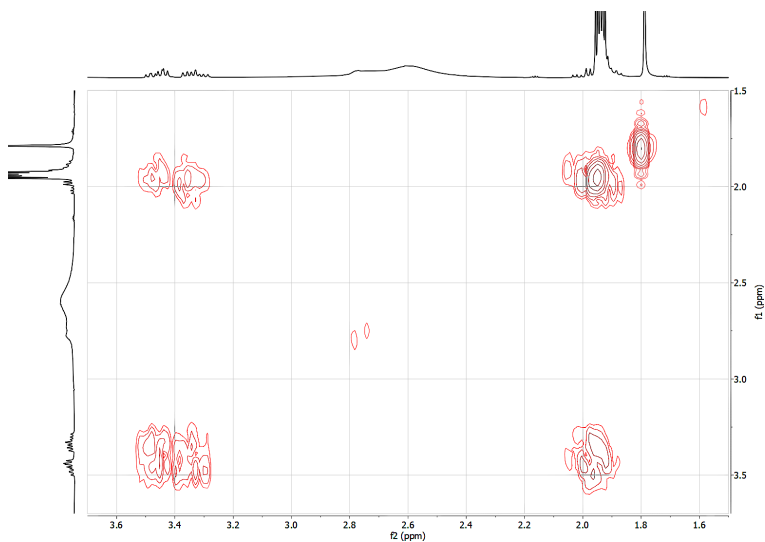


Figure AII.16. ^1H - ^1H -COSY NMR spectrum of $[2_s]\text{Cl}$ dissolved in CD_3CN . The synthesis was done in absence of triethylamine. The spectrum shows the correlation of protons in $\text{N-CH}_2\text{-CH}_2\text{-S}$ (3.18–3.50 ppm) with the solvent peak (1.9 ppm), indicating that the solvent peak obscures the proton peak of interest.

Table AII.1. Crystallographic data for all crystals in the present work.

	[1s]Cl	[2s-Ag-2s](SbF ₆) ₃	[2ssquin]
Chemical formula	C ₂₃ H ₂₂ CoN ₄ OS· 3(CH ₄ O)·Cl	C ₅₀ H ₅₁ AgCo ₂ N ₉ O ₂ S ₂ · 3(F ₆ Sb)·0.969(C ₂ H ₃ N)	C ₄₈ H ₄₈ Cl ₂ Co ₂ N ₈ O ₂ S ₂ · 0.903(C ₂ H ₃ N)
<i>M_r</i>	593.01	1846.88	1058.87
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
Cell lengths (<i>a</i> , <i>b</i> , <i>c</i>) (Å)	8.8184(3), 13.0506(5), 13.3362(5)	15.7072(5), 27.0793(6), 19.3101(6)	18.4673(4), 14.9350(4), 19.1135(4)
Cell angles (α, β, γ) (°)	63.783(4), 73.530(3), 84.488(3)	90, 112.171(3), 90	90, 97.898(2), 90
Cell volume (Å ³)	1319.66(10)	7606.1 (4)	5221.7(2)
<i>Z</i>	2	4	4
μ (mm ⁻¹)	7.11	1.87	0.86
Crystal size (mm)	0.41 × 0.33 × 0.18	0.52 × 0.37 × 0.22	0.35 × 0.22 × 0.20
Temperature (K)	110(2)	110(2)	110(2)
Diffractometer	SuperNova, Dual, Cu at zero, Atlas detector	SuperNova, Dual, Cu at zero, Atlas detector	SuperNova, Dual, Cu at zero, Atlas detector
Radiation type	Cu <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
<i>T</i> _{min} , <i>T</i> _{max}	0.161, 0.410	0.295, 1.000	0.425, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	16974, 5155, 5078	61799, 21893, 14227	62110, 11982, 9923
<i>R</i> _{int}	0.025	0.048	0.045
(sin θ/λ) _{max} (Å ⁻¹)	0.616	0.650	0.650
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.028, 0.071, 1.05	0.072, 0.231, 1.07	0.048, 0.128, 1.03
No. of reflections	5155	21893	11982
No. of parameters	340	1385	618
No. of restraints	-	2501	2
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.28, -0.46	1.75, -1.28	0.69, -0.59

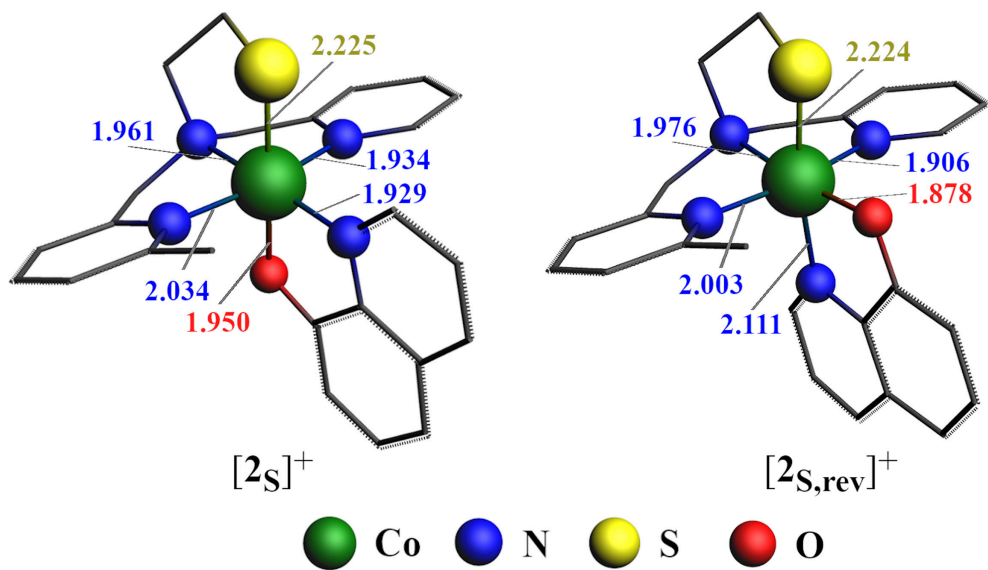


Figure AII.17. Optimized geometries of $[2_S]^+$ and $[2_{S,rev}]^+$ with selected bond distances (Å).

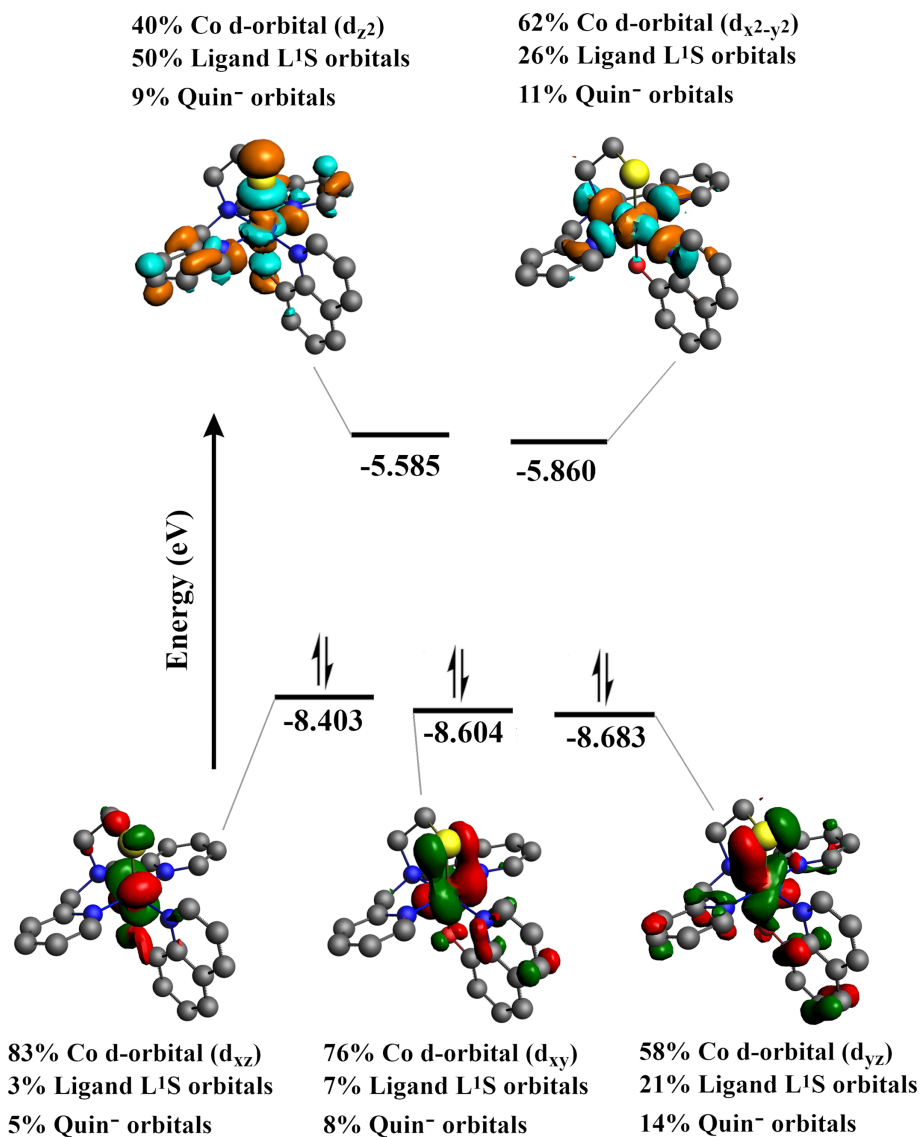


Figure AII.18. Several frontier orbitals of $[1s]^+$ associated with Co d -orbitals along with their energies, orbital visualization, and orbital composition.

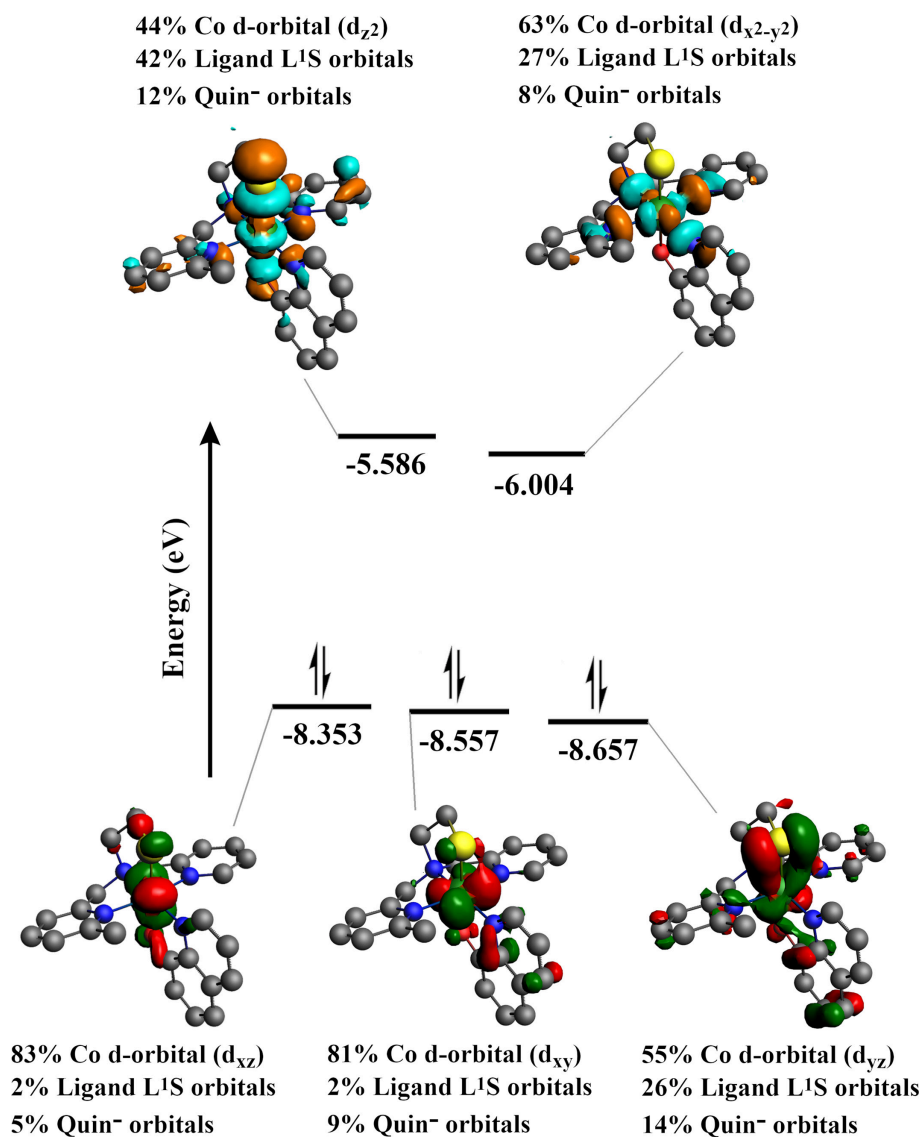


Figure AII.19. Several frontier orbitals of $[2s]^+$ associated with Co d -orbitals along with their energies, orbital visualization, and orbital composition.

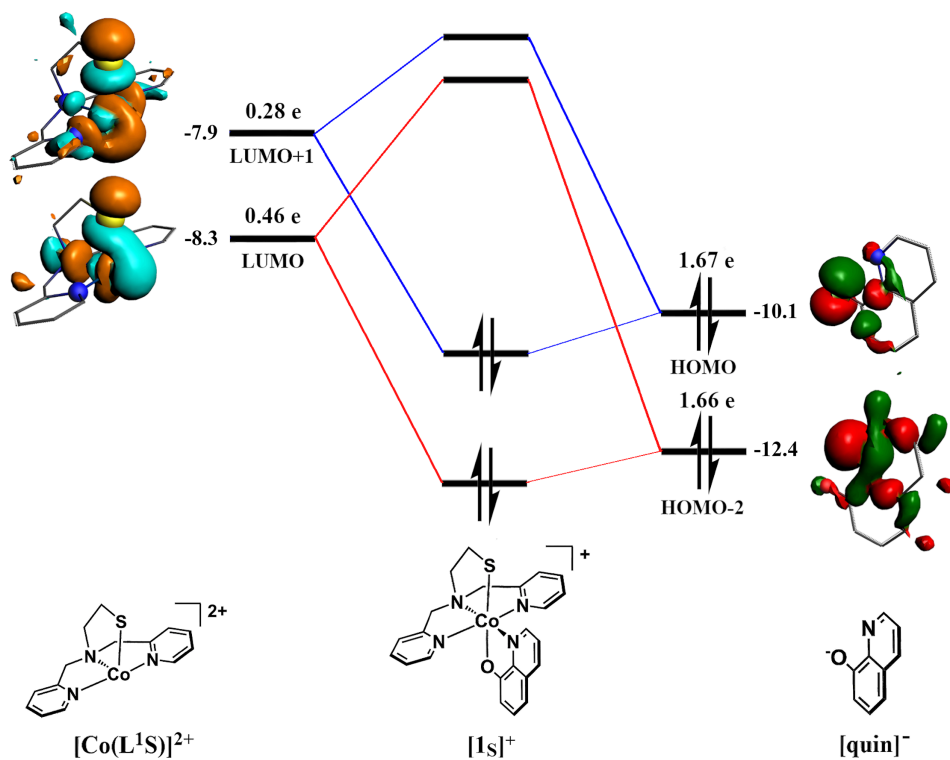


Figure AII.20. Molecular orbital diagram for the interaction between the fragments $[\text{Co}(\text{L}^1\text{S})]^{2+}$ and $[\text{quin}]^-$ in $[1\text{s}]^+$. Fragment molecular orbital energies (in eV) obtained from the Kohn-Sham Fock matrix diagonal elements (see references ¹⁻³ for details).

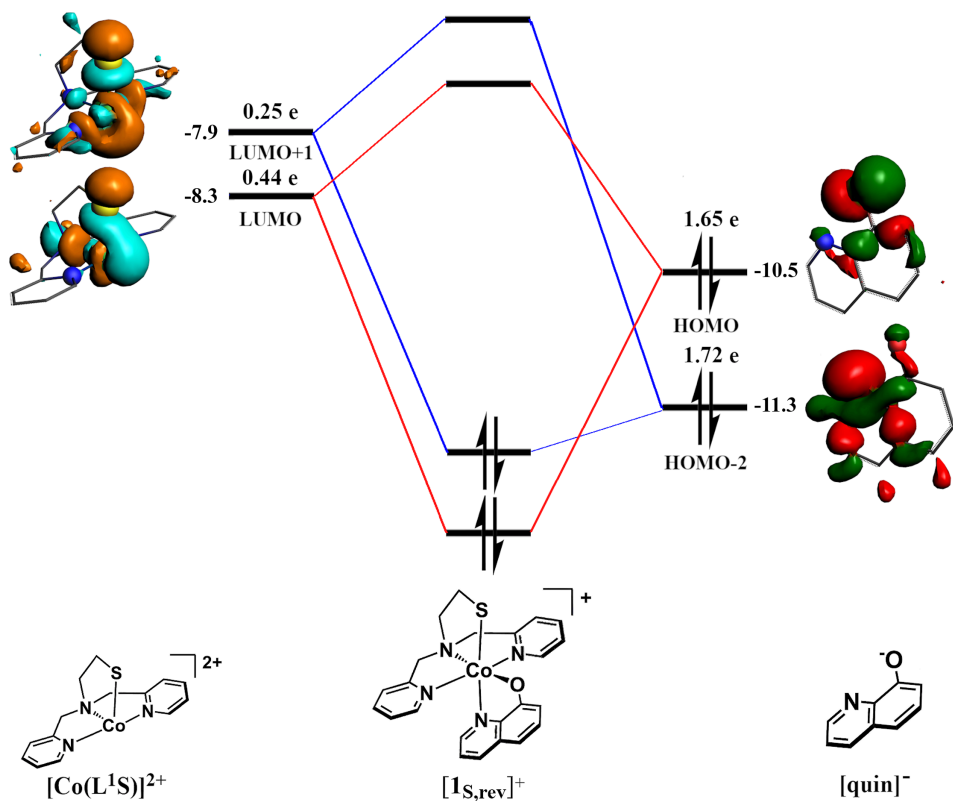


Figure AII.21. Molecular orbital diagram for the interaction between the fragments $[\text{Co}(\text{L}^1\text{S})]^{2+}$ and $[\text{quin}]^-$ in $[\text{1s,rev}]^+$. Fragment molecular orbital energies (in eV) obtained from the Kohn-Sham Fock matrix diagonal elements (see references ¹⁻³ for details).

References

1. Bickelhaupt, F. M., Solà, M. and Fonseca Guerra, C. *J. Mol. Model.* **2006**, 12 (5), 563-568.
2. Bickelhaupt, F. M., Solà, M. and Fonseca Guerra, C. *Inorg. Chem.* **2007**, 46 (13), 5411-5418.
3. Bickelhaupt, F. M., Solà, M. and Guerra, C. F. *J. Comput. Chem.* **2007**, 28 (1), 238-250.

Appendix III

Supplementary Information for Chapter 4

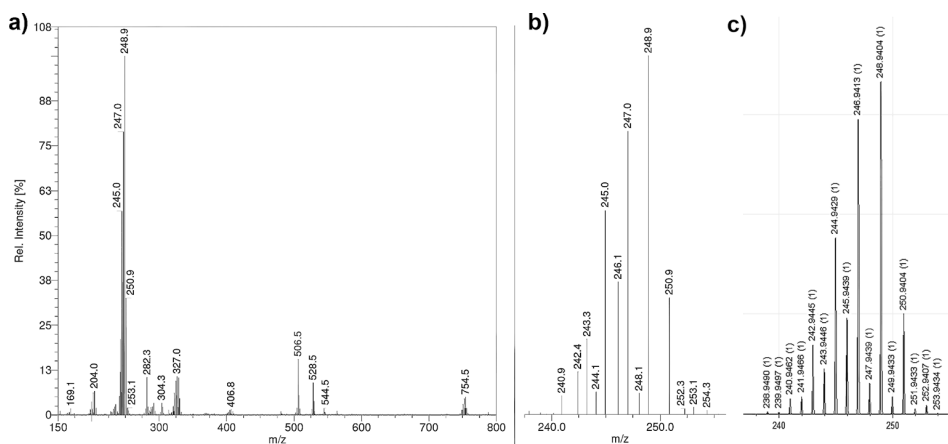


Figure AIII.1. ESI-MS spectrum of a) selenocystamine hydrochloride; b) the experimental isotopic distribution of the main signal; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[(\text{NH}_2\text{C}_2\text{H}_4\text{Se})_2 + \text{H}]^+$ m/z 248.9 (248.94).

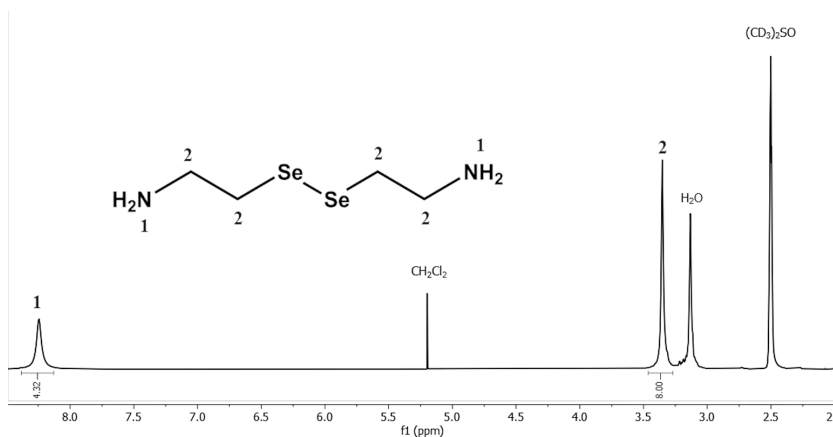


Figure AIII.2. ^1H -NMR spectrum of selenocystamine hydrochloride in $(\text{CD}_3)_2\text{SO}$.

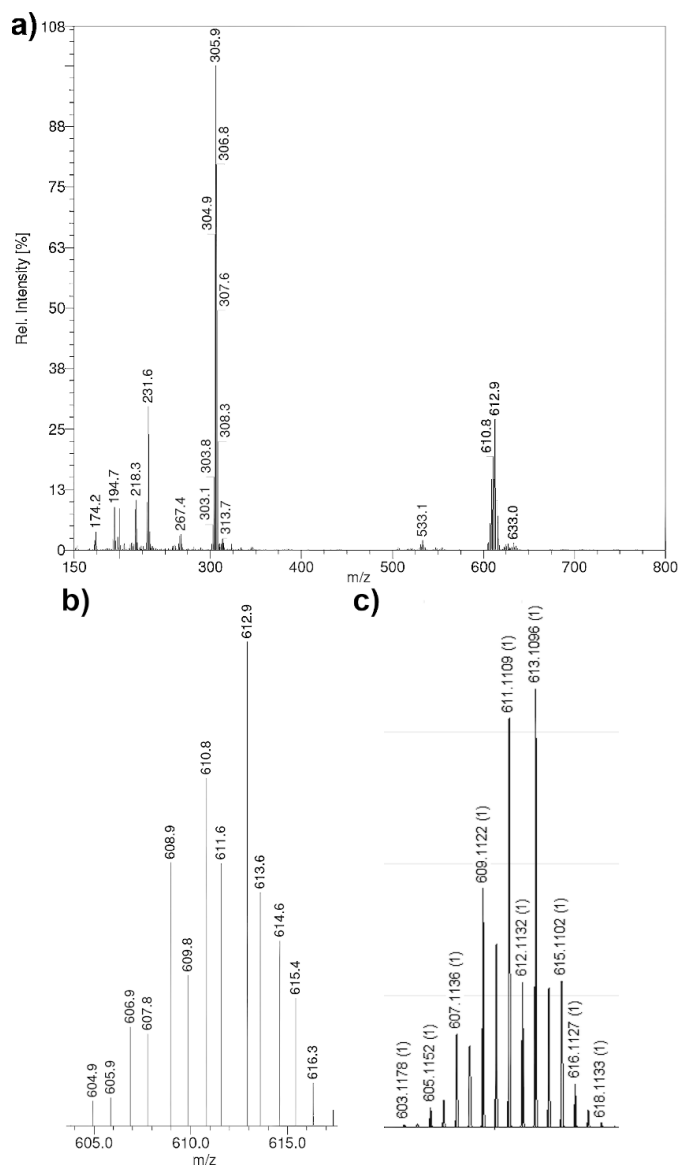


Figure AIII.3. ESI-MS spectrum of a) $L^1\text{SeSeL}^1$; b) the experimental isotopic distribution of the main signal; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[L^1\text{SeSeL}^1 + \text{H}]^+$ m/z 612.9 (613.1) and for $[L^1\text{SeSeL}^1 + 2\text{H}]^{2+}$ m/z 306.8 (307.06).

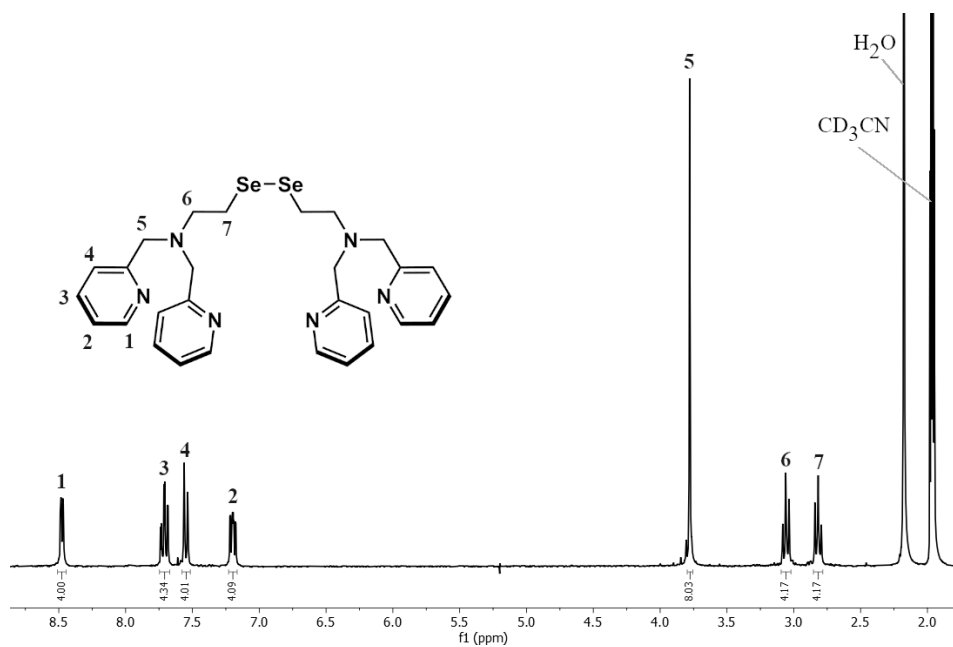


Figure AIII.4. ^1H -NMR spectrum of L^1SeSeL^1 in CD_3CN .

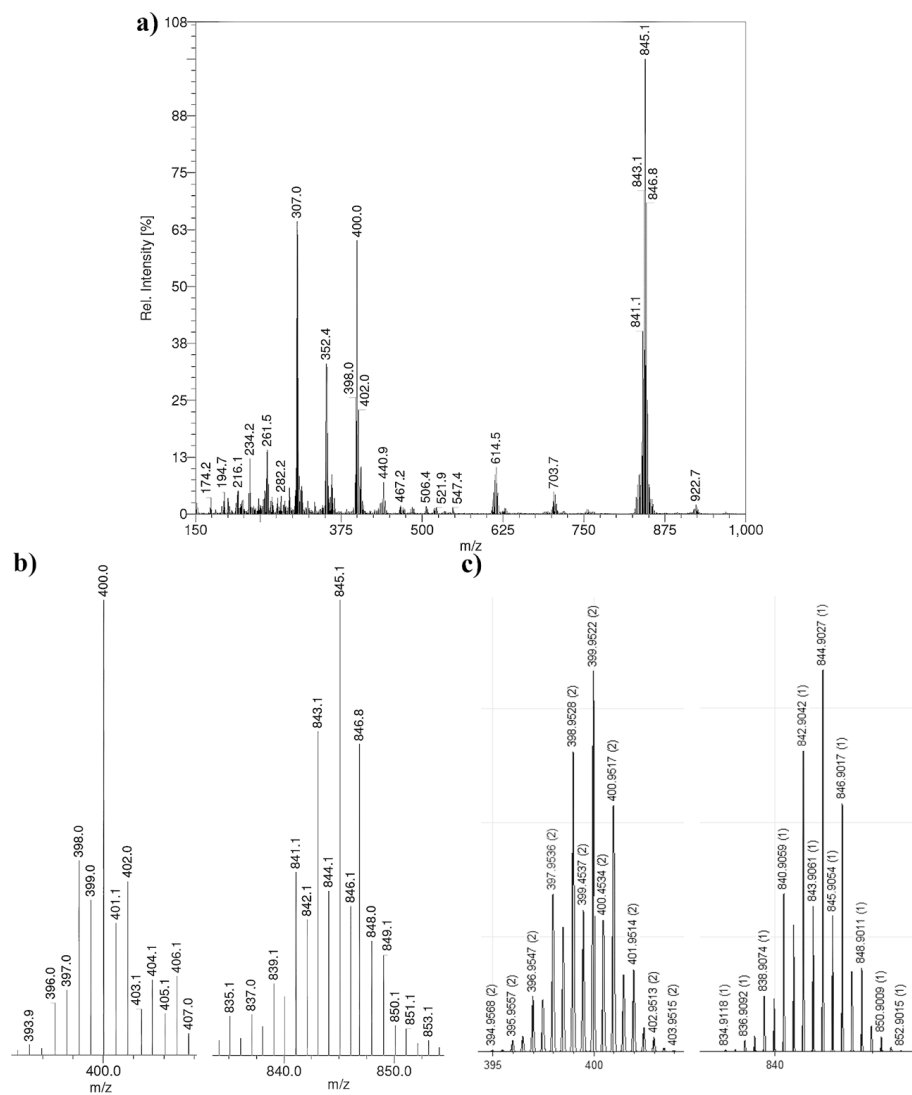


Figure AIII.5. ESI-MS spectrum of a) $[\text{Co}_2(\text{L}^1\text{SeSeL}^1)(\text{Cl})_4]$ (**1**); b) the experimental isotopic distribution of the main peaks; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[\mathbf{1} - 2\text{Cl}]^{2+}$ m/z 400.0 (399.95) and for $[\mathbf{1} - 2\text{Cl} + \text{HCOO}]^+$ m/z 845.1 (844.90).

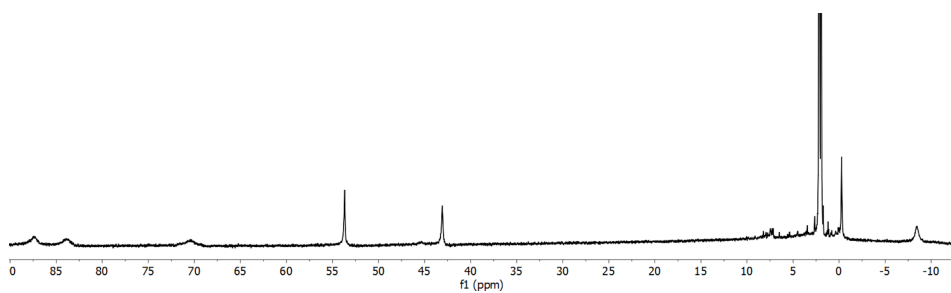


Figure AIII.6. ^1H -NMR spectrum of compound [1] in CD_3CN .

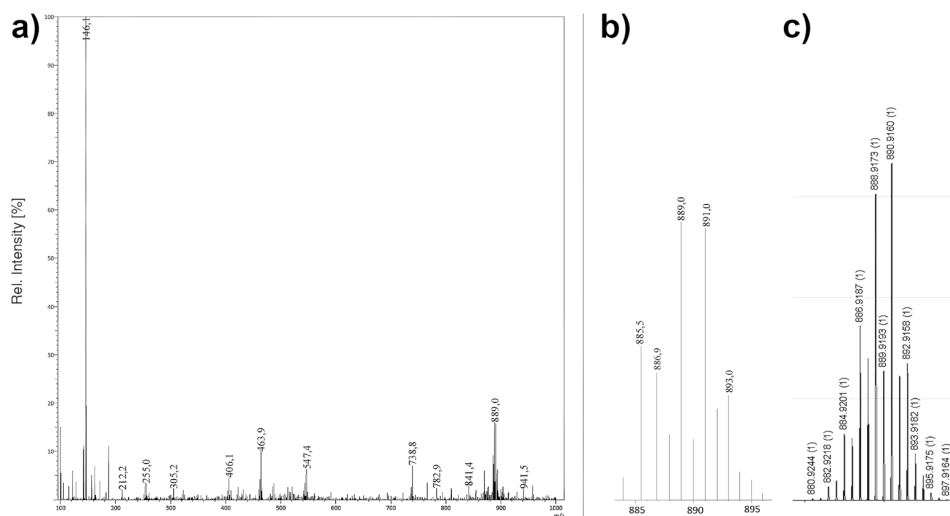


Figure AIII.7. ESI-MS spectrum of a) $[\text{Co}(\text{L}^1\text{Se})(\text{NCS})_2]$ ([2]); b) the experimental isotopic distribution of the main signal; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[2 - \text{SCN}^- + \text{MeCN}]^+ m/z$ 463.9 (463.99), for $[2 \times 2 - 2\text{SCN}^- + \text{HCOO}^-]^+ m/z$ 889.0 (888.92).

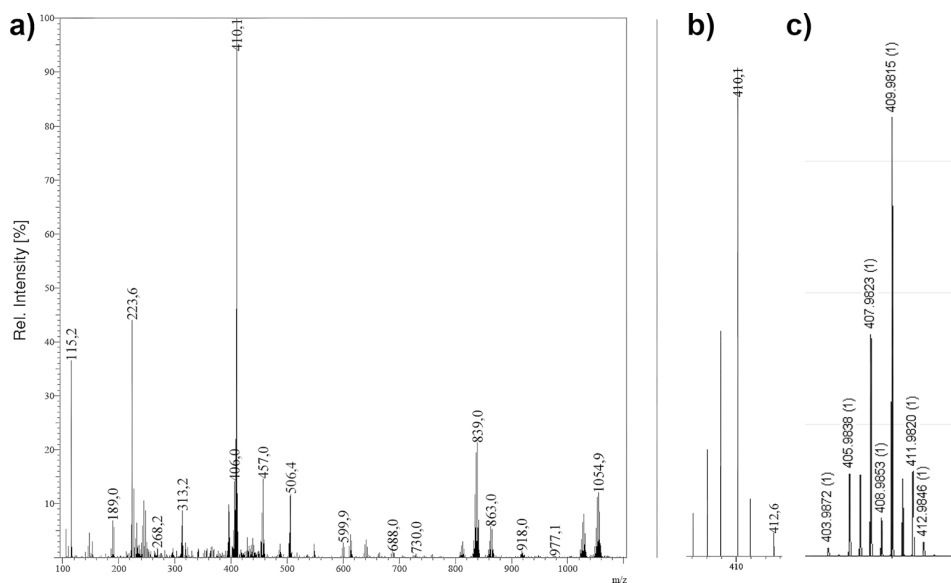


Figure AIII.8. ESI-MS spectrum of a) $[\text{Co}(\text{L}^1\text{Se})(\text{MeCN})_2](\text{SbF}_6)_2$ (**[3]**)(SbF_6)₂; b) the experimental isotopic distribution of the main signal; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[\mathbf{3}]^{2+}$ m/z 223.6 (223.52), for $[\mathbf{3} - 2\text{MeCN} + \text{HCOO}]^+ m/z$ 410.1 (409.98), for the dimer $[2 \times \mathbf{3} - 4\text{MeCN} + 3\text{HCOO}]^+ m/z$ 863.0 (862.96), and $[2 \times \mathbf{3} - 4\text{MeCN} + 2\text{HCOO}^- + \text{SbF}_6]^- m/z$ 1054.9 (1054.86).

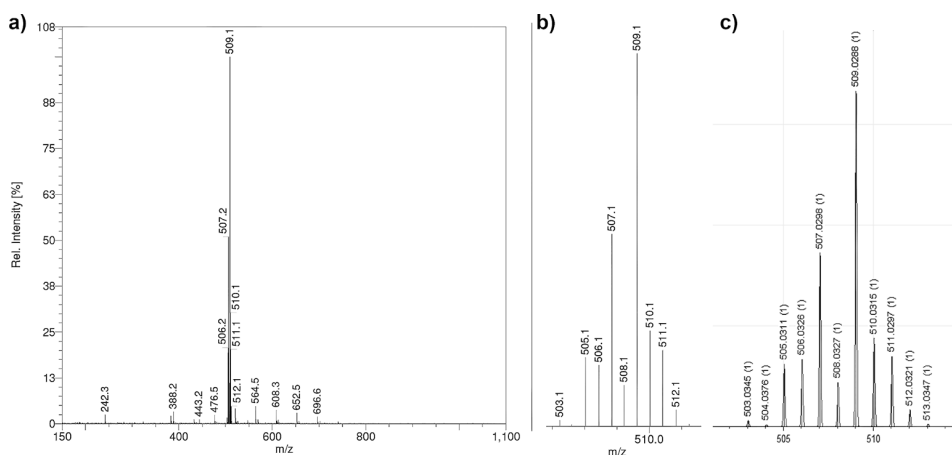


Figure AIII.9. ESI-MS spectrum of a) compound $[\text{Co}(\text{L}^1\text{Se})(\text{quin})]\text{Cl}$ (**[4]**Cl); b) the experimental isotopic distribution of the main signal; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[\mathbf{4}]^+ m/z$ 509.1 (509.03).

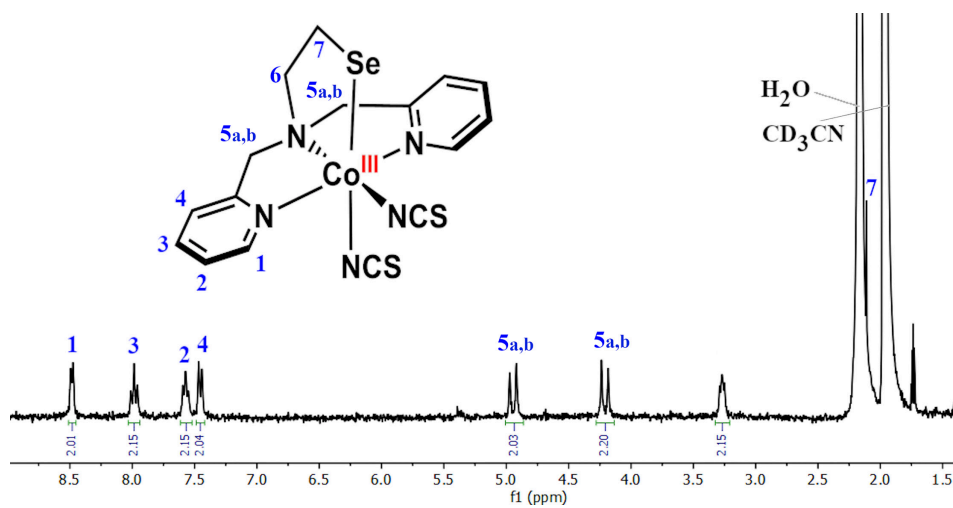


Figure AIII.10. ^1H -NMR spectrum of compound [2] dissolved in CD_3CN .

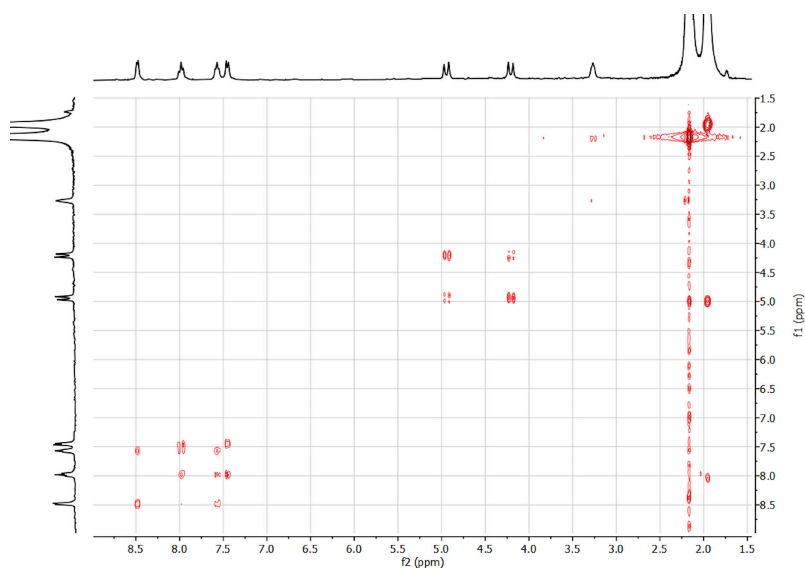


Figure AIII.11. ^1H - ^1H COSY NMR spectrum of compound [2] dissolved in CD_3CN .

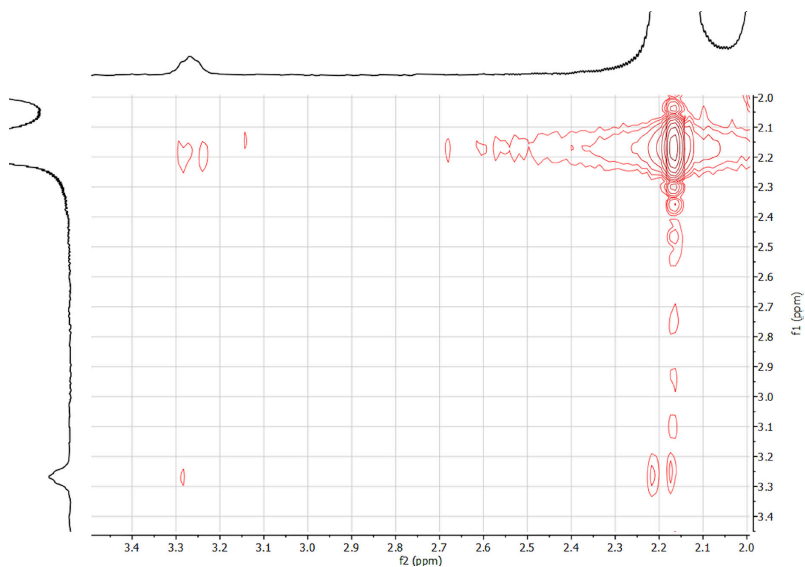


Figure AIII.12. ^1H - ^1H COSY NMR spectrum at 2.0-3.5 ppm of compound [2] dissolved in CD_3CN . The correlation of the $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{Se}$ (about 3.3 ppm) with $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{Se}$ (about 2.1-2.2 ppm) is shown.

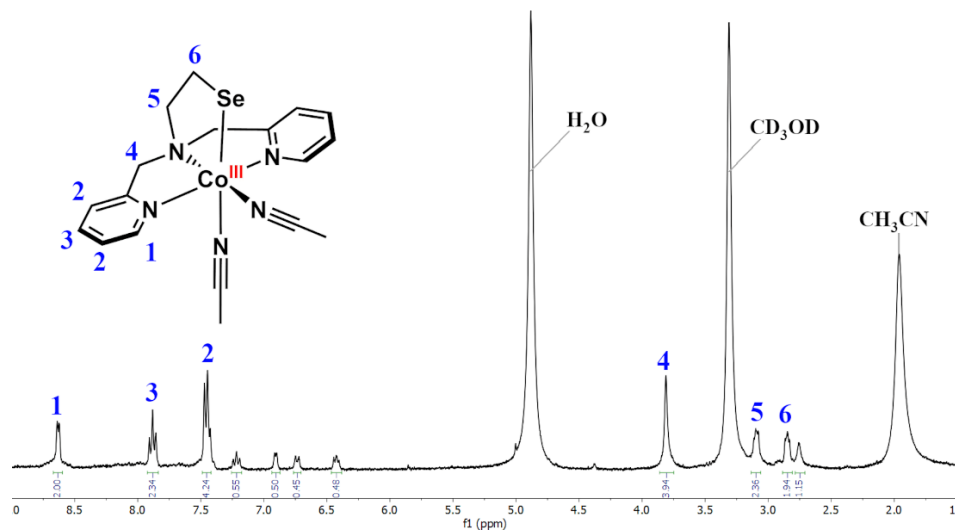


Figure AIII.13. ^1H -NMR spectrum [3](SbF_6) $_2$ dissolved in CD_3OD . The spectrum shows unassigned aromatic peaks at 6.4-7.25 ppm and an aliphatic peak at 2.75 ppm, most likely arises from the degradation of the ligand.

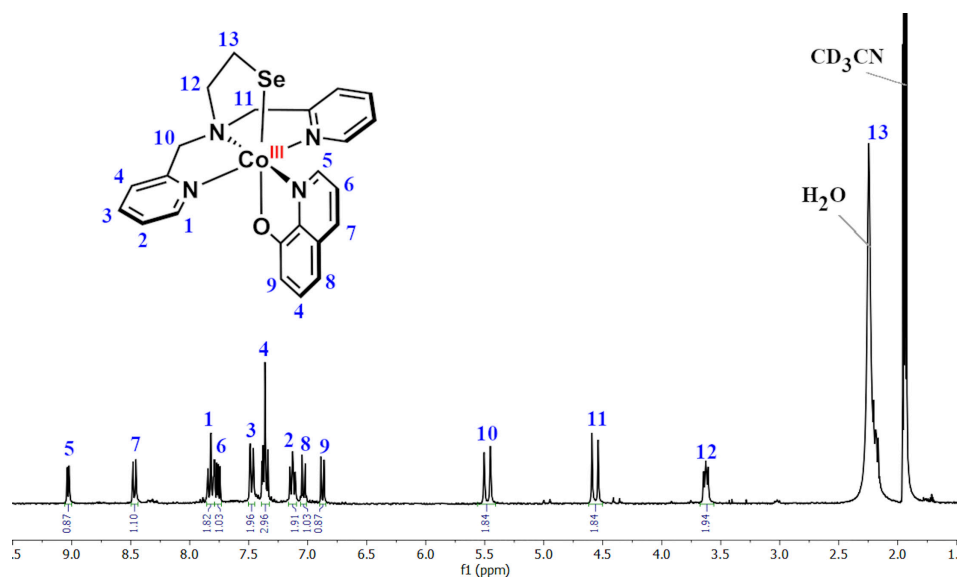


Figure AIII.14. ^1H -NMR spectrum of compound [4]Cl dissolved in CD_3CN .

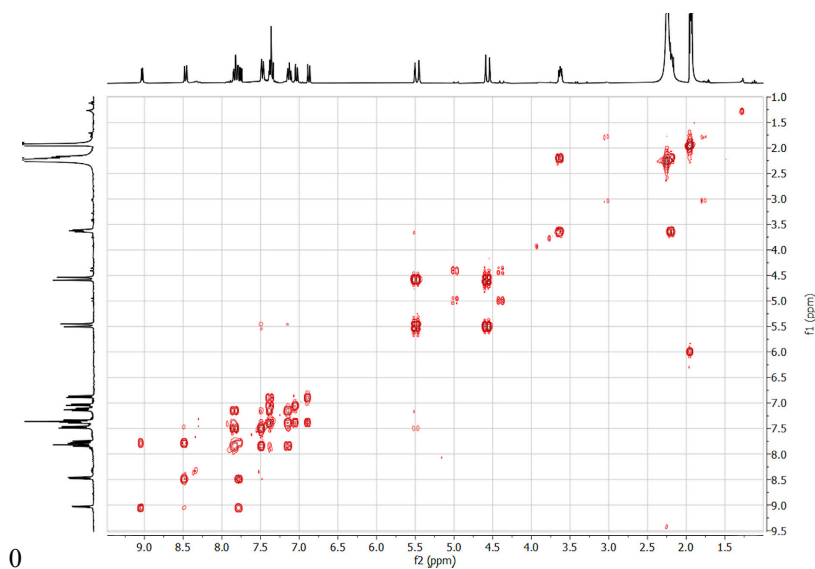


Figure AIII.15. ^1H - ^1H COSY NMR spectrum of compound [4]Cl dissolved in CD_3CN .

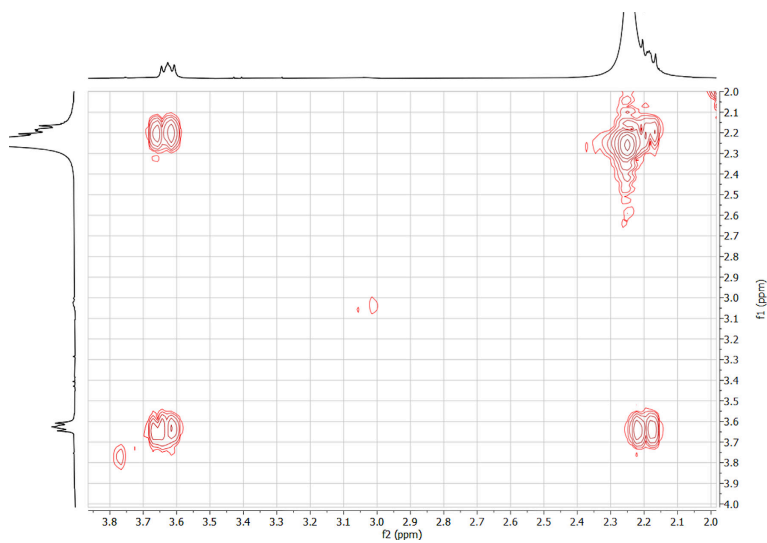


Figure AIII.16. ^1H - ^1H COSY NMR spectrum at 2.0-4.0 ppm of compound [4]Cl dissolved in CD_3CN . The correlation of the $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{Se}$ (about 3.6 ppm) with $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{Se}$ (about 2.2 ppm) is shown.

Table AIII.1. Crystallographic data for all crystals in the present work.

	[1]	[2]	[4]Cl
Chemical formula	C ₂₈ H ₃₂ Cl ₄ Co ₂ N ₆ Se ₂ · C ₄ H ₁₀ O	C ₁₆ H ₁₆ CoN ₅ S ₂ Se	C ₂₃ H ₂₂ CoN ₄ OSe· 2(CHCl ₃)·Cl
<i>M_r</i>	944.29	480.35	782.52
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> −1	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>
Cell lengths (<i>a</i> , <i>b</i> , <i>c</i>) (Å)	8.3598(3) 13.7008(6) 17.2414(14)	11.1298(4) 16.5289(5) 19.6469(7)	13.5307(3) 13.2033(3) 17.4772(4)
Cell angles (α, β, γ) (°)	91.225(5) 101.881(4) 92.102(3)	90 90 90	90 105.487(3) 90
Cell volume (Å ³)	1930.31(19)	3614.3(2)	3008.93(13)
<i>Z</i>	2	8	4
μ (mm ^{−1})	3.06	3.20	2.43
Crystal size (mm)	0.22 × 0.13 × 0.03	0.21 × 0.14 × 0.06	0.26 × 0.22 × 0.04
Temperature (K)	110	110	110
Diffractometer	SuperNova, Dual, Cu at zero, Atlas detector	SuperNova, Dual, Cu at zero, Atlas detector	SuperNova, Dual, Cu at zero, Atlas detector
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
<i>T</i> _{min} , <i>T</i> _{max}	0.470, 1.000	0.552, 1.000	0.467, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	25557, 7594, 5429	32659, 4155, 3485	39269, 6915, 5863
<i>R</i> _{int}	0.071	0.049	0.048
(sin θ/λ) _{max} (Å ^{−1})	0.617	0.650	0.650
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.048, 0.105, 1.04	0.026, 0.058, 1.06	0.030, 0.068, 1.03
No. of reflections	7594	4155	6915
No. of parameters	426	226	443
No. of restraints	−	−	289
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ^{−3})	0.88, −0.55	0.59, −0.37	0.94, −0.81

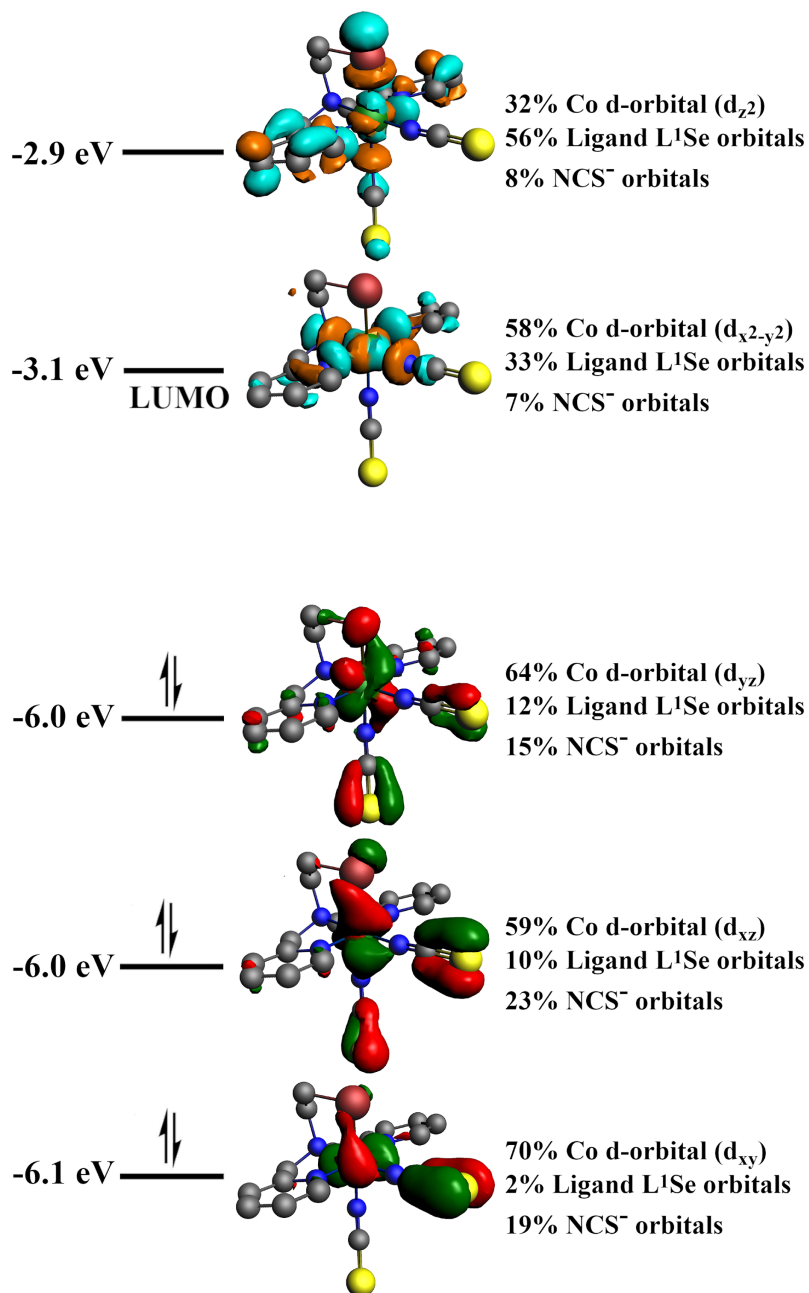


Figure AIII.17. Several frontier orbitals of [2] associated with Co *d*-orbitals along with their energies, orbital visualization, and orbital composition.

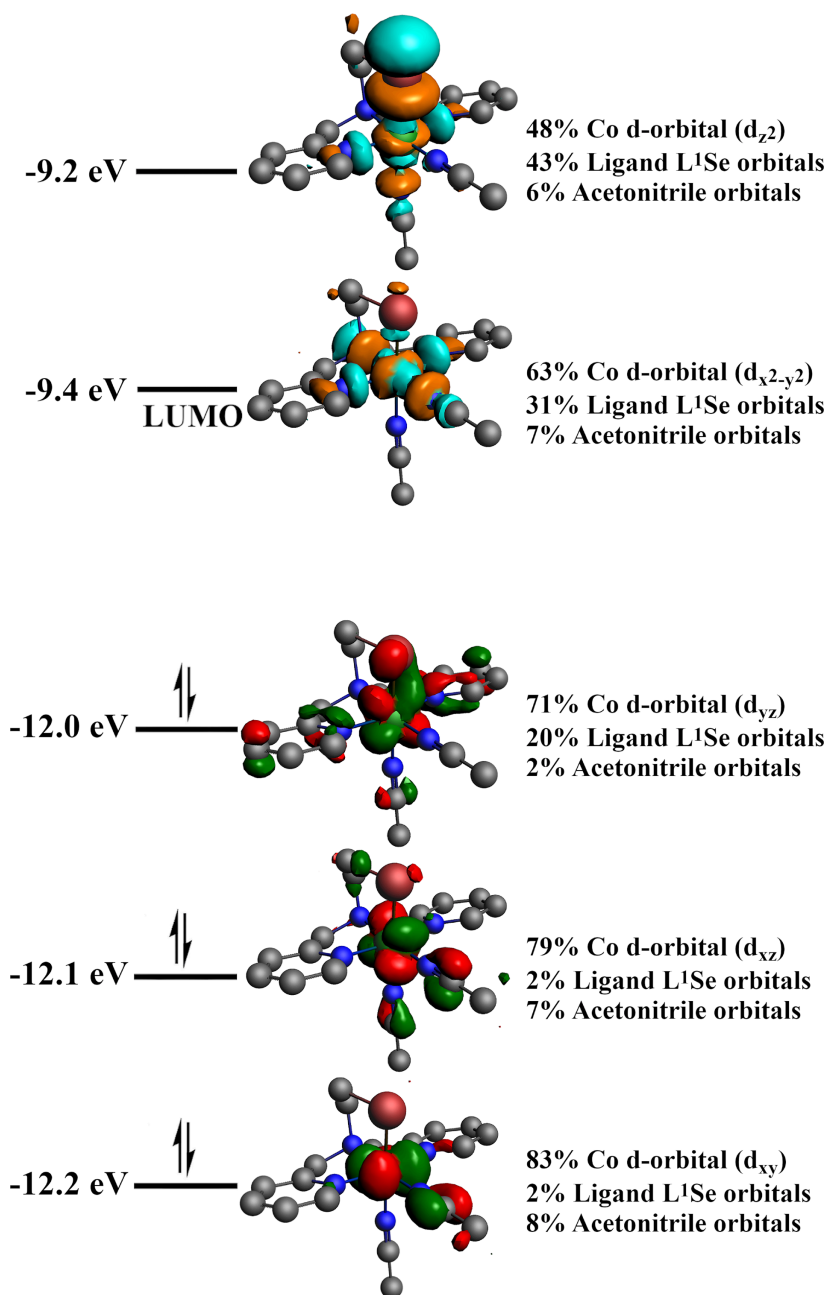


Figure AIII.18. Several frontier orbitals of $[3]^{2+}$ associated with Co d -orbitals along with their energies, orbital visualization, and orbital composition.

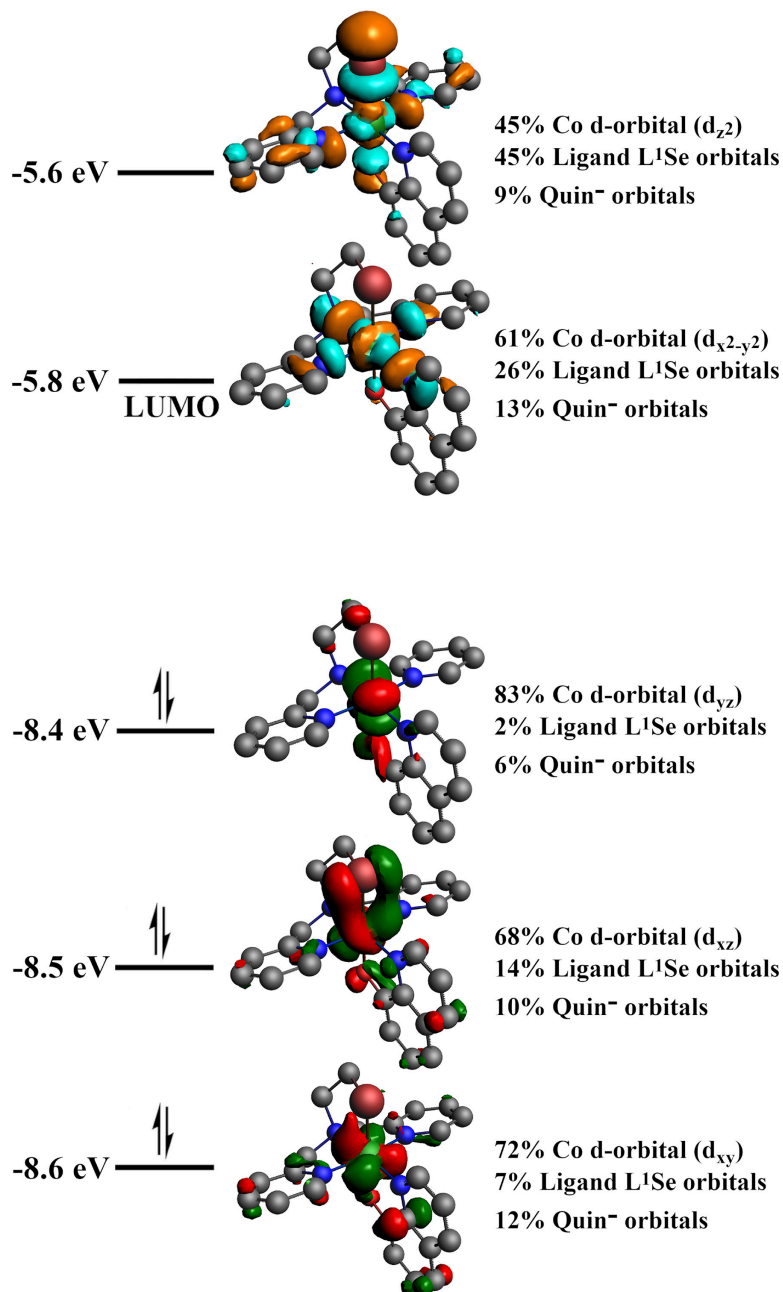


Figure AIII.19. Several frontier orbitals of $[4]^+$ associated with Co d -orbitals along with their energies, orbital visualization, and orbital composition.

Appendix IV

Supplementary Information for Chapter 5

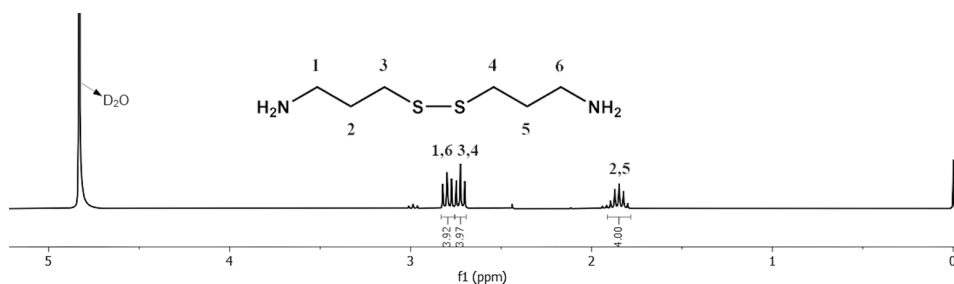


Figure AIV.1. ^1H -NMR spectrum of bis(3-aminopropyldisulfide) in D_2O .

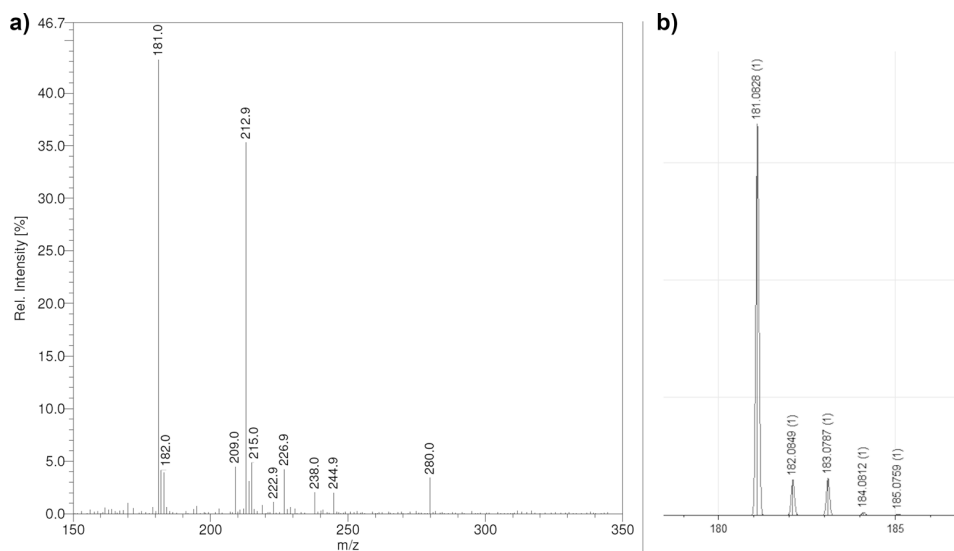


Figure AIV.2. ESI-MS spectrum of a) bis(3-aminopropyldisulfide) dissolved in H_2O ; b) simulated spectrum at m/z 180–185. ESI-MS found (calcd.) for $[\text{bis(3-aminopropyldisulfide)} + \text{H}]^+$ m/z 181.0 (181.08).

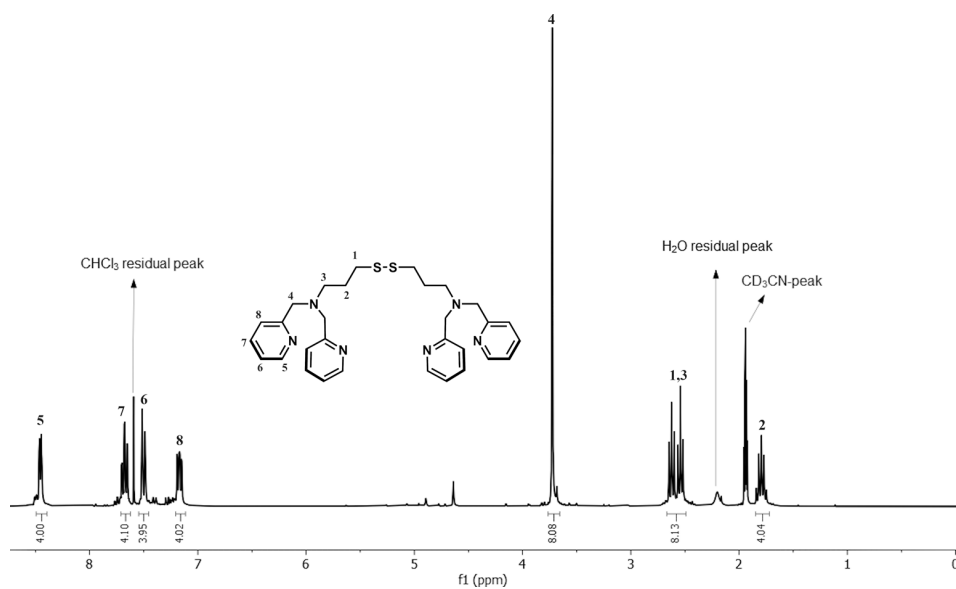


Figure AIV.3. ^1H -NMR spectrum of $\text{L}^{\text{p}}\text{SSL}^{\text{p}}$ in CD_3CN .

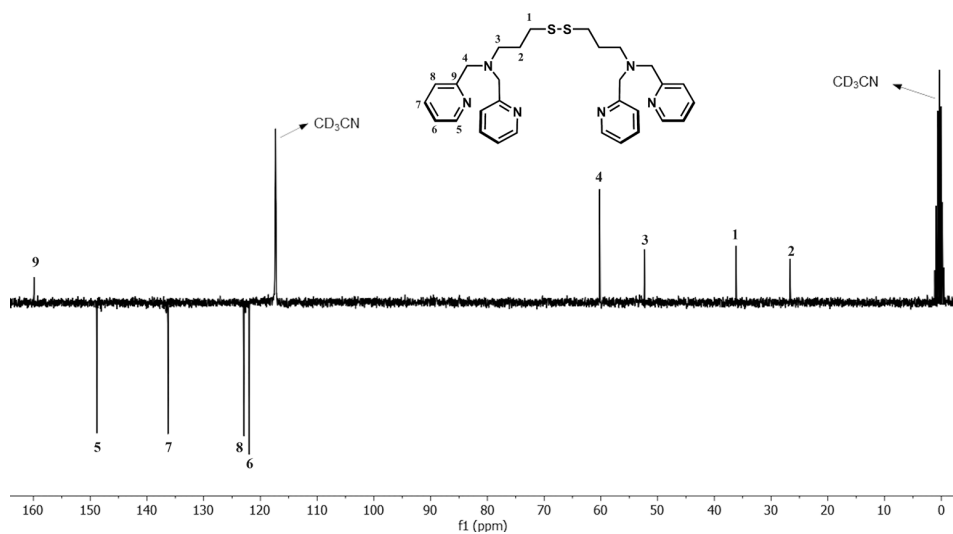


Figure AIV.4. ^{13}C -NMR spectrum of $\text{L}^{\text{p}}\text{SSL}^{\text{p}}$ in CD_3CN .

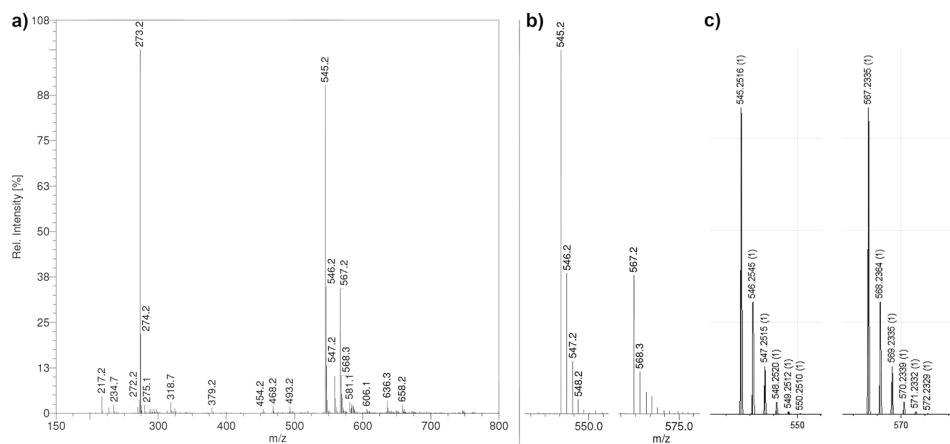


Figure AIV.5. ESI-MS spectrum of a) L^pSSLP dissolved in methanol; b) the experimental isotopic distribution; c) simulated isotopic distribution at m/z 540–575. ESI-MS found (calcd.) for [L^pSSLP + Na]⁺ m/z 567.2 (567.2), for [L^pSSLP + H]⁺ m/z 545.2 (545.2), for [L^pSSLP + 2H]²⁺ m/z 273.2 (273.1).

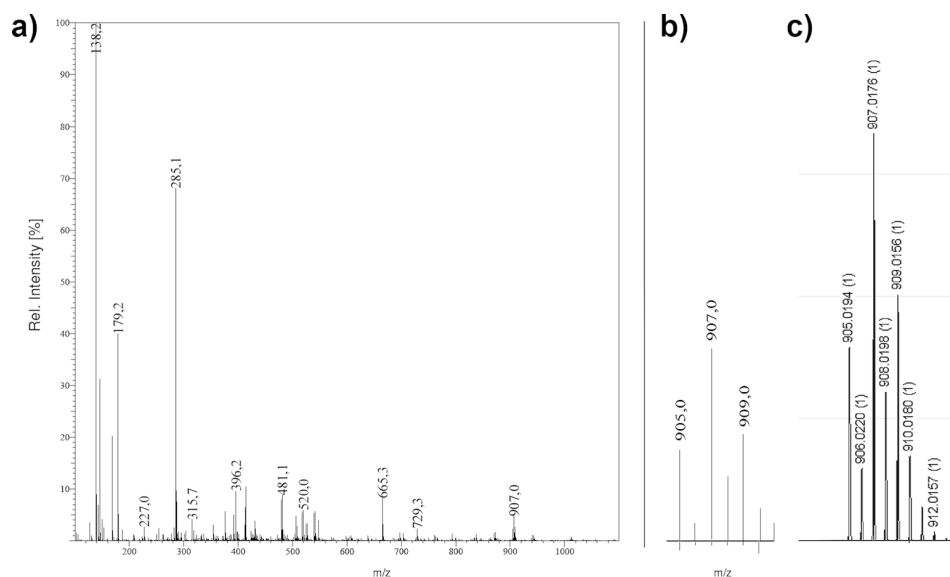


Figure AIV.6. ESI-MS spectrum of a) [1Br⁻] dissolved in acetonitrile; b) the experimental isotopic distribution; c) simulated isotopic distribution. ESI-MS found (calcd.) for [1Br⁻ - 2Br⁻ + HCOO⁻]⁺ m/z 907.0 (907.02) and for [1Br⁻ - 3Br⁻ + HCOO⁻]²⁺ m/z 414.1 (413.5).

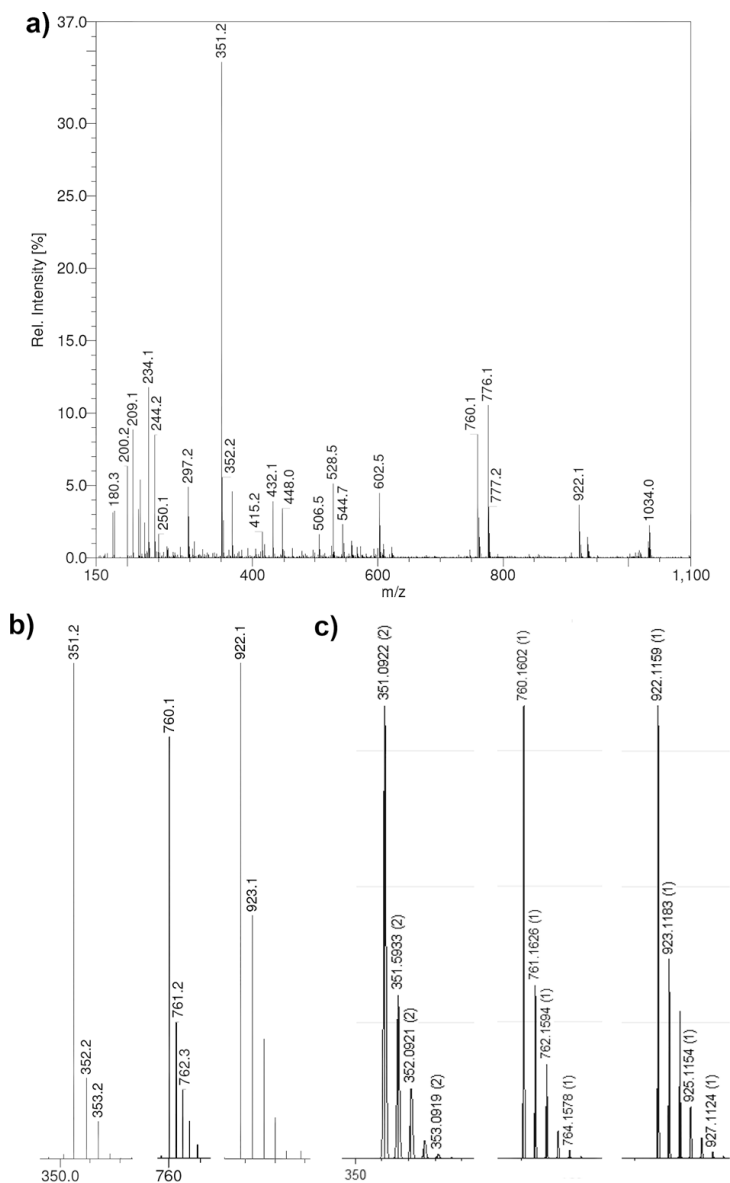


Figure AIV.7. ESI-MS spectrum of a) [1NCS] dissolved in methanol; b) the experimental isotopic distributions; c) simulated isotopic distributions at different m/z . ESI-MS found (calcd.) for $[1NCS - NCS^- + HCOO^- + H^+]^+$ m/z 922.1 (922.1), for $[1NCS - 3NCS^-]^+$ (partial reduction from the ESI-MS) m/z 760.1 (760.16), and for $[1NCS - 4NCS^-]^{2+}$ (partial reduction from the ESI-MS) m/z 351.09 (351.1).

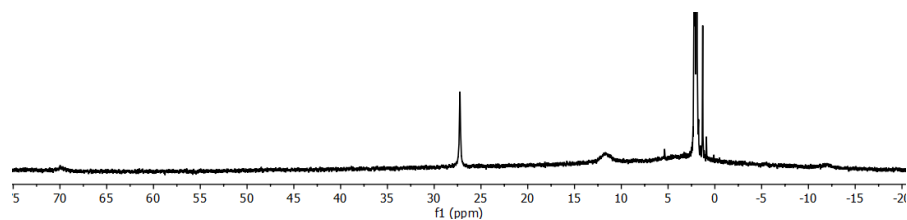


Figure AIV.8. ^1H -NMR spectrum of $[\mathbf{1}_{\text{NCS}}]$ dissolved in CD_3CN .

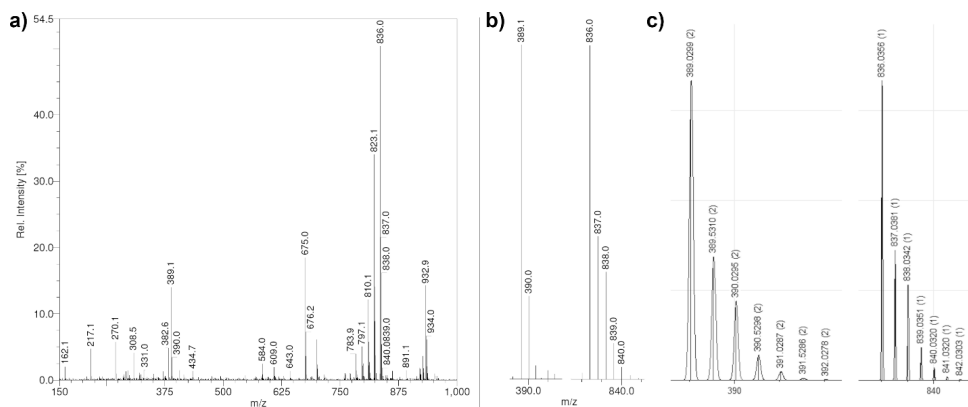


Figure AIV.9. ESI-MS spectrum of a) $[\mathbf{2}_{\text{NCS}}]$ dissolved in acetonitrile; b) the experimental isotopic distribution of the main signals; c) simulated isotopic distribution of the main signals. ESI-MS found (calcd.) for $[\mathbf{2}_{\text{NCS}} - \text{NCS}]^+ m/z$ 836.0 (836.0), for $[\mathbf{2}_{\text{NCS}} - 2\text{NCS}]^{2+} m/z$ 389.1 (389.0).

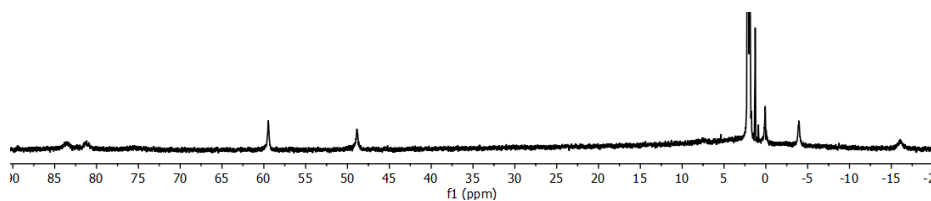


Figure AIV.10. ^1H -NMR spectrum of $[\mathbf{2}_{\text{NCS}}]$ dissolved in CD_3CN .

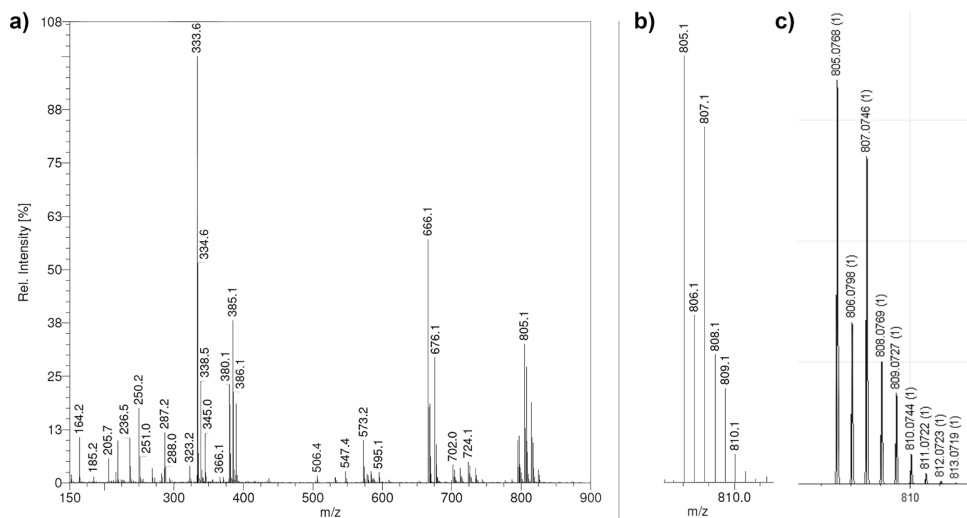


Figure AIV.11. ESI-MS spectrum of compound a) [3Cl] dissolved in methanol; b) the experimental isotopic distribution; c) simulated isotopic distribution at m/z 800–815. ESI-MS found (calcd.) for $[3\text{Cl} - 2\text{Cl}^- + \text{HCOO}]^+$ m/z 805.1 (805.08), for $[3\text{Cl} - 3\text{Cl}^- + \text{HCOO}]^{2+}$ m/z 385.1 (385.1), and for $[3\text{Cl} - 2\text{Cl}^-]^{2+}$ m/z 380.1 (380.04).

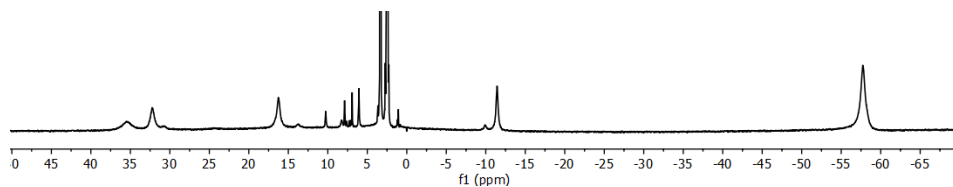


Figure AIV.12. ^1H -NMR spectrum of compound [3Cl] dissolved in $(\text{CD}_3)_2\text{SO}$.

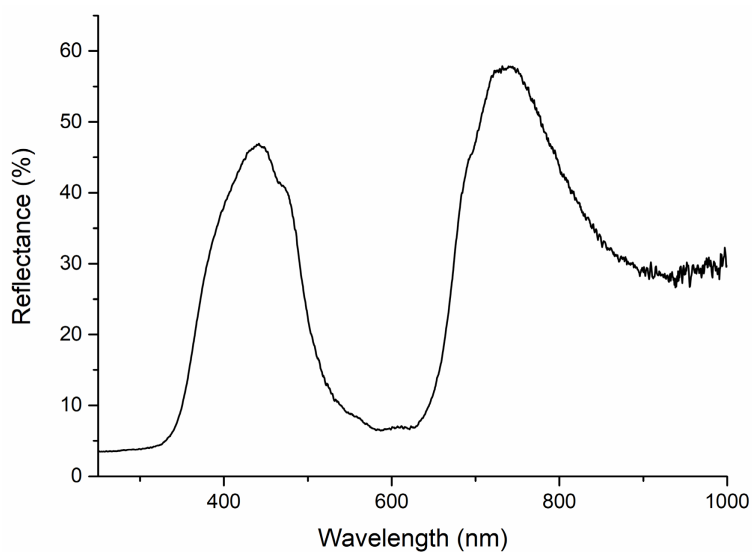


Figure AIV.13. Solid state reflectance spectrum of compound [1Br].

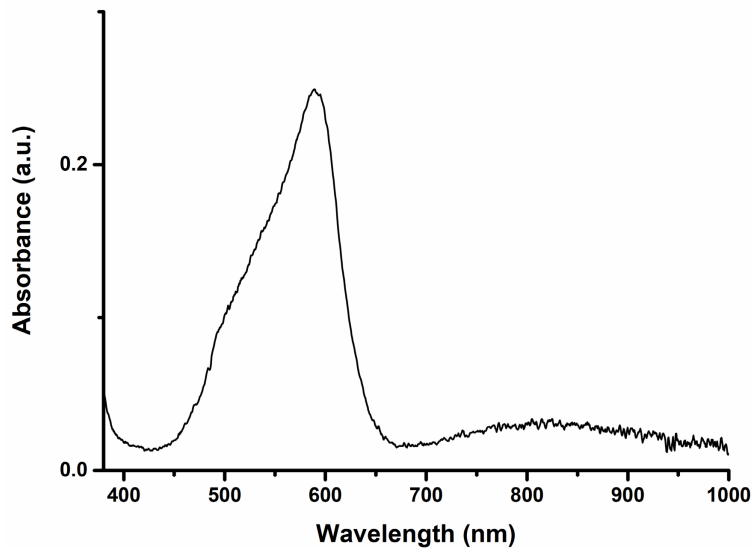


Figure AIV.14. UV-Visible spectrum of 2.5 mM solution of [1NCS] in acetone, recorded using a transmission dip probe with path length of 1.4 mm.

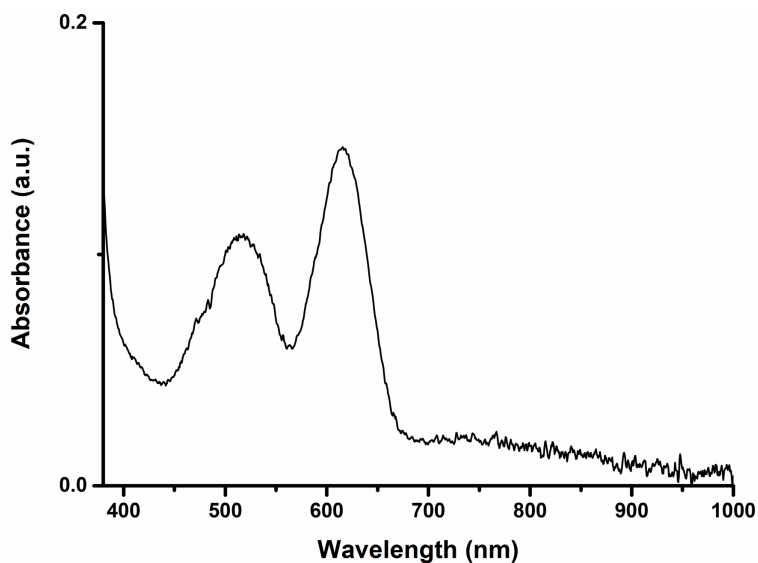


Figure AIV.15. UV-Visible spectrum of 2.5 mM solution of [2NCS] in acetone, recorded using a transmission dip probe with path length of 1.4 mm.

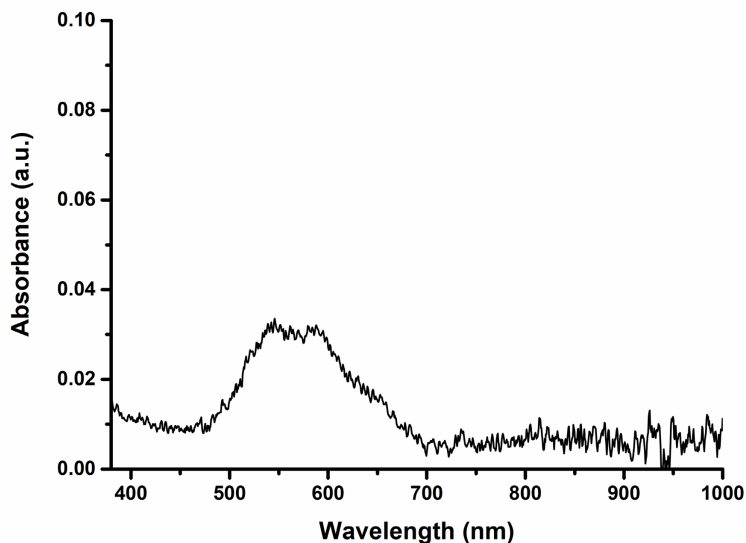


Figure AIV.16. UV-Visible spectrum of 2.5 mM solution of [3Cl] in acetonitrile, recorded using a transmission dip probe with path length of 1.4 mm.

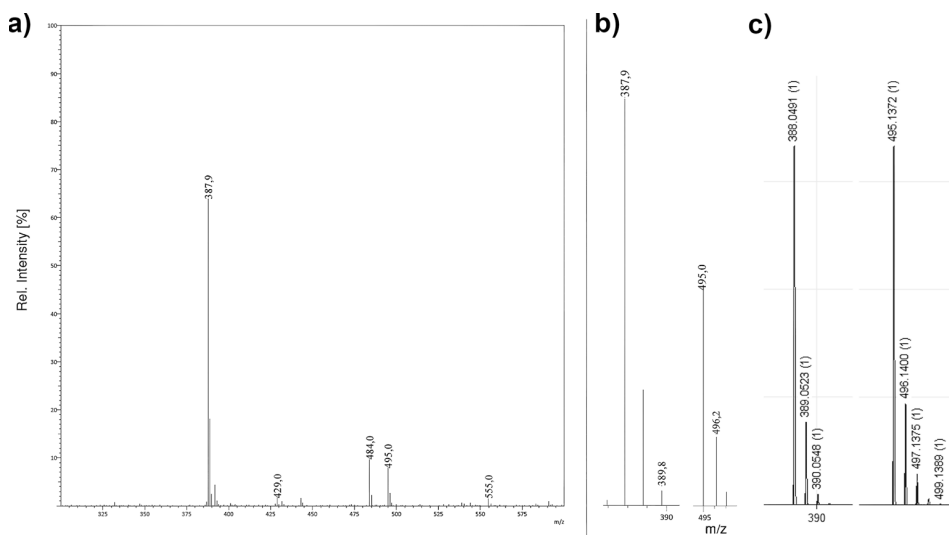


Figure AIV.17. ESI-MS spectrum of a) the reaction of Hquin, K_2CO_3 , and *in situ* formed $[Co_2(L^{mpz}SSL^{mpz})(Br)_4]$ dissolved in acetonitrile; b) the experimental isotopic distribution; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[Co(L^{mpz}S)(quin)]^+$ m/z 495.0 (495.1), for $[Co(quin)_2(MeCN)]^+$ m/z 387.9 (388.0).

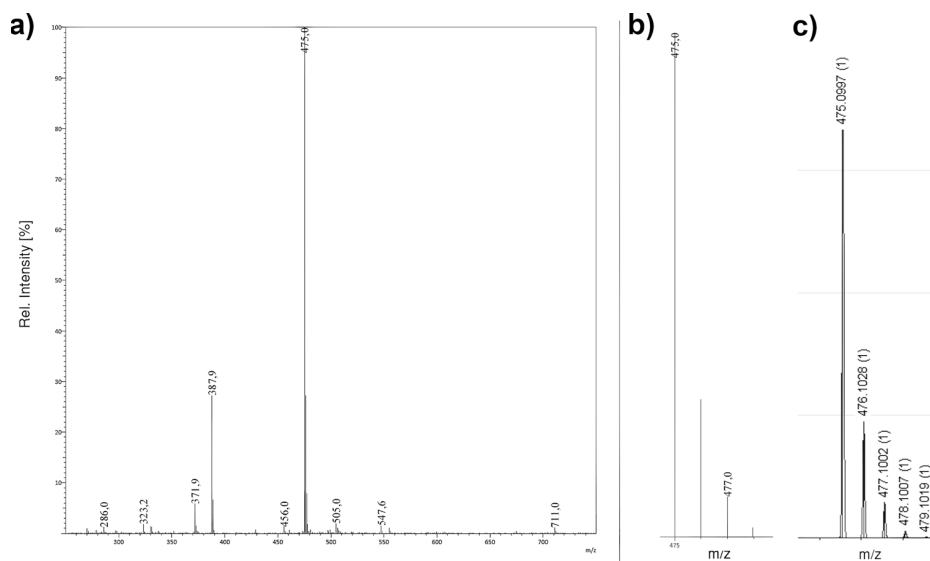


Figure AIV.18. ESI-MS spectrum of a) the reaction of Hquin, K_2CO_3 , and *in situ* formed $[Co_2(L^pSSL^p)(Cl)_4]$ dissolved in acetonitrile; b) the experimental isotopic distribution; c) simulated isotopic distribution. ESI-MS found (calcd.) for $[Co(L^pS)(quin)]^+$ m/z 475.0 (475.1), for $[Co(quin)_2(MeCN)]^+$ m/z 387.9 (388.0).

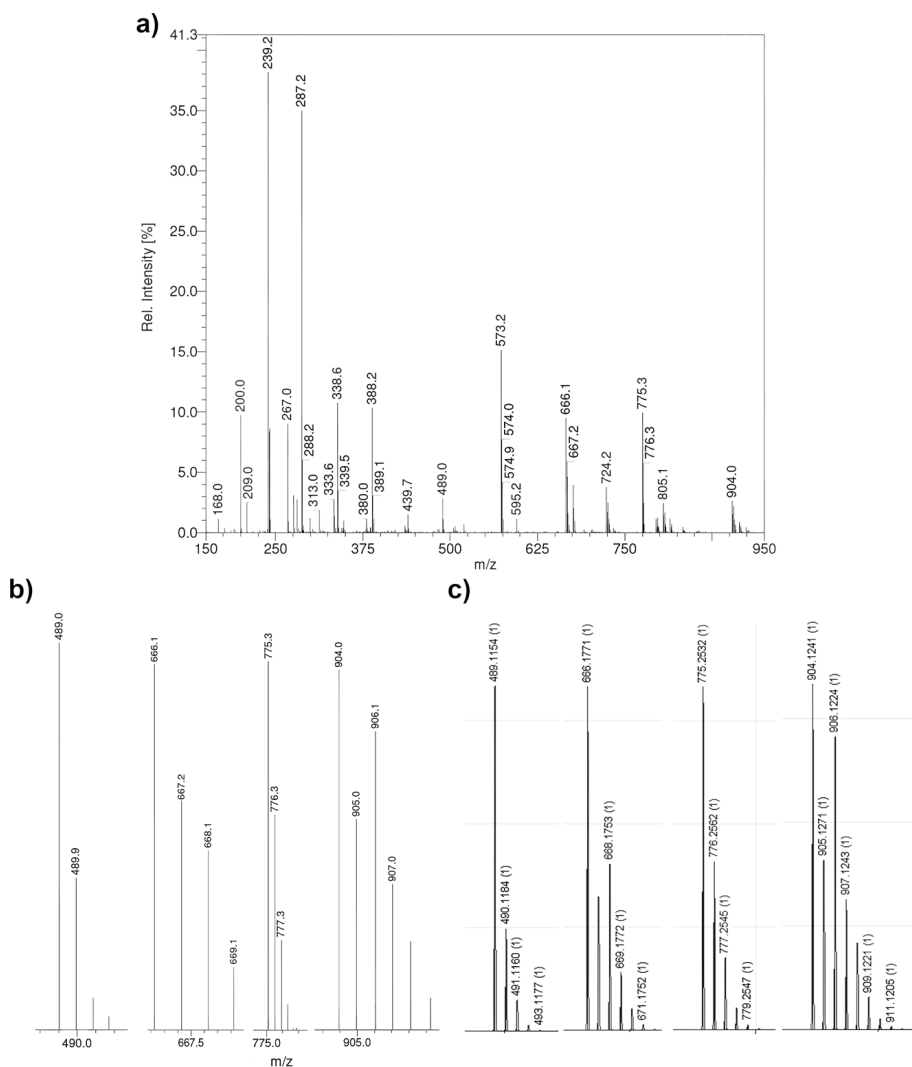


Figure AIV.19. ESI-MS spectrum of a) the reaction of Hquin, K_2CO_3 , and *in situ* formed $[Co_2(L^3SSL^3)(Cl)_4]$ dissolved in methanol; b) the experimental isotopic distribution; c) simulated isotopic distribution spectra. ESI-MS found (calcd.) for $[Co(L^3S)(quin)]^+$ m/z 489.0 (489.1), for $[Co(quin)_2(MeCN)]^+$ m/z 387.9 (388.0), for $[L^3SSL^3 + H]^+$ m/z 573.2 (573.3), for $[L^3SSL^3 + 2H]^2+$ m/z 287.2 (287.2), for $[L^3SSL^3 + Co + Cl]^+$ m/z 666.1 (666.2), for $[L^3SSL^3 + Co + quin]^+$ m/z 775.3 (775.3), and for $[Co_2(L^3SSL^3)(Cl)_2(quin)]^+$ m/z 904.0 (904.1).

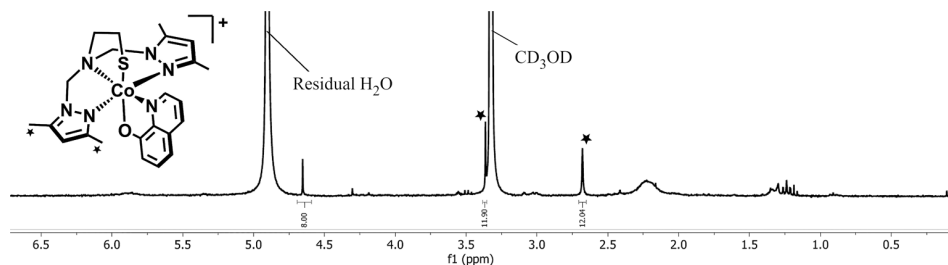


Figure AIV.20. ^1H -NMR spectrum of the brown powder of presumably $[\text{Co}(\text{L}^{\text{mpzS}})(\text{quin})]\text{Br}$ dissolved in MeOD_4 . The aromatic region contains no signal.

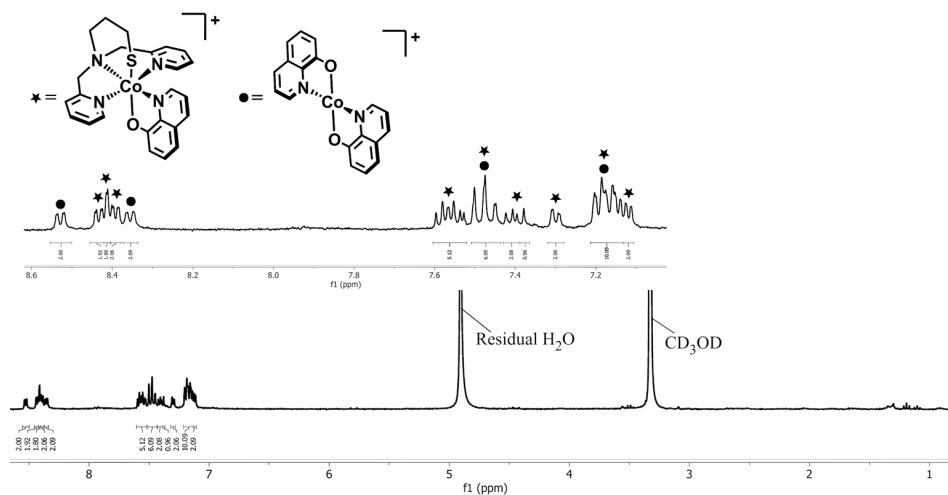


Figure AIV.21. ^1H -NMR spectrum of the brown powder of presumably $[\text{Co}(\text{L}^{\text{pS}})(\text{quin})]\text{Cl}$ dissolved in MeOD_4 . Inset shows the peaks in the aromatic region (between 7.0 – 8.6 ppm). The peaks assigned are for the species $[\text{Co}(\text{L}^{\text{pS}})(\text{quin})]^+$ and $[\text{Co}(\text{quin})_2]^+$. However, the aliphatic peaks of the ligand L^{pS} are missing.

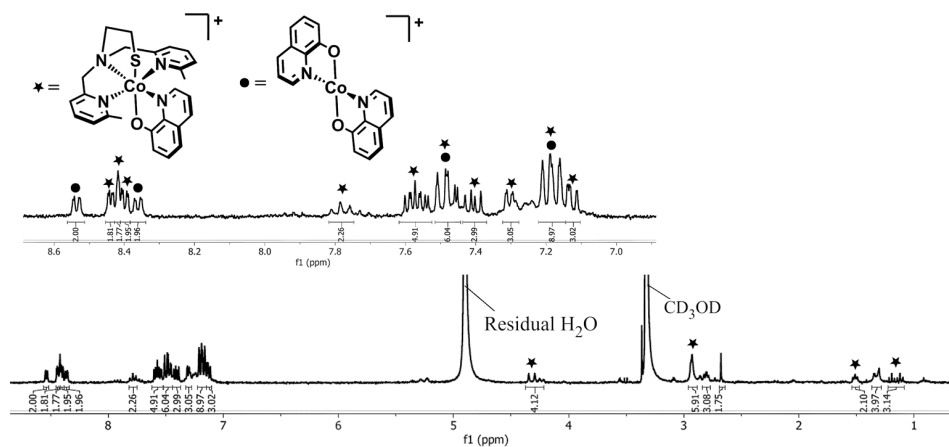


Figure AIV.22. ^1H -NMR spectrum of the brown powder of presumably $[\text{Co}(\text{L}^3\text{S})(\text{quin})]\text{Cl}$ dissolved in MeOD_4 . Inset shows the peaks in the aromatic region (between 7.0 – 8.6 ppm). The peaks assigned are for the species $[\text{Co}(\text{L}^3\text{S})(\text{quin})]^+$ and $[\text{Co}(\text{quin})_2]^+$.

Table AIV.1. Crystallographic data for compound [**1_{NCS}**] and [**1_{Br}**].

	[1_{NCS}]	[1_{Br}]
Chemical formula	C ₃₂ H ₄₄ Co ₂ N ₁₄ S ₆ ·2(C ₂ H ₃ N)	C ₂₈ H ₄₄ Br ₄ Co ₂ N ₁₀ S ₂
<i>M_r</i>	1017.14	1022.35
Crystal system	Monoclinic	Triclinic
Space group	<i>C2/c</i>	<i>P</i> -1
Cell lengths (<i>a</i> , <i>b</i> , <i>c</i>) (Å)	27.4033 (3), 10.05127 (11), 19.6772 (3)	8.6620 (3), 14.5167 (4), 15.3806 (4)
Cell angles (α, β, γ) (°)	90, 101.5415 (11), 90	82.892 (2), 82.030 (2), 89.653 (2)
Cell volume (Å ³)	5310.26 (12)	1900.49 (10)
<i>Z</i>	4	2
μ (mm ⁻¹)	7.43	5.22
Crystal size (mm)	0.38 × 0.28 × 0.22	0.14 × 0.07 × 0.04
Temperature (K)	110	110
Diffractometer	SuperNova, Dual, Cu at zero, Atlas detector	SuperNova, Dual, Cu at zero, Atlas detector
Radiation type	Cu <i>K</i> α	Mo <i>K</i> α
<i>T_{min}</i> , <i>T_{max}</i>	0.180, 0.396	0.632, 0.976
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	21714, 5193, 4734	32103, 7468, 6234
<i>R_{int}</i>	0.033	0.039
(sin θ/λ) _{max} (Å ⁻¹)	0.616	0.617
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.090, 1.04	0.038, 0.094, 1.03
No. of reflections	5193	7468
No. of parameters	276	423
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.45, -0.40	2.45, -1.37

Table AIV.2. Crystallographic data for compound [2_{NCS}] and [3_{Cl}].

	[2]	[3]
Chemical formula	C ₃₄ H ₃₆ Co ₂ N ₁₀ S ₆	C ₃₂ H ₄₀ Cl ₄ Co ₂ N ₆ S ₂ ·2(C ₂ H ₃ N)
<i>M</i> _r	894.95	914.59
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>I</i> 2/ <i>a</i>
Cell lengths (<i>a</i> , <i>b</i> , <i>c</i>) (Å)	13.3213 (3), 11.5322 (3), 26.3107 (7)	15.3973 (3), 8.62095 (19), 31.1728 (6)
Cell angles (α, β, γ) (°)	90, 98.684 (2), 90	90, 97.3686 (19), 90
Cell volume (Å ³)	3995.62 (18)	4103.69 (15)
<i>Z</i>	4	4
μ (mm ⁻¹)	1.18	1.21
Crystal size (mm)	0.20 × 0.16 × 0.07	0.32 × 0.09 × 0.06
Temperature (K)	110	110
Diffractometer	SuperNova, Dual, Cu at zero, Atlas detector	SuperNova, Dual, Cu at zero, Atlas detector
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
<i>T</i> _{min} , <i>T</i> _{max}	0.645, 1.000	0.613, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	47666, 9172, 7483	36703, 4706, 4209
<i>R</i> _{int}	0.037	0.031
(sin θ/λ) _{max} (Å ⁻¹)	0.650	0.650
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.037, 0.094, 1.06	0.029, 0.075, 1.06
No. of reflections	9172	4706
No. of parameters	469	313
No. of restraints	-	171
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.74, -0.56	0.75, -0.30

Table AIV.3. Complete bond distances and bond angles in [1Br].

Atoms	Distance (Å)	Atoms	Bond angles (°)	Atoms	Bond angles (°)
Co1–S1	2.6084(12)	S1–Co1–N1	81.46(9)	N2–Co2–N32	74.37(13)
Co1–N1	2.264(3)	S1–Co1–N12	91.93(10)	N2–Co2–N42	74.51(13)
Co1–N12	2.129(3)	S1–Co1–N22	76.37(9)	N2–Co2–Br3	88.32(9)
Co1–N22	2.165(3)	S1–Co1–Br1	170.98(3)	N2–Co2–Br4	173.84(9)
Co1–Br1	2.4860(7)	S1–Co1–Br2	88.11(3)	Br4–Co2–N32	101.20(10)
Co1–Br2	2.5299(7)	Br1–Co1–N1	93.23(9)	Br4–Co2–N42	103.85(10)
Co2–N2	2.378(4)	Br1–Co1–N12	93.77(10)	Br4–Co2–Br3	97.83(3)
Co2–N32	2.072(4)	Br1–Co1–N22	95.31(9)	N32–Co2–N42	113.02(15)
Co2–N42	2.060(4)	Br1–Co1–Br2	97.18(2)	N32–Co2–Br3	129.64(12)
Co2–Br3	2.4242(7)	N1–Co1–N12	75.34(12)	N42–Co2–Br3	106.78(10)
Co2–Br4	2.4419(8)	N1–Co1–N22	75.77(12)		
S1–S2	2.0454(14)	N1–Co1–Br2	169.56(9)		
Co2–S2	6.090(1)	N12–Co1–N22	150.12(13)		

Table AIV.4. Complete bond distances and bond angles in [1ncs].

Atoms	Distance (Å)	Atoms	Bond angles (°)
Co1–N1	2.3701(17)	N1–Co1–N12	74.71(6)
Co1–N12	2.0444(17)	N1–Co1–N22	74.79(6)
Co1–N22	2.0400(17)	N1–Co1–N3	87.66(7)
Co1–N3	1.9788(18)	N1–Co1–N4	174.40(7)
Co1–N4	1.9952(19)	N4–Co1–N12	102.43(8)
S1–S1	2.0396(10)	N4–Co1–N22	102.70(7)
Co1–S1	6.0600(7)	N4–Co1–N3	97.94(8)
Co1–Co1	11.6906(6)	N3–Co1–N12	119.70(7)
		N3–Co1–N22	112.80(7)
		N12–Co1–N22	116.76(7)

Table AIV.5. Complete bond distances and bond angles in [2ncs].

Atoms	Distance (Å)	Atoms	Bond angles (°)	Atoms	Bond angles (°)
Co1–N1	2.2785(19)	N1–Co1–N11	77.09(7)	N2–Co2–N31	77.37(7)
Co1–N11	2.0661(19)	N1–Co1–N21	77.60(7)	N2–Co2–N41	78.38(8)
Co1–N21	2.0530(19)	N1–Co1–N51	174.26(8)	N2–Co2–N71	174.77(8)
Co1–N51	2.018(2)	N1–Co1–N61	87.42(8)	N2–Co2–N81	89.66(8)
Co1–N61	1.990(2)	N51–Co1–N11	99.20(8)	N71–Co2–N31	101.27(9)
Co2–N2	2.2337(19)	N51–Co1–N21	100.04(8)	N71–Co2–N41	97.35(9)
Co2–N31	2.032(2)	N51–Co1–N61	98.11(9)	N71–Co2–N81	95.44(9)
Co2–N41	2.0509(19)	N61–Co1–N11	113.19(9)	N81–Co2–N31	116.85(8)
Co2–N71	1.995(2)	N61–Co1–N21	127.31(8)	N81–Co2–N41	130.82(8)
Co2–N81	1.993(2)	N11–Co1–N21	112.01(7)	N31–Co2–N41	106.76(8)
S1–S2	2.0272(9)				
Co1–S1	6.2951(7)				
Co2–S2	5.6117(8)				
Co1–Co2	7.0894(7)				

Table AIV.6. Complete bond distances and bond angles in [3C].

Atoms	Distance (Å)	Atoms	Bond angles (°)
Co1–N1	2.1406(14)	N1–Co1–N11	79.18(6)
Co1–N11	2.1631(14)	N1–Co1–N21	78.41(6)
Co1–N21	2.1918(15)	N1–Co1–Cl1	112.91(4)
Co1–Cl1	2.3235(5)	N1–Co1–Cl2	123.28(4)
Co1–Cl2	2.2976(5)	N21–Co1–N11	157.28(6)
S1–S1	2.0311(12)	N21–Co1–Cl1	95.81(4)
Co1–S1	4.8457(9)	N21–Co1–Cl2	93.52(4)
		N11–Co1–Cl1	96.29(4)
		N11–Co1–Cl2	95.63(4)
		Cl1–Co1–Cl2	123.78(2)