

SUPPLEMENTARY MATERIALS

New Azide-Bridged Polymeric Manganese (III) Schiff Base Complex with Allylamine-Derived Ligand: Structural Characterization and Activity Spectra

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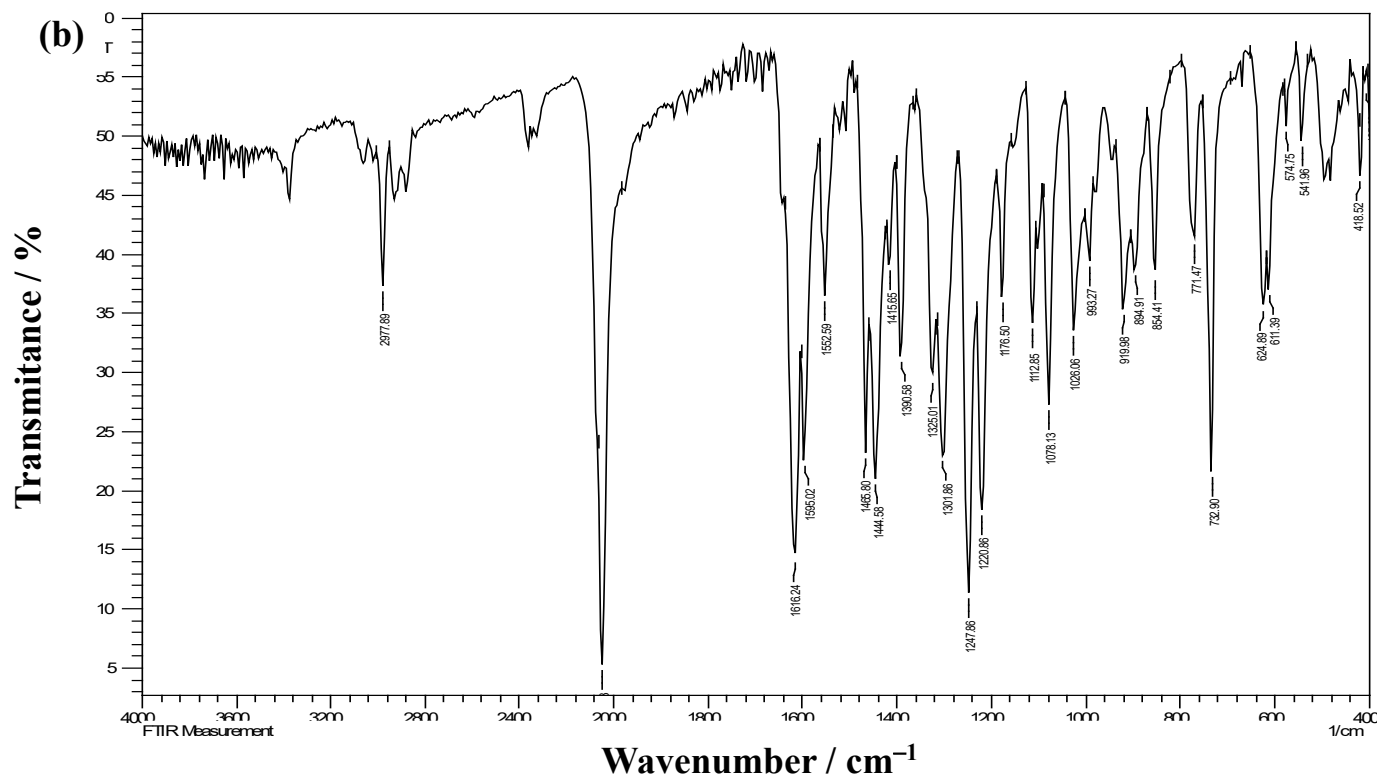
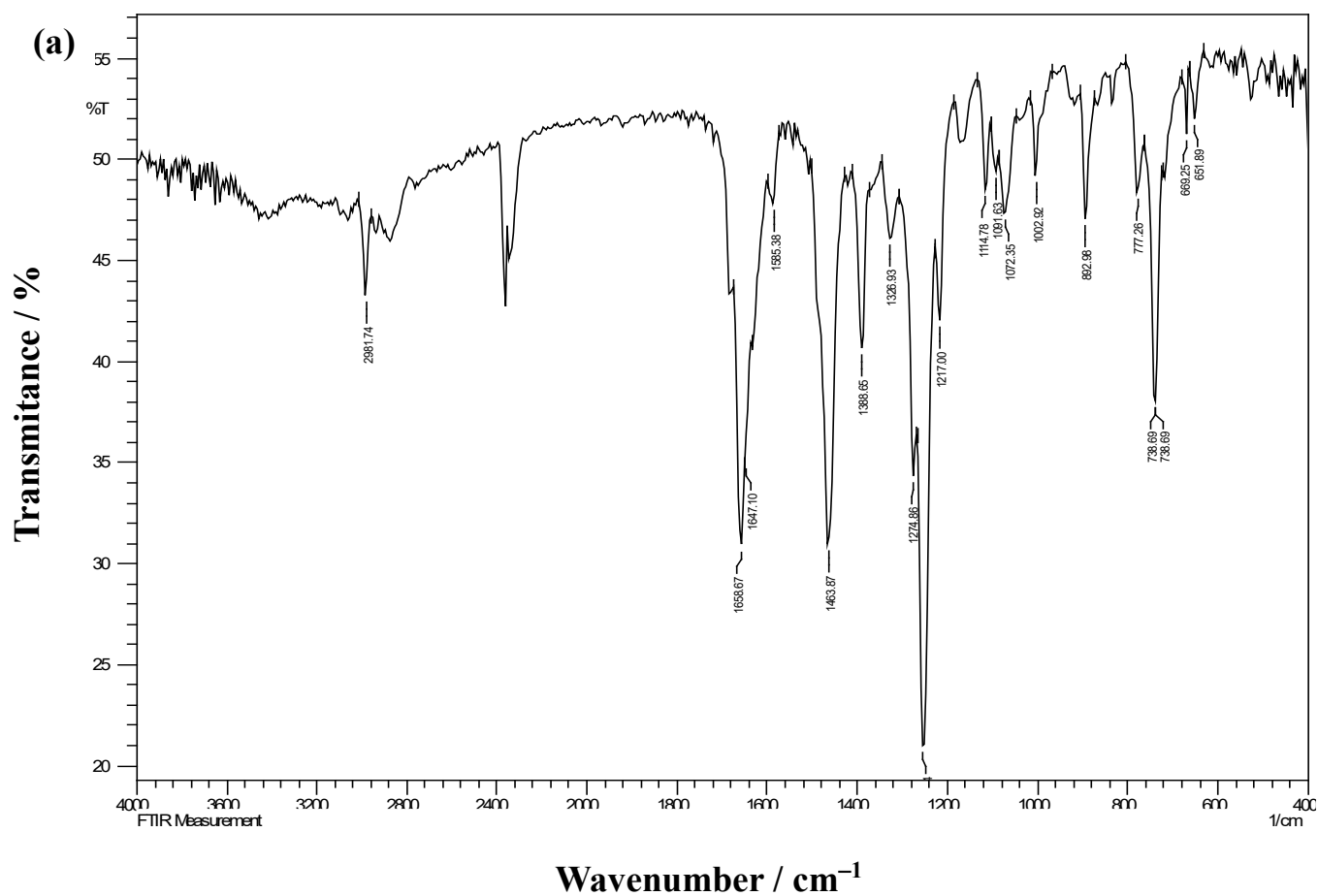


Figure S1. (a). IR spectra of the Schiff base ligand dispersed in a KBr pellet. (b). IR spectra of the Mn (III) complex dispersed in a KBr pellet.

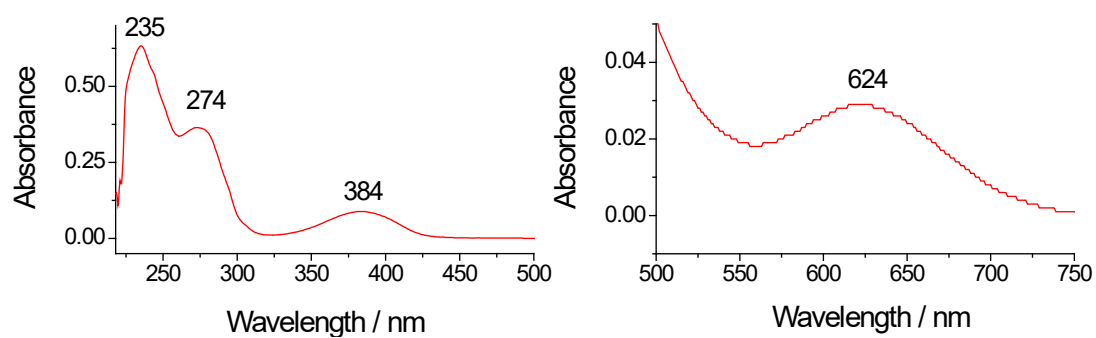


Figure S2. UV-Vis spectrum of the complex in DMF solvent ($c = 1 \times 10^{-5}$ M).

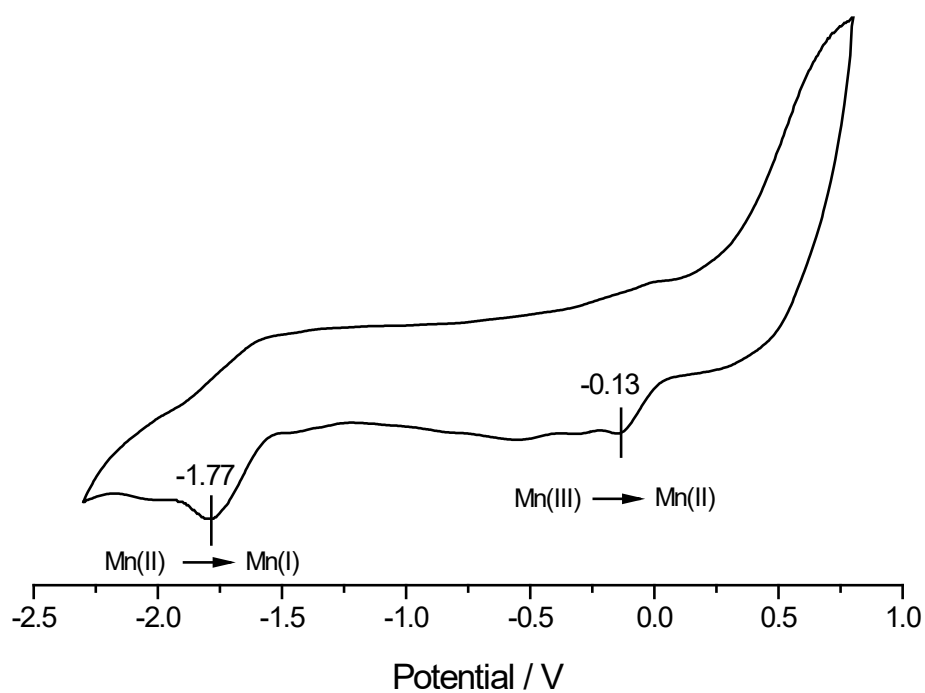
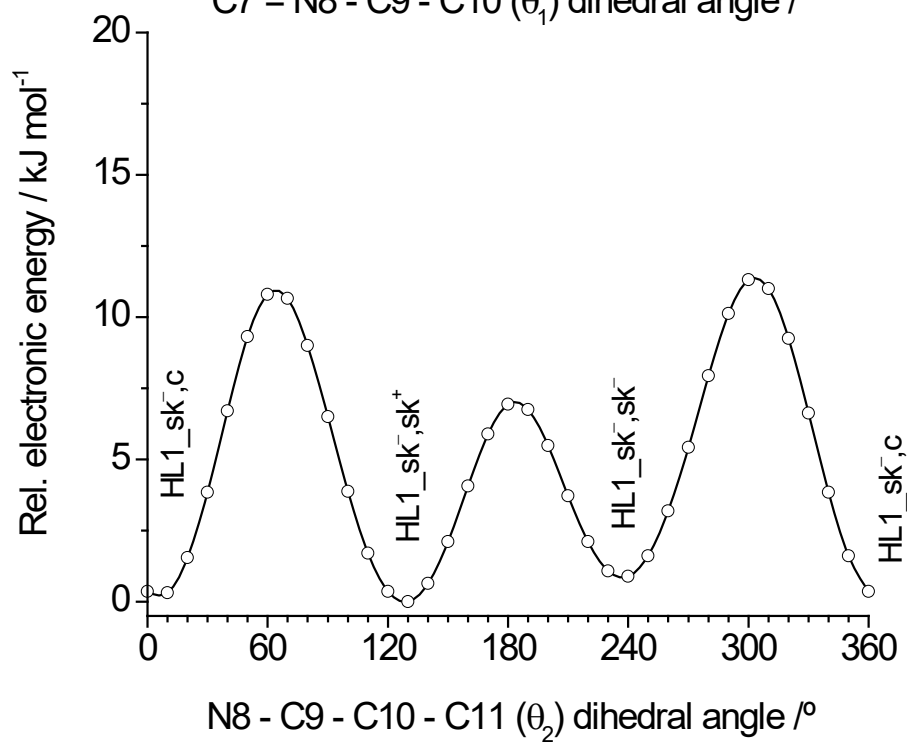
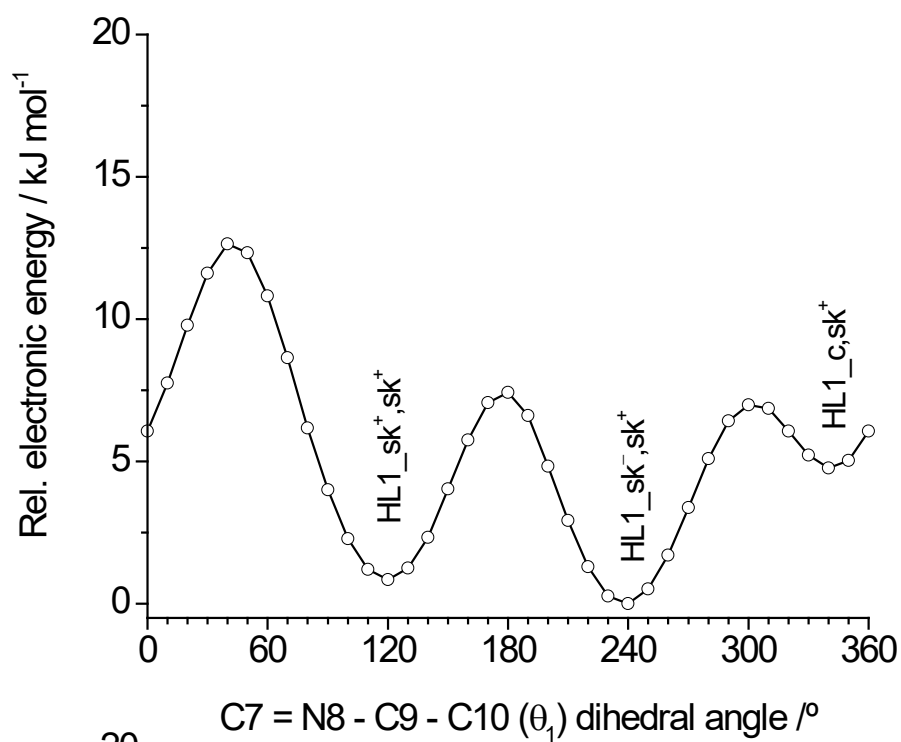


Figure S3. Cyclic voltammogram of a 10^{-3} mol L⁻¹ solution of the complex in DMF solution containing 0.1 mol L⁻¹ TBAH (scan rate = 100 mVs⁻¹).

(a)



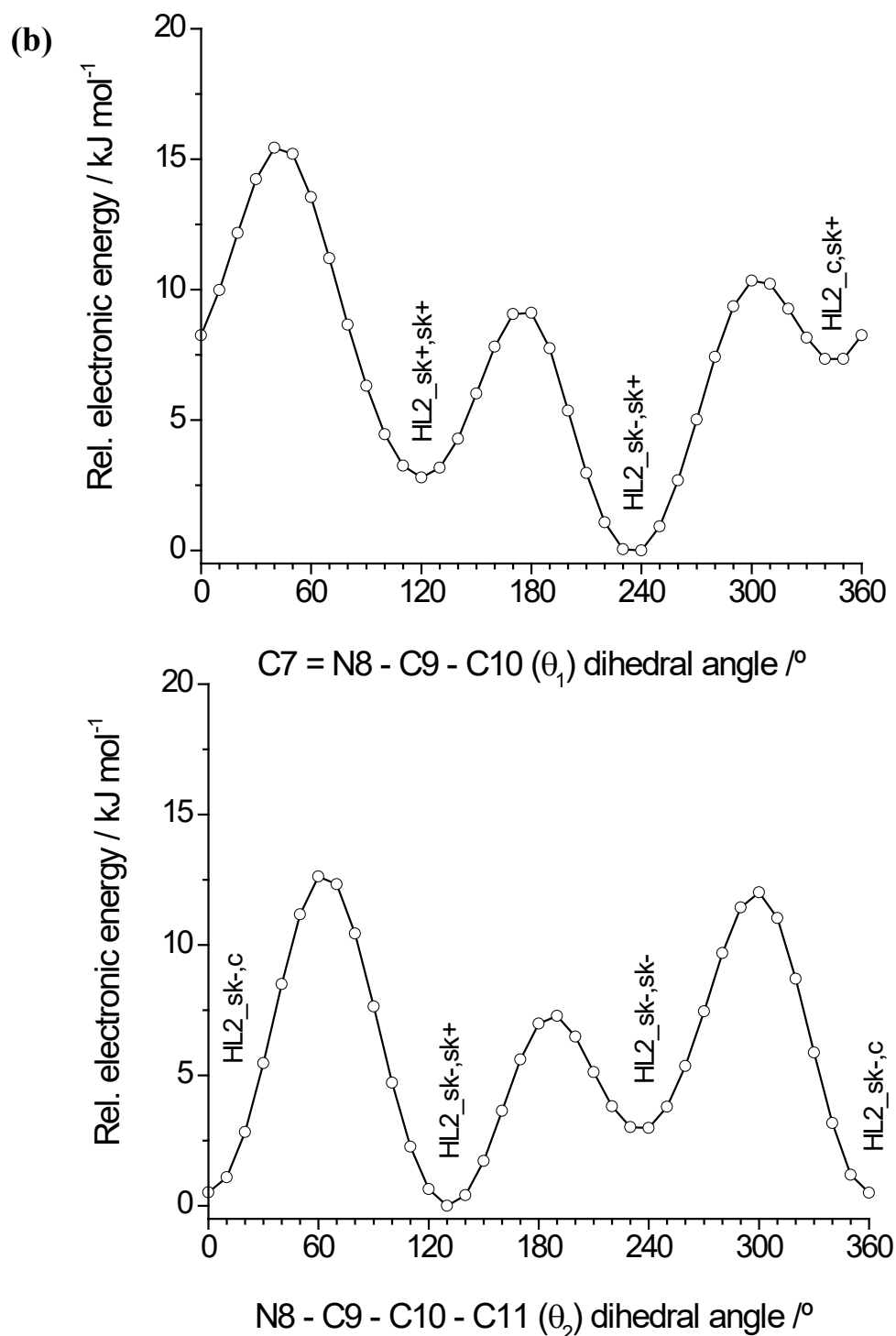


Figure S4. (a) Relaxed potential energy scans around the C7=N8-C9-C10 (θ_1) and N8-C9-C10-C11 (θ_2) dihedral angles calculated at the B3LYP/6-311++G(d,p) level of theory for the Schiff base ligand (HL) with the O1H pointing towards the N8 atom (HL1, see Figure S6). (b) Relaxed potential energy scans around the C7=N8-C9-C10 (θ_1) and N8-C9-C10-C11 (θ_2) dihedral angles calculated at the B3LYP/6-311++G(d,p) level of theory for the Schiff base ligand (HL) with the O1H pointing towards the O2 atom (HL2, see Figure S6). The dihedral angles were incrementally fixed in steps of 10°, while all

other internal coordinates were fully optimized. In both scans the energy of conformer HL1_sk⁻, sk⁺ was set as zero.

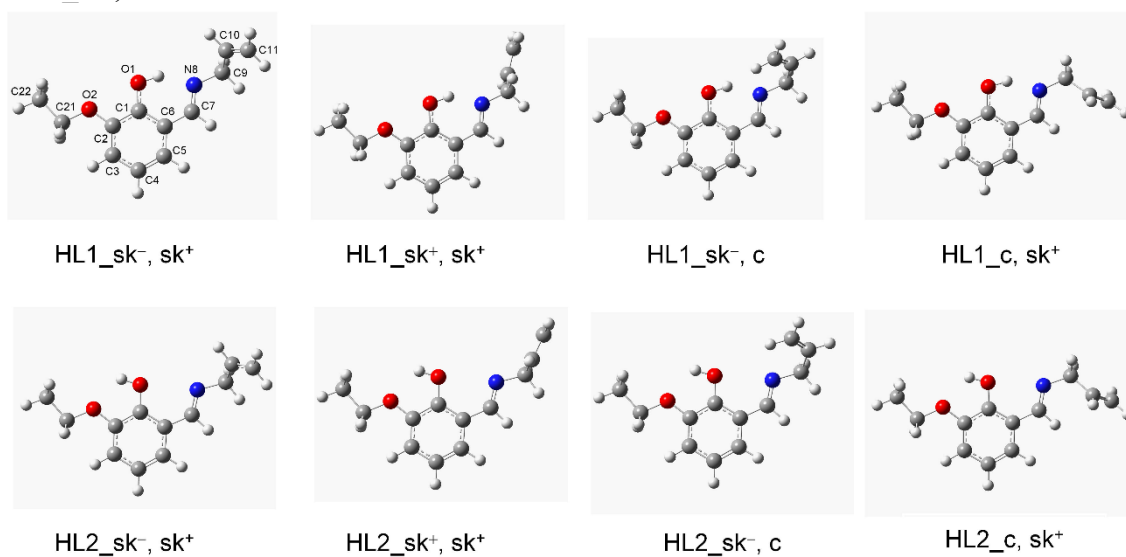


Figure S5. Geometries of the conformers of the Schiff base ligand (HL) fully optimized at the B3LYP/6-311++G(d,p) level of theory. The conformers are identified by the orientation around the C7=N8-C9-C10 (θ_1) and N8-C9-C10=C11 (θ_2) torsions, which define the arrangement of the allyl fragment. The orientation of the ethoxy fragment with respect to the ring is similar across all conformers (trans) and, therefore, is not used for labeling the conformers. Note that each conformer has a mirror image counterpart, resulting in double degeneracy, with both forms being energetically and symmetrically similar.

Table S1. Wavenumbers ($\tilde{\nu}$ / cm^{-1}) and intensity of the bands observed in the IR spectra of the schiff base ligand and polymeric Mn(III) complex.^a

Ligand	Intensity	Complex	Intensity
~3440	br.	3373.3	w
2981.7	w	2976.0	m
1658.7	s	2923.9	m
1647.1	s	2046.3	s
1585.4	w	1614.2	s
1463.9	s	1552.6	m
1388.6	m	1521.7	w
1326.9	w	1465.8	s
1274.9	m	1444.6	s
1253.6	s	1413.7	w
1217.0	w	1390.6	m
1114.8	w	1325.0	s
1091.6	w	1301.9	s
1072.4	w	1247.9	s
1002.9	w	1220.9	s
893.0	w	1174.6	w
777.3	w	1168.8	w
738.7	m	1110.9	w
669.3	w	1099.4	w
651.9	w	1078.1	m
		1026.1	w
		993.3	w
		920.0	w
		894.9	w
		854.4	w
		771.5	w
		732.9	s
		684.7	vw
		624.9	m
		543.9	vw
		495.7	w

^a Intensities are given in qualitative terms: s = strong; m = medium; w = weak; br. = broad.

Table S2. B3LYP/6-311++G(d,p) wavenumbers ($\tilde{\nu}$ / cm^{-1}) and IR intensities (I / km mol^{-1}) calculated for the most stable conformer of the Schiff base ligand (HL1_{sk}⁻, sk⁺) fully optimized at the same level of theory.

$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I
3050.4	13.8	1377.6	30.5	819.2	0.1
3045.9	2.3	1371.4	24.8	775.8	11.0
3038.6	547.8	1339.1	20.7	746.9	27.1
3025.8	19.2	1321.5	36.8	728.8	53.2
3005.4	1.2	1288.9	7.8	667.5	2.5
2986.3	5.4	1284.2	80.9	607.5	14.0
2969.1	11.5	1276.6	0.6	575.8	1.5
2958.1	25.4	1252.7	437.2	566.1	2.2
2948.5	25.4	1229.5	0.5	543.2	0.3
2885.4	23.0	1221.1	11.8	531.0	1.1
2873.5	32.4	1175.4	10.5	469.8	1.2
2865.6	17.1	1153.8	3.5	407.6	3.3
2855.6	68.7	1144.7	12.2	366.3	1.0
2840.2	38.9	1117.7	41.3	347.2	3.8
2825.5	62.9	1092.5	21.7	337.4	0.7
1670.1	45.4	1075.5	67.8	314.4	5.0
1652.8	198.3	1026.1	34.2	299.6	0.7
1625.0	55.3	1009.3	17.3	280.1	1.5
1582.9	21.6	1004.6	30.1	244.5	0.3
1497.7	11.4	994.1	5.7	192.3	3.1
1492.1	0.3	941.0	7.5	170.0	0.1
1471.6	21.0	931.7	40.8	148.4	0.6
1463.4	246.1	929.0	5.8	109.5	1.0
1453.4	7.1	916.6	16.2	98.3	1.1
1450.7	16.0	888.5	24.8	90.1	0.4
1431.5	22.6	863.9	0.3	61.2	1.0
1426.3	8.1	836.9	72.7	39.0	3.2

^a Wavenumbers were multiplied by 0.950 (above 2000 cm^{-1}) or 0.980 (below 2000 cm^{-1}).

Table S3. B3LYP/def2-SVP wavenumbers ($\tilde{\nu}$ / cm^{-1}) and IR intensities (I / km mol^{-1}) calculated for the $\text{Mn}^{\text{III}}(\text{L})_2(\text{N}_3)_2^-$ fragment of the polymeric Manganese (III) Schiff Base complex fully optimized at the same level.

$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I
3106.7	36.5	1305.9	4.0	580.1	7.5
3094.2	62.0	1258.5	4.1	567.9	21.9
3072.9	71.1	1250.5	3.0	535.1	3.1
3048.9	16.1	1237.9	933.3	461.7	66.1
3029.0	13.0	1219.6	23.8	429.2	44.5
3028.1	29.1	1203.4	196.3	418.7	10.3
3017.0	68.7	1147.5	85.3	406.4	159.7
3015.3	28.4	1138.4	8.2	364.1	8.3
2965.2	43.8	1119.1	70.0	355.1	2.9
2935.8	49.3	1112.4	5.0	322.8	31.4
2921.9	88.8	1082.7	30.4	318.1	83.5
2916.2	50.1	1072.8	76.6	294.0	9.3
2901.3	93.3	1019.6	31.9	271.9	2.7
2864.9	137.8	1004.7	8.7	257.8	2.7
2172.3	1877.9	1004.2	61.6	238.3	24.9
1662.0	607.7	971.8	16.7	225.7	10.7
1656.4	34.4	926.0	0.1	217.6	2.6
1594.5	214.9	922.3	2.3	181.1	6.1
1546.0	51.3	900.0	39.7	173.5	1.7
1472.8	865.0	890.4	120.1	147.0	0.3
1454.4	67.1	880.2	5.7	134.9	0.9
1438.7	200.2	859.7	4.4	104.9	1.5
1427.3	10.1	842.0	65.7	98.8	0.2
1411.8	22.3	804.0	0.2	84.1	0.7
1405.7	11.4	770.0	8.6	69.9	1.5
1386.3	36.3	758.8	59.0	67.1	2.8
1382.2	48.4	719.4	76.2	56.0	4.2
1376.2	10.1	680.5	0.9	29.9	0.1
1370.0	154.2	654.2	40.0	25.2	2.6
1344.3	60.6	612.3	20.4	21.4	0.2
1336.8	51.9	596.9	29.6	16.4	2.7
1324.8	315.8	582.8	66.4	13.8	0.2

^a Wavenumbers were multiplied by 0.967.

Table S4. Electronic energies (ΔE_{el}), electronic energies corrected for zero-point vibrational energy [$\Delta(E_{\text{el}} + \text{ZPVE})$], and Gibbs energies at 298.15 K (ΔG), calculated for the conformers of the Schiff base ligand HL at the B3LYP/6-311++G(d,p) level of theory.^a

Conformer	ΔE_{el}	$\Delta(E_{\text{el}} + \text{ZPVE})$	$\Delta G(298\text{K})$
HL1_sk ⁻ , sk ⁺	0.000	0.000	0.000
HL1_sk ⁺ , sk ⁺	0.861	0.730	0.627
HL1_sk ⁻ , c	0.194	0.226	0.764
HL1_c, sk ⁺	4.773	4.986	5.548
HL2_sk ⁻ , sk ⁺	35.040	33.375	30.687
HL2_sk ⁻ , c	35.544	33.869	31.346
HL2_sk ⁺ , sk ⁺	37.941	36.153	33.173
HL2_c, sk ⁺	42.376	40.995	38.681

^a HL1 conformers have the O1H group pointing to N8, while HL2 conformers have the O1H group pointing to O2. Labels “c” (cis, $\sim 0^\circ$) and “sk[±]” (skew[±], $\sim \pm 120^\circ$), refer to the orientation around the C7=N8-C9-C10 (θ_1) and N8-C9-C10=C11 (θ_2) dihedral angles. In the conformer’s designation, the first label refers to θ_1 and the second to θ_2 . All relative energies (kJ mol^{-1}) are expressed with respect to the most stable conformer (HL1_sk⁻, sk⁺). Absolute energy values computed for HL1_sk⁻, sk⁺: $E_{\text{el}} = -671.660865 E_h$; $E_{\text{el}} + \text{ZPVE} = -671.412937 E_h$; $G(298.15\text{K}) = -671.456126 E_h$.