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Supporting Information

X-ray Structure of a Ni(II)-Tri-Phenoxyl Radical Complex **

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Experimental section

The pro-ligand LH was synthesized as previously reported. (G. M. Zats, H. Arora, R. Lavi, D. Yufit, L. Benisvy, *Dalton Trans.* **2011**, *40*, 10889)

Synthesis of NiL_2 (1). To a solution of LH (0.05 g, 0.175 mmol) in methanol (10 mL), a solution of $Ni(BF_4)_2 \cdot 6H_2O$ (0.03 g, 0.0875 mmol) in methanol (10 mL) was added. Then, Et_3N (24 μL) was added to the reaction mixture, causing an immediate green microcrystalline precipitate to be formed. After a ten minutes of stirring, the solid was collected by filtration, washed with cold methanol, and dried under vacuum, to give green crystalline solid of NiL_2 (**1**) in 70 % yield (78 mg). The slow diffusion of hexane onto a dichloromethane solution, gave, after a few days, large light-green rectangles single crystals of **1** suitable for X-ray crystallography.

^1H NMR ($CDCl_3$, 300 MHz): δ 10.82 (bs, 2H, NH), 7.31 (bs, 2H, Ar), 7.16 (bs, 2H, Ar), 6.38 (bs, 2H, Py), 2.38 (s, 6H, CH_3), 1.40 (s, 18H, *^{t}Bu*), 1.25 (s, 18H, *^{t}Bu*). MS: ES(+) *m/z* 629 (M). UV/vis (CH_2Cl_2) λ_{max}/nm (Ɛ/$M^{-1}cm^{-1}$): 400(610), 484(120) and 630 (170)). Elemental analysis: Calc. for $C_{36}H_{50}N_4O_2Ni$: C 68.69, H 8.01, N 8.91; Found: C 68.67, H 7.83, N 8.79.

Synthesis of $[NiL_3][SbF_6]_2$ (2). Under nitrogen, to a solution of **1** (0.05 g, 0.07 mmol) in distilled CH_2Cl_2 (15 mL) was added to a suspension of $AgSbF_6$ (0.025 g, 0.07 mmol) in distilled CH_2Cl_2 at -10^o C. During this time the colour of the solution changes from green to dark greenish brown, concomitantly with the formation of a silver mirror. The mixture was stirred for further 1 h at room temperature and then filtered with cannula. The solvent was evaporated under vacuo yielding a dark greenish brown crystalline powder of $[NiL_3][SbF_6]_2$ (**2**) in 46 % yield (45 mg). Slow diffusion of hexane into a saturated CH_2Cl_2 solution of **2** at 4^o C for two days under inert atmosphere, yields dark-brown cube-like single crystals suitable for X-ray crystallography. Elemental analysis: Calc. for **2** ($C_{54}H_{75}N_6O_3NiSb_2F_{12}$): C 47.78, H 5.45, N 6.06; Found: C 47.31, H 5.85, N 5.80. MS: ES (+) *m/z*: 912 $[Ni(L)_3(H^+)]^+$, 1148 $\{[Ni(LH)_3][SbF_6]\}^+$. UV/vis (CH_2Cl_2): λ_{max}/nm (Ɛ/M^{-1} cm^{-1}): 420 nm (7500), 840 (2100).

X-ray crystallography.

The X-ray single crystal data have been collected on a Bruker SMART CCD 6000 (compound **1**) and Bruker ApexDuo (compound **2**) diffractometers (graphite monochromator, λMoKα, λ =0.71073Å) equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats at the temperatures 120.0(2) and 110(2)K respectively. Both structures were solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2[1] and SHELXTL[2] software. All non-disordered non-hydrogen atoms were refined anisotropically, the hydrogen atoms were placed in the calculated positions and refined in riding mode. Disordered atoms in structure **1** were refined isotropically with fixed SOF=0.6 and 0.4. Chloroform solvent molecule in the structure **2** was refined with fixed SOF=0.8. Crystal data and parameters of refinement are listed in Table SI1, bond lengths and angles are in the Tables SI2-SI6. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-1005503, 1005504.

1. O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H. Puschmann, *J. Appl. Cryst.* (2009), 42, 339-341.
2. G.M. Sheldrick, *Acta Cryst.* (2008), A64, 112-122

Physical Methods:

Elemental analyses of the compounds isolated in these studies were accomplished in the University of Bar Ilan. EI mass spectra were recorded on a Q-Tof micro (UK)-micromass-Waters UK spectrometer. ^{1}H NMR spectra were recorded on a Bruker DPX300. UV/Vis spectra were recorded on a Varian Cary 5000 UV/Vis/NIR spectrophotometer. The measurements were carried out using a quartz cuvette with optical pathlength of 0.1 cm.

Figures and Tables

Table SI1. Crystallographic data for crystals of **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{36}H_{50}N_4O_2Ni$	$[C_{54}H_{75}N_6NiO_3]^{2+}$ x $2(SbF_6)^{1-}$ x $2.4(CH_2Cl_2)$
Formula weight	629.51	1590.23
Temperature / K	120.0	110.0
Crystal system	Monoclinic	trigonal
Space group	$P2_1/c$	R-3
a / Å, b / Å, c / Å	17.3610(6), 10.3225(4), 9.2567(3)	15.0749(6), 54.398(2)
α/°, β/°, γ/°	90.00, 92.410(10), 90.00	90.0, 90.0, 120.0
Volume / Å^3	1657.42(10)	10705.9(9)
Z	2	6
ρ_{calc} / mg mm^{-3}	1.261	1.480
μ / mm^{-1}	0.622	1.266
F(000)	676	4822.8
Reflections collected	19777	18973
Independent reflections, R_{int}	4400, 0.0427	4873, 0.0287
Data/restraints/parameters	4400/0/263	4873/15/269
Goodness-of-fit on F^2	1.010	1.175
Final R_1 indexes [I>2σ (I)]	0.0448	0.0468
Final wR_2 indexes [all data]	0.1261	0.1178
Largest diff. peak/hole / e Å^{-3}	0.773/-0.489	1.24/-1.63

Table SI2. Bond lengths/Å for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	O1	1.8689(13)	C6	C14	1.545(3)
Ni1	N1	1.8501(17)	C7	C8	1.398(3)
O1	C5	1.333(2)	C8	C9	1.382(3)
N1	N2	1.354(2)	C8	C10	1.534(3)
N1	C3	1.339(2)	C10	C11	1.542(5)
N2	C1	1.340(3)	C10	C11A	1.483(8)
C1	C2	1.380(3)	C10	C12	1.534(5)
C1	C18	1.490(3)	C10	C12A	1.574(7)
C2	C3	1.417(3)	C10	C13	1.496(5)
C3	C4	1.459(3)	C10	C13A	1.576(7)
C4	C5	1.421(3)	C14	C15	1.542(3)
C4	C9	1.401(3)	C14	C16	1.540(3)
C5	C6	1.433(3)	C14	C17	1.534(3)
C6	C7	1.387(3)			

Table SI3. Bond angles/° for **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Ni1	O1[1]	180.0	C5	O1	Ni1	131.00(13)
O1	C5	C4	122.67(17)	C5	C4	C3	121.15(17)
O1	C5	C6	119.99(17)	C5	C6	C14	121.31(17)
N1	Ni1	O1[1]	89.13(7)	C6	C7	C8	124.42(19)
N1	Ni1	O1	90.87(7)	C7	C6	C5	118.67(18)
N1[1]	Ni1	N1	180.00(4)	C7	C6	C14	120.02(17)
N1	C3	C2	108.73(17)	C7	C8	C10	122.04(18)
N1	C3	C4	121.42(17)	C8	C9	C4	122.1(2)
N2	N1	Ni1	121.16(13)	C9	C4	C3	117.76(18)
N2	C1	C2	106.65(17)	C9	C4	C5	120.99(18)
N2	C1	C18	120.74(18)	C9	C8	C7	116.53(19)
C1	N2	N1	111.89(16)	C9	C8	C10	121.42(19)
C1	C2	C3	106.13(17)	C15	C14	C6	110.31(17)
C2	C1	C18	132.60(19)	C16	C14	C6	112.19(18)
C2	C3	C4	129.75(18)	C16	C14	C15	105.82(18)
C3	N1	Ni1	131.06(13)	C17	C14	C6	109.73(17)
C3	N1	N2	106.60(16)	C17	C14	C15	112.22(18)
C4	C5	C6	117.33(18)	C17	C14	C16	106.50(18)

[1]-X,1-Y,1-Z

Table SI4. Bond lengths/Å for **2**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ni1	N2[1]	2.047(3)		C12	C15	1.546(6)
Ni1	N2[2]	2.047(3)		C16	C17	1.410(6)
Ni1	N2	2.047(3)		C17	C18	1.523(5)
Ni1	O10	2.025(3)		C17	C22	1.407(6)
Ni1	O10[1]	2.025(3)		C18	C19	1.530(6)
Ni1	O10[2]	2.025(3)		C18	C20	1.547(6)
N2	N3	1.359(4)		C18	C21	1.538(6)
N2	C7	1.344(5)		Sb23	F24[3]	1.861(2)
N3	C4	1.344(5)		Sb23	F24	1.861(2)
C4	C5	1.496(6)		Sb23	F24[4]	1.861(2)
C4	C6	1.365(6)		Sb23	F25[4]	1.885(2)
C6	C7	1.407(5)		Sb23	F25	1.885(2)
C7	C8	1.461(5)		Sb23	F25[3]	1.885(2)
C8	C9	1.461(5)		Sb26	F27[5]	1.864(4)
C8	C22	1.376(5)		Sb26	F27[6]	1.864(4)
C9	O10	1.258(5)		Sb26	F27	1.864(4)
C9	C11	1.469(5)		Sb26	F28[6]	1.871(4)
C11	C12	1.533(5)		Sb26	F28[5]	1.871(4)
C11	C16	1.368(6)		Sb26	F28	1.871(4)
C12	C13	1.537(6)		C29	Cl30	1.713(9)
C12	C14	1.537(6)		C29	Cl31	1.701(10)

[1]1-Y,+X-Y,+Z; [2]1+Y-X,1-X,+Z; [3]1-Y,1+X-Y,+Z; [4]+Y-X,1-X,+Z; [5]+Y-X,-X,+Z; [6]-Y,+X-Y,+Z

Table SI5. Bond angles/[o] for **2**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N2[1]	Ni1	N2	100.63(11)		C11	C16	C17	123.1(4)
N2[2]	Ni1	N2	100.63(11)		C16	C17	C18	123.0(4)
N2[2]	Ni1	N2[1]	100.63(11)		C22	C17	C16	118.4(4)
O10[1]	Ni1	N2[1]	85.49(11)		C22	C17	C18	118.6(4)
O10	Ni1	N2	85.49(11)		C17	C18	C19	113.0(3)
O10	Ni1	N2[2]	170.73(12)		C17	C18	C20	108.6(4)
O10[2]	Ni1	N2[1]	170.73(12)		C17	C18	C21	108.3(3)
O10[2]	Ni1	N2	84.92(12)		C19	C18	C20	108.7(4)
O10[1]	Ni1	N2[2]	84.92(12)		C19	C18	C21	108.3(4)
O10[2]	Ni1	N2[2]	85.49(11)		C21	C18	C20	109.9(4)
O10[1]	Ni1	N2	170.73(12)		C8	C22	C17	122.9(4)
O10	Ni1	N2[1]	84.92(12)		F24[3]	Sb23	F24[4]	91.45(12)
O10[1]	Ni1	O10[2]	88.14(11)		F24	Sb23	F24[3]	91.45(12)
O10[1]	Ni1	O10	88.14(11)		F24	Sb23	F24[4]	91.45(12)
O10	Ni1	O10[2]	88.14(11)		F24	Sb23	F25[4]	91.25(12)
N3	N2	Ni1	123.3(2)		F24[3]	Sb23	F25[3]	177.24(12)
C7	N2	Ni1	126.1(3)		F24[3]	Sb23	F25	91.25(13)
C7	N2	N3	105.3(3)		F24[3]	Sb23	F25[4]	89.02(11)
C4	N3	N2	112.3(3)		F24	Sb23	F25	177.24(12)
N3	C4	C5	121.8(4)		F24[4]	Sb23	F25[4]	177.24(12)
N3	C4	C6	106.3(4)		F24[4]	Sb23	F25	89.02(11)
C6	C4	C5	131.9(4)		F24	Sb23	F25[3]	89.02(11)
C4	C6	C7	106.8(4)		F24[4]	Sb23	F25[3]	91.25(12)
N2	C7	C6	109.2(3)		F25[4]	Sb23	F25	88.25(12)
N2	C7	C8	124.0(3)		F25[4]	Sb23	F25[3]	88.25(12)
C6	C7	C8	126.8(4)		F25[3]	Sb23	F25	88.25(12)
C9	C8	C7	122.7(3)		F27[5]	Sb26	F27	90.4(2)
C22	C8	C7	119.1(4)		F27[5]	Sb26	F27[6]	90.4(2)
C22	C8	C9	118.2(3)		F27	Sb26	F27[6]	90.4(2)
C8	C9	C11	119.0(3)		F27	Sb26	F28[5]	178.9(2)
O10	C9	C8	121.7(3)		F27[6]	Sb26	F28	178.9(2)
O10	C9	C11	119.3(3)		F27[5]	Sb26	F28	90.6(2)
C9	O10	Ni1	133.8(3)		F27[6]	Sb26	F28[5]	90.6(2)
C9	C11	C12	119.3(3)		F27[5]	Sb26	F28[6]	178.9(2)
C16	C11	C9	118.2(3)		F27	Sb26	F28	89.71(19)
C16	C11	C12	122.4(3)		F27[6]	Sb26	F28[6]	89.71(19)
C11	C12	C13	111.7(3)		F27[5]	Sb26	F28[5]	89.71(19)
C11	C12	C14	109.3(3)		F27	Sb26	F28[6]	90.6(2)
C11	C12	C15	110.7(3)		F28[6]	Sb26	F28	89.2(2)
C13	C12	C15	107.2(3)		F28[6]	Sb26	F28[5]	89.2(2)
C14	C12	C13	107.6(3)		F28[5]	Sb26	F28	89.2(2)
C14	C12	C15	110.3(3)		Cl31	C29	Cl30	114.3(6)

[1]1-Y,+X-Y,+Z; [2]1+Y-X,1-X,+Z; [3]+Y-X,1-X,+Z; [4]1-Y,1+X-Y,+Z; [5]+Y-X,-X,+Z; [6]-Y,+X-Y,+Z

Figure SI1. Room-temperature ^{1}H NMR ($CDCl_3$, 300 MHz) spectra of **1**.