

Metal ion directed template synthesis using 2-acetyl-1,3-indandione and ethylenediamine: steric and electronic restrictions

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Crystallographic data

Table S1 Crystallographic data for complex **2**.

Summary chemical formula	C ₂₆ H ₂₆ N ₄ NiO ₄
<i>M_r</i>	517.22
Crystal system, color, habit	monoclinic, orange, prism
Space group	P2 ₁ /n
Crystal dimensions (mm ³)	0.36 × 0.30 × 0.20
Unit cell parameters:	
<i>a</i> /Å	14.9563(16)
<i>b</i> /Å	10.9514(12)
<i>c</i> /Å	17.6484(15)
angles	α 90 β 103.484(3) γ 90
<i>V</i> /Å ³	2811.0(5)
<i>Z</i>	4
ρ (calculated) / g cm ⁻³	1.222
μ /mm ⁻¹	0.725
<i>F</i> (000)	1080

θ - range/°	1.61 – 22.19 (compl. 0.997)
Reflections collected, unique ($R_{\text{int.}}$), observed [$I > 2\sigma(I)$]	3519, 2884 (0.0401)
Number of parameters refined	318
$R(F_0)$	0.0409
$R_w(F_0^2)$	0.0971
Goodness of fit on F^2 , S	1.066
Max., and min. electron density, $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} / e \text{ \AA}^{-3}$	0.39, -0.35

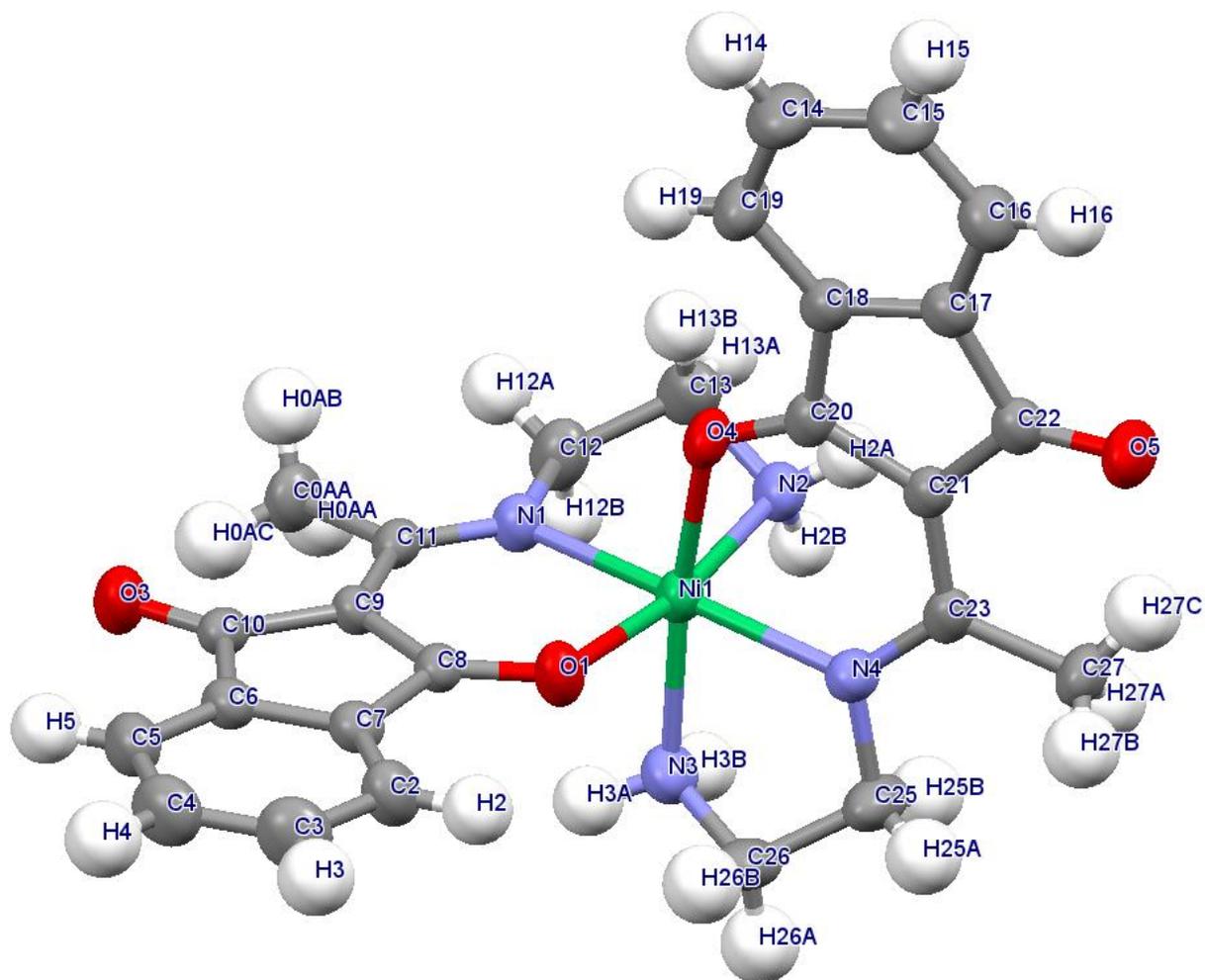


Figure S1 Crystal structure of complex **2** with atoms numbering and ellipsoids representing 50 % probability.

Table S2 Bond lengths in complex **2** with atoms numbering from Figure S1.

bond	Length (Å)	bond	Length (Å)
Ni1 - O1	2.059(3)	C2 - C3	1.385(6)
Ni1 - O4	2.075(2)	C4 - C3	1.374(6)
Ni1 - N1	2.092(3)	C5 - C4	1.389(6)
Ni1 - N4	2.090(3)	C6 - C5	1.374(5)
Ni1 - N3	2.109(3)	C7 - C6	1.379(5)
Ni1 - N2	2.105(3)	C7 - C2	1.376(6)
O1 - C8	1.258(4)	C7 - C8	1.491(4)
O3 - C10	1.236(4)	C8 - C9	1.427(5)
O4 - C20	1.258(4)	C6 - C10	1.504(6)
N1 - C11	1.297(4)	C11 - C9	1.438(5)
N1 - C12	1.475(6)	C11 - C0AA	1.513(5)
O5 - C22	1.235(4)	C10 - C9	1.456(5)
N4 - C23	1.308(5)	C12 - C13	1.511(6)
N4 - C25	1.464(5)	C15 - C14	1.373(6)
N2 - C13	1.463(5)	C16 - C15	1.395(6)
N2 - H2A	0.89	C18 - C20	1.493(5)
N2 - H2B	0.891	C17 - C16	1.380(6)
N3 - C26	1.474(5)	C17 - C18	1.388(5)
N3 - H3A	0.891	C17 - C22	1.498(5)
N3 - H3B	0.89	C19 - C14	1.392(6)
C2 - H2	0.931	C19 - C18	1.381(5)
C3 - H3	0.929	C21 - C20	1.439(4)
C4 - H4	0.931	C22 - C21	1.457(5)
C5 - H5	0.929	C23 - C21	1.443(5)
C14 - H14	0.93	C23 - C27	1.518(5)

C15 - H15	0.93	C26 - C25	1.506(6)
C16 - H16	0.93	C0AA - H0AA	0.959
C19 - H19	0.931	C0AA - H0AB	0.958
C12 - H12A	0.969	C0AA - H0AC	0.96
C12 - H12B	0.971	C27 - H27A	0.96
C13 - H13A	0.969	C27 - H27B	0.96
C13 - H13B	0.97	C27 - H27C	0.96
C25 - H25A	0.971	C26 - H26A	0.971
C25 - H25B	0.971	C26 - H26B	0.97

Table S3 Bond angles in complex **2** with atoms numbering from Figure S1.

Bond angles	[^o]	Bond angles	[^o]
O1 - Ni1 - O4	88.3(1)	Ni1 - N2 - C13	106.0(2)
O1 - Ni1 - N1	89.7(1)	N1 - C12 - C13	108.3(3)
O1 - Ni1 - N4	97.5(1)	N2 - C13 - C12	108.9(3)
O1 - Ni1 - N3	87.7(1)	O1 - C8 - C7	120.7(3)
O1 - Ni1 - N2	170.5(1)	O1 - C8 - C9	130.8(3)
O4 - Ni1 - N1	96.8(1)	O3 - C10 - C6	122.3(3)
O4 - Ni1 - N4	89.6(1)	O3 - C10 - C9	130.5(3)
O4 - Ni1 - N3	169.8(1)	O5 - C22 - C21	130.7(3)
O4 - Ni1 - N2	87.6(1)	C17 - C22 - C21	107.1(3)
N1 - Ni1 - N4	170.5(1)	C16 - C15 - C14	120.7(4)
N1 - Ni1 - N3	92.5(1)	C23 - C21 - C20	125.4(3)
N1 - Ni1 - N2	82.3(1)	C22 - C21 - C20	107.8(3)
N4 - Ni1 - N3	81.7(1)	N4 - C23 - C21	120.6(3)
N4 - Ni1 - N2	91.0(1)	N4 - C23 - C27	120.9(3)

N3 - Ni1 - N2	97.7(1)	C21 - C23 - C27	118.5(3)
Ni1 - O1 - C8	123.2(2)	O5 - C22 - C17	122.2(3)
Ni1 - O4 - C20	123.0(2)	N3 - C26 - C25	109.0(3)
Ni1 - N1 - C11	129.6(2)	N4 - C25 - C26	108.6(3)
Ni1 - N1 - C12	109.9(2)	O4 - C20 - C18	121.7(3)
C11 - N1 - C12	119.9(3)	O4 - C20 - C21	130.4(3)
Ni1 - N4 - C23	127.5(2)	C18 - C20 - C21	107.9(3)
Ni1 - N4 - C25	111.2(2)	C19 - C14 - C15	121.2(4)
C23 - N4 - C25	118.9(3)	C16 - C17 - C18	120.8(3)
Ni1 - N3 - C26	105.4(2)	C16 - C17 - C22	130.6(3)
N1 - C11 - C9	120.0(3)	C18 - C17 - C22	108.6(3)
C7 - C6 - C10	108.2(3)	C18 - C19 - C14	118.0(4)
C7 - C6 - C5	120.7(3)	C17 - C18 - C20	108.5(3)
C8 - C7 - C6	108.6(3)	C19 - C18 - C20	130.5(3)
C8 - C7 - C2	130.3(3)	C8 - C9 - C11	126.0(3)
C6 - C7 - C2	121.1(3)	C8 - C9 - C10	107.5(3)
C7 - C8 - C9	108.5(3)	C11 - C9 - C10	126.6(3)
C7 - C2 - C3	118.5(4)	C10 - C6 - C5	131.1(3)
C4 - C3 - C2	120.3(4)	C6 - C10 - C9	107.2(3)
C5 - C4 - C3	121.2(4)	C6 - C5 - C4	118.2(4)

Computational data

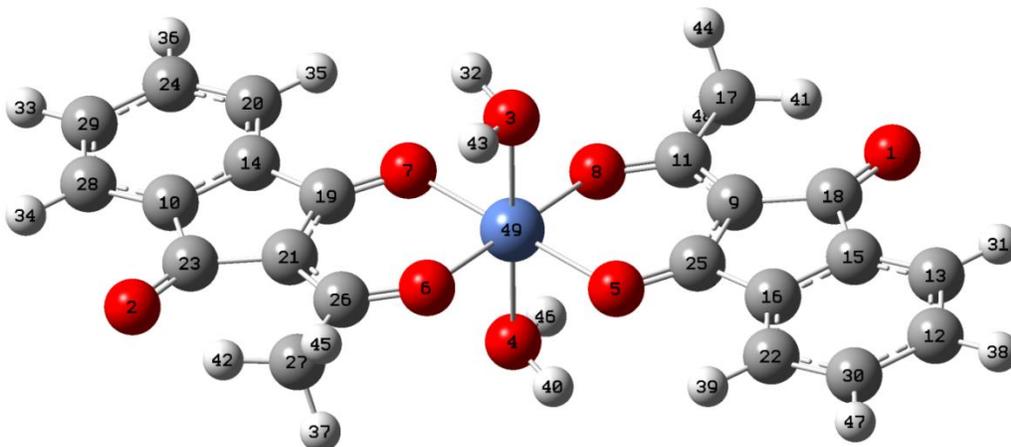


Figure S2 Optimized structure (UB3LYP/6-31G(d,p) ; S=1) of complex **1** (atom numbering and coordination bonds are visualized for clarity).

Table S4 Selected bond lengths (in Å) and bond angles (in °) in complex **1** as obtained from the DFT (UB3LYP/6-31G(d,p); S=1) optimizations (for atoms numbering see Figure S2).

Bond	Length (Å)	Bond angle	degree (°)
Ni – O3	2.1237	O3 – Ni – O7	88.16
Ni - O4	2.1237	O3 – Ni – O8	94.98
Ni – O5	2.0085	O3 – Ni – O6	85.02
Ni – O6	2.0035	O3 – Ni – O5	91.82
Ni – O7	2.0082	O3 – Ni – O4	179.97
Ni – O8	2.0033	O7 – Ni – O6	91.53
O5 – C25	1.2611	Ni– O6 – C26	127.55
O8 - C11	1.2731	O6 – C26 – C21	122.72
O7 – C19	1.2608	C26 – C21 – C19	124.00
O6 – C26	1.2733	C21 – C19 – O7	129.55
C26 – C21	1.4165	C19 – O7 – Ni	121.79
C21 – C19	1.4341	O7 – Ni – O5	179.98

Table S5 Fragment from the output file with the XYZ coordinates of the optimized structure of complex **1** along with computational details, as obtained from the DFT (UB3LYP/6-31G(d,p); S=1) (for atoms numbering see Figure S2).

Stoichiometry C22H18NiO8(3)

Framework group C1[X(C22H18NiO8)]

Deg. of freedom 141

Full point group C1 NOp 1

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	

1	8	0	5.090760	2.602827	0.120357	
2	8	0	-5.091661	-2.601629	-0.122641	
3	8	0	0.171016	-0.023796	2.117594	
4	8	0	-0.170478	0.021532	-2.115666	
5	8	0	1.810461	-0.842050	-0.218518	
6	8	0	-0.768812	-1.838212	0.217653	
7	8	0	-1.810173	0.840741	0.221145	
8	8	0	0.768466	1.836467	-0.215686	
9	6	0	3.049642	1.252327	-0.045877	
10	6	0	-5.183089	-0.189172	-0.032960	
11	6	0	1.987202	2.186954	-0.103693	
12	6	0	6.897749	-1.470716	0.054528	
13	6	0	6.533302	-0.117608	0.095174	
14	6	0	-4.212882	0.813028	0.070259	
15	6	0	5.183253	0.190470	0.030702	
16	6	0	4.213460	-0.812188	-0.071304	

17	6	0	2.249718	3.671314	-0.038793
18	6	0	4.498984	1.531761	0.048852
19	6	0	-2.872090	0.168959	0.117523
20	6	0	-4.563219	2.156375	0.110596
21	6	0	-3.050097	-1.252175	0.045485
22	6	0	4.564536	-2.155419	-0.111157
23	6	0	-4.499437	-1.530860	-0.050772
24	6	0	-5.925725	2.476362	0.045670
25	6	0	2.872090	-0.168893	-0.117612
26	6	0	-1.988079	-2.187542	0.105233
27	6	0	-2.251727	-3.671717	0.040789
28	6	0	-6.532886	0.119601	-0.098360
29	6	0	-6.896617	1.472868	-0.057333
30	6	0	5.927287	-2.474747	-0.047157
31	1	0	7.274327	0.671538	0.174451
32	1	0	-0.565089	0.511214	2.447862
33	1	0	-7.945659	1.750040	-0.106483
34	1	0	-7.274245	-0.669200	-0.178539
35	1	0	-3.802236	2.926340	0.188651
36	1	0	-6.235323	3.516925	0.074798
37	1	0	-1.872686	-4.046843	-0.917307
38	1	0	7.946972	-1.747273	0.103046
39	1	0	3.803884	-2.925803	-0.188136
40	1	0	0.565419	-0.514082	-2.445494
41	1	0	3.309917	3.908009	-0.112998
42	1	0	-3.311768	-3.907821	0.119481
43	1	0	-0.057842	-0.944467	2.316037
44	1	0	1.865356	4.046848	0.916974

45	1	0	-1.675382	-4.169559	0.826382
46	1	0	0.058811	0.941914	-2.315004
47	1	0	6.237424	-3.515172	-0.075964
48	1	0	1.677024	4.168336	-0.827646
49	28	0	-0.000135	-0.000781	0.000972

Rotational constants (GHZ): 0.3297445 0.0701078 0.0602200

Standard basis: 6-31G(d,p) (6D, 7F)

There are 576 symmetry adapted basis functions of A symmetry.

Two-electron integral symmetry is turned on.

576 basis functions, 1070 primitive gaussians, 579 cartesian basis functions

122 alpha electrons 120 beta electrons

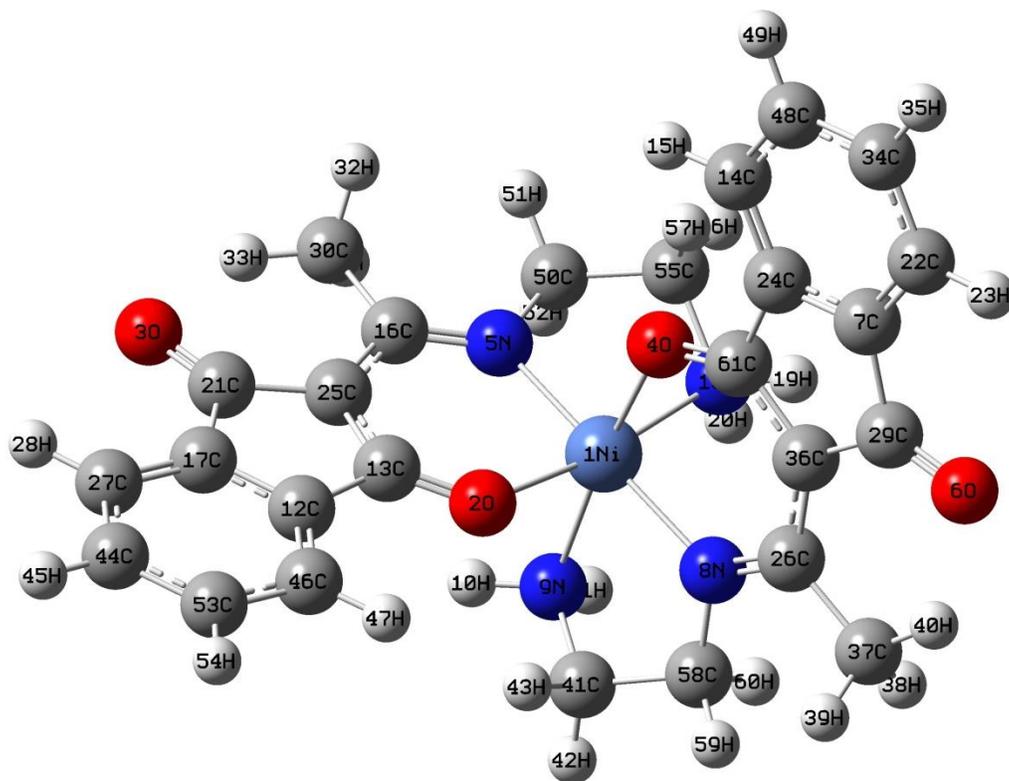


Figure S3 Optimized structure (UB3LYP/6-31G(d,p) and UB3LYP/6-311G(d,p) ; S=1) of complex **2** (labels, atom numbering and coordination bonds are visualized for clarity).

Table S6 Fragment from the output file with the XYZ coordinates of the optimized structure of complex **2**, along with computational details, as obtained from the DFT (UB3LYP/6-31G(d,p); S=1) calculations (for atoms numbering see Figure S3).

Stoichiometry C₂₆H₂₆N₄NiO₄(3)

Framework group C1[X(C₂₆H₂₆N₄NiO₄)]

Deg. of freedom 177

Full point group C1 NOp 1

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	

1	28	0	-0.000060	-1.235351	0.010244	
2	8	0	1.240651	0.165501	-0.779850	
3	8	0	5.179979	0.511858	1.889424	
4	8	0	-1.238608	0.181694	0.774600	
5	7	0	1.167660	-1.382866	1.706863	
6	8	0	-5.182794	0.476844	-1.893545	
7	6	0	-4.434825	1.533134	0.135093	
8	7	0	-1.169350	-1.412562	-1.682524	
9	7	0	1.229152	-2.658059	-1.073246	
10	1	0	2.205318	-2.470356	-0.856963	
11	1	0	1.074256	-3.647825	-0.889730	
12	6	0	3.272882	1.433723	-0.926104	
13	6	0	2.349360	0.467496	-0.261065	
14	6	0	-3.115767	2.199856	2.059169	
15	1	0	-2.204012	2.134775	2.644626	
16	6	0	2.363711	-0.876755	1.908987	

17	6	0	4.435975	1.528491	-0.160712
18	7	0	-1.229971	-2.638595	1.117246
19	1	0	-2.206133	-2.456104	0.896487
20	1	0	-1.073327	-3.631156	0.951273
21	6	0	4.295790	0.634147	1.042193
22	6	0	-5.484442	2.359368	0.501703
23	1	0	-6.383286	2.408982	-0.105022
24	6	0	-3.270257	1.453102	0.899960
25	6	0	2.966937	0.000185	0.943456
26	6	0	-2.366238	-0.911341	-1.891781
27	6	0	5.486407	2.347319	-0.541342
28	1	0	6.384092	2.408688	0.066018
29	6	0	-4.297036	0.615536	-1.050494
30	6	0	3.137870	-1.198504	3.173350
31	1	0	3.168719	-2.279964	3.344593
32	1	0	2.642527	-0.749022	4.042865
33	1	0	4.151391	-0.807346	3.117645
34	6	0	-5.339077	3.120947	1.671276
35	1	0	-6.141147	3.782041	1.987033
36	6	0	-2.968020	-0.016428	-0.942033
37	6	0	-3.142789	-1.258111	-3.148067
38	1	0	-3.172390	-2.342681	-3.298623
39	1	0	-2.650109	-0.824552	-4.027128
40	1	0	-4.156757	-0.867384	-3.097517
41	6	0	0.935400	-2.346563	-2.488333
42	1	0	1.384802	-3.068620	-3.182784
43	1	0	1.359830	-1.361067	-2.688514
44	6	0	5.343398	3.085868	-1.725882

45	1	0	6.146181	3.740576	-2.052937
46	6	0	3.120735	2.157612	-2.100026
47	1	0	2.210096	2.081111	-2.685832
48	6	0	-4.171312	3.042829	2.437551
49	1	0	-4.081770	3.645253	3.337045
50	6	0	0.574260	-2.242397	2.727865
51	1	0	0.769499	-1.891184	3.748067
52	1	0	0.990933	-3.263437	2.668024
53	6	0	4.177135	2.992908	-2.492782
54	1	0	4.089478	3.577652	-3.404048
55	6	0	-0.938306	-2.301763	2.526901
56	1	0	-1.388598	-3.011292	3.233581
57	1	0	-1.363100	-1.312874	2.708733
58	6	0	-0.577449	-2.290925	-2.688259
59	1	0	-0.774162	-1.958611	-3.714500
60	1	0	-0.994024	-3.310675	-2.608970
61	6	0	-2.348155	0.473980	0.252101

Rotational constants (GHZ): 0.1604149 0.0748308 0.0731400

Standard basis: 6-31G(d,p) (6D, 7F)

There are 676 symmetry adapted basis functions of A symmetry.

Two-electron integral symmetry is turned on.

676 basis functions, 1238 primitive gaussians, 679 cartesian basis functions

136 alpha electrons 134 beta electrons

Table S7 Fragment from the output file with the XYZ coordinates of the optimized structure of complex **2**, along with computational details, as obtained from the DFT (UB3LYP/6-311G(d,p); S=1) calculations (for atoms numbering see Figure S3).

Stoichiometry C₂₆H₂₆N₄NiO₄(3)

Framework group C1[X(C₂₆H₂₆N₄NiO₄)]

Deg. of freedom 177

Full point group C1 NOp 1

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Type	X	Y	Z	

1	28	0	-0.000580	-1.366635	0.008844	
2	8	0	-1.203438	0.073856	0.826841	
3	8	0	-5.104221	0.682640	-1.830288	
4	8	0	1.209247	0.053997	-0.833874	
5	7	0	-1.244946	-1.496297	-1.649761	
6	8	0	5.097260	0.713234	1.830188	
7	6	0	4.286000	1.652746	-0.225129	
8	7	0	1.239724	-1.470561	1.672541	
9	7	0	-1.158111	-2.795460	1.159305	
10	1	0	-2.148615	-2.644792	0.992798	
11	1	0	-0.975545	-3.778178	0.973674	
12	6	0	-3.130542	1.489028	0.964848	
13	6	0	-2.282206	0.450270	0.309305	
14	6	0	2.931092	2.168712	-2.165311	
15	1	0	2.029270	2.021779	-2.748028	
16	6	0	-2.406528	-0.918887	-1.839812	

17	6	0	-4.282556	1.662032	0.202346
18	7	0	1.153810	-2.815084	-1.120496
19	1	0	2.144300	-2.659534	-0.958624
20	1	0	0.973870	-3.795160	-0.919061
21	6	0	-4.215389	0.745638	-0.990884
22	6	0	5.270007	2.545483	-0.610031
23	1	0	6.158358	2.679672	-0.003663
24	6	0	3.137796	1.465147	-0.989848
25	6	0	-2.937297	0.016132	-0.886885
26	6	0	2.400169	-0.889023	1.856919
27	6	0	-5.264366	2.562486	0.574691
28	1	0	-6.155736	2.685172	-0.029686
29	6	0	4.212549	0.759851	0.985384
30	6	0	-3.221710	-1.218345	-3.082865
31	1	0	-3.328903	-2.297737	-3.223668
32	1	0	-2.713534	-0.823795	-3.969448
33	1	0	-4.203847	-0.759613	-3.024265
34	6	0	5.073064	3.262441	-1.797319
35	1	0	5.822951	3.973023	-2.127230
36	6	0	2.934765	0.028607	0.889258
37	6	0	3.210126	-1.164989	3.108797
38	1	0	3.317476	-2.241517	3.269947
39	1	0	2.697804	-0.754540	3.985723
40	1	0	4.192192	-0.706687	3.046124
41	6	0	-0.806343	-2.466291	2.559557
42	1	0	-1.203879	-3.196377	3.274068
43	1	0	-1.245391	-1.492068	2.773991
44	6	0	-5.061174	3.302553	1.746643

45	1	0	-5.809163	4.019771	2.066337
46	6	0	-2.917718	2.215375	2.125262
47	1	0	-2.013078	2.079397	2.706266
48	6	0	3.919599	3.077613	-2.562620
49	1	0	3.788329	3.648834	-3.475024
50	6	0	-0.719973	-2.413833	-2.658360
51	1	0	-0.950658	-2.099746	-3.680780
52	1	0	-1.161310	-3.416784	-2.534177
53	6	0	-3.903917	3.132324	2.509608
54	1	0	-3.767886	3.721237	3.409986
55	6	0	0.798063	-2.508556	-2.524947
56	1	0	1.193321	-3.250344	-3.228583
57	1	0	1.236848	-1.538132	-2.756402
58	6	0	0.711298	-2.369995	2.695545
59	1	0	0.939138	-2.038212	3.712980
60	1	0	1.152547	-3.375140	2.590186
61	6	0	2.285735	0.439689	-0.318341

Rotational constants (GHZ): 0.1513273 0.0784856 0.0745559

Standard basis: 6-311G(d,p) (5D, 7F)

There are 814 symmetry adapted basis functions of A symmetry.

Two-electron integral symmetry is turned on.

814 basis functions, 1377 primitive gaussians, 854 cartesian basis functions

136 alpha electrons 134 beta electrons

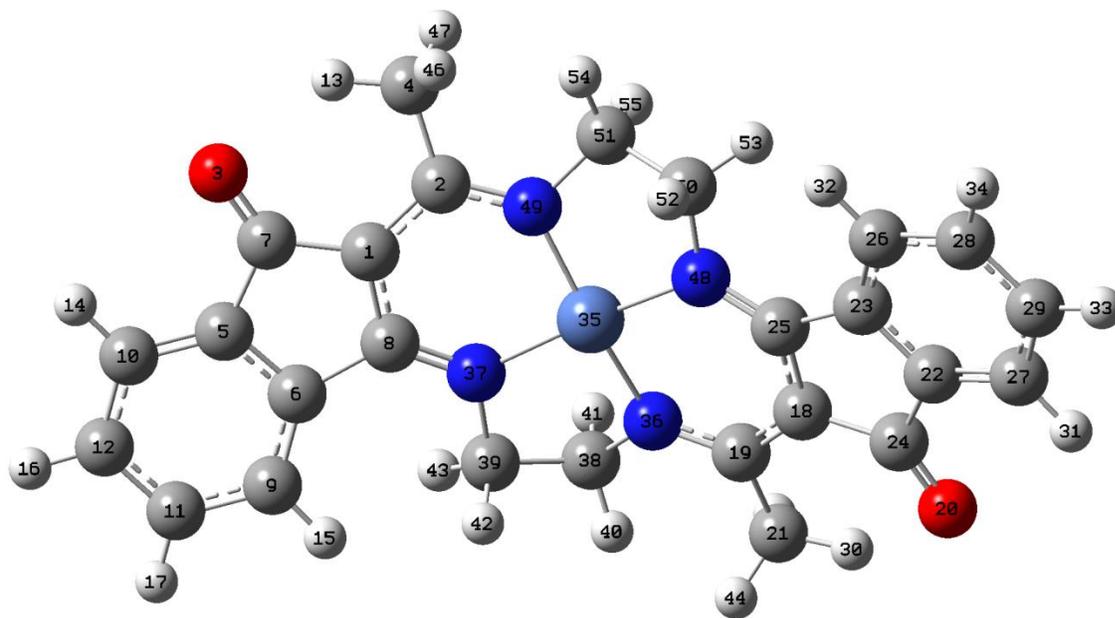


Figure S4 Optimized structure (RB3LYP/6-31G(d,p) ; S=0) of the fully cyclized cyclam-like complex (labels, atom numbering and coordination bonds are visualized for clarity).

Table S8 Selected bond lengths and interatomic distances (in Å) in the optimized structure of the fully cyclized cyclam-like complex, as obtained from the DFT-RB3LYP (S=0) calculations with different basis sets (for atoms numbering see Figure S4).

RB3LYP/6-31G(d,p)		RB3LYP/6-311+G(d,p)	
Bonds/distances	(Å)	Bonds/distances	(Å)
Ni35 – N36	1.8730	Ni35 – N36	1.8977
Ni35 – N37	1.8705	Ni35 – N37	1.8957
Ni35 – N48	1.8704	Ni35 – N48	1.8977
Ni35 – N49	1.8730	Ni35 – N49	1.8957
C19 – N36	1.3238	C19 – N36	1.3203
C8 – N37	1.3148	C8 – N37	1.3102
C25 – N48	1.3148	C25 – N48	1.3102
C2 – N49	1.3238	C2 – N49	1.3203
N36.....N48	2.73083	N36.....N48	2.7703
N49.....N48	2.58044	N49.....N48	2.6055

Table S9 Fragment from the output file with the XYZ coordinates of the optimized structure of the fully cyclized cyclam-like complex, along with computational details, as obtained from the DFT (RB3LYP/6-31G(d,p); S=0) calculations (for atoms numbering see Figure S4).

Stoichiometry C₂₆H₂₂N₄NiO₂

Framework group C1[X(C₂₆H₂₂N₄NiO₂)]

Deg. of freedom 159

Full point group C1 NOp 1

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	-2.978324	-1.252307	0.123963
2	6	0	-1.946901	-2.152646	0.485880
3	8	0	-4.972922	-2.659328	-0.138923
4	6	0	-2.299055	-3.604550	0.738558
5	6	0	-5.050495	-0.281066	-0.472723
6	6	0	-4.122193	0.769477	-0.388805
7	6	0	-4.380083	-1.579955	-0.146267
8	6	0	-2.809798	0.168918	0.025543
9	6	0	-4.533901	2.060464	-0.728437
10	6	0	-6.368527	-0.084711	-0.846479
11	6	0	-5.868171	2.268538	-1.109167
12	6	0	-6.781766	1.215336	-1.161139
13	1	0	-3.365102	-3.762530	0.589928
14	1	0	-7.043839	-0.933141	-0.895429
15	1	0	-3.860055	2.906006	-0.726819
16	1	0	-7.809144	1.405506	-1.457111

17	1	0	-6.189480	3.272061	-1.372078
18	6	0	2.978246	1.252182	0.124131
19	6	0	1.946759	2.152533	0.485862
20	8	0	4.972698	2.659394	-0.138577
21	6	0	2.299039	3.604391	0.738596
22	6	0	5.050513	0.281145	-0.472515
23	6	0	4.122295	-0.769489	-0.388712
24	6	0	4.380043	1.579919	-0.145734
25	6	0	2.809844	-0.169062	0.025713
26	6	0	4.534114	-2.060382	-0.728594
27	6	0	6.368545	0.084968	-0.846370
28	6	0	5.868389	-2.268276	-1.109403
29	6	0	6.781891	-1.214990	-1.161243
30	1	0	3.365120	3.762236	0.590039
31	1	0	7.043781	0.933466	-0.895200
32	1	0	3.860351	-2.905981	-0.727146
33	1	0	7.809277	-1.405024	-1.457278
34	1	0	6.189774	-3.271726	-1.372503
35	28	0	0.000057	-0.000048	0.452023
36	7	0	0.698394	1.730515	0.611643
37	7	0	-1.685301	0.795539	0.292771
38	6	0	-0.357115	2.640798	1.059506
39	6	0	-1.623682	2.259722	0.314159
40	1	0	-0.120018	3.691800	0.881811
41	1	0	-0.514167	2.514472	2.140085
42	1	0	-1.580791	2.653636	-0.710906
43	1	0	-2.495638	2.689308	0.815627
44	1	0	1.753499	4.263308	0.053870

45	1	0	2.028691	3.893948	1.759931
46	1	0	-1.753397	-4.263383	0.053840
47	1	0	-2.028716	-3.894107	1.759893
48	7	0	1.685339	-0.795697	0.292885
49	7	0	-0.698579	-1.730541	0.611716
50	6	0	1.623594	-2.259868	0.314368
51	6	0	0.356931	-2.640791	1.059665
52	1	0	1.580759	-2.653855	-0.710668
53	1	0	2.495461	-2.689483	0.815957
54	1	0	0.119788	-3.691793	0.882026
55	1	0	0.513918	-2.514408	2.140245

Rotational constants (GHZ): 0.2760358 0.0717839 0.0597433

Standard basis: 6-31G(d,p) (6D, 7F)

There are 629 symmetry adapted cartesian basis functions of A symmetry.

There are 626 symmetry adapted basis functions of A symmetry.

626 basis functions, 1154 primitive gaussians, 629 cartesian basis functions

125 alpha electrons 125 beta electrons

Table S10 Fragment from the output file with the XYZ coordinates of the optimized structure of the fully cyclized cyclam-like complex, along with computational details, as obtained from the DFT (RB3LYP/6-311+G(d,p); S=0) calculations (for atoms numbering see Figure S4).

Stoichiometry C₂₆H₂₂N₄NiO₂

Framework group C1[X(C₂₆H₂₂N₄NiO₂)]

Deg. of freedom 159; Full point group C1 NOp 1

Standard orientation:

Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z

1	6	0	-3.007118	1.244456	-0.160489
2	6	0	-1.961059	2.151828	-0.463347
3	8	0	-5.013098	2.643283	-0.041439
4	6	0	-2.306675	3.594265	-0.769446
5	6	0	-5.103092	0.279382	0.358611
6	6	0	-4.167934	-0.764623	0.361728
7	6	0	-4.421421	1.570933	0.025035
8	6	0	-2.838458	-0.173605	-0.015734
9	6	0	-4.586042	-2.041200	0.739762
10	6	0	-6.434842	0.087533	0.677774
11	6	0	-5.933327	-2.244490	1.066591
12	6	0	-6.853869	-1.199504	1.027943
13	1	0	-3.382174	3.740343	-0.765050
14	1	0	-7.118432	0.928503	0.661601
15	1	0	-3.909523	-2.878961	0.809983
16	1	0	-7.891045	-1.384754	1.283429
17	1	0	-6.259325	-3.236132	1.359710
18	6	0	3.007095	-1.244413	-0.160571
19	6	0	1.961046	-2.151776	-0.463426
20	8	0	5.013015	-2.643303	-0.041697
21	6	0	2.306741	-3.594190	-0.769545
22	6	0	5.103093	-0.279416	0.358502
23	6	0	4.167954	0.764612	0.361712
24	6	0	4.421386	-1.570934	0.024877
25	6	0	2.838452	0.173643	-0.015779
26	6	0	4.586109	2.041145	0.739854
27	6	0	6.434857	-0.087624	0.677639

28	6	0	5.933411	2.244376	1.066656
29	6	0	6.853927	1.199374	1.027893
30	1	0	3.382253	-3.740195	-0.765144
31	1	0	7.118424	-0.928612	0.661390
32	1	0	3.909623	2.878919	0.810179
33	1	0	7.891115	1.384578	1.283366
34	1	0	6.259440	3.235985	1.359850
35	28	0	-0.000017	0.000018	-0.352438
36	7	0	0.700971	-1.758262	-0.487486
37	7	0	-1.709742	-0.807560	-0.217182
38	6	0	-0.359841	-2.695176	-0.867661
39	6	0	-1.631200	-2.270066	-0.158395
40	1	0	-0.122981	-3.727504	-0.606333
41	1	0	-0.510698	-2.652315	-1.954412
42	1	0	-1.598284	-2.597493	0.888305
43	1	0	-2.491765	-2.734448	-0.643458
44	1	0	1.870183	-4.263872	-0.021805
45	1	0	1.904434	-3.881322	-1.745081
46	1	0	-1.870070	4.263911	-0.021701
47	1	0	-1.904342	3.881383	-1.744977
48	7	0	1.709726	0.807600	-0.217200
49	7	0	-0.700990	1.758302	-0.487446
50	6	0	1.631175	2.270109	-0.158419
51	6	0	0.359800	2.695219	-0.867652
52	1	0	1.598290	2.597542	0.888281
53	1	0	2.491715	2.734492	-0.643517
54	1	0	0.122931	3.727546	-0.606321
55	1	0	0.510627	2.652353	-1.954407

Rotational constants (GHZ): 0.2823768 0.0708146 0.0587813

Standard basis: 6-311+G(d,p) (5D, 7F)

There are 894 symmetry adapted basis functions of A symmetry.

Two-electron integral symmetry is turned on.

894 basis functions, 1422 primitive gaussians, 933 cartesian basis functions

125 alpha electrons 125 beta electrons

Table S11 Calculated Mulliken charges for complexes 1 and 2 – data shown for C- and O-atoms from coordinated carbonyl and enolic, as obtained from the DFT-UB3LYP/6-31G(d,p) (S=1) (for atoms numbering see Figures S2 and S3).

Complex 1		Complex 2	
Enolic C-O		Imine C-N	
C26/C11	0.406	C16/C26	0.345
O6/O8	-0.618	N5/N8	-0.618
Carbonyl C=O		Carbonyl C=O	
C19/C25	0.373	C13/C61	0.368
O7/O5	-0.629	O20/O40	-0.619

Infrared spectra in KBr and CsI

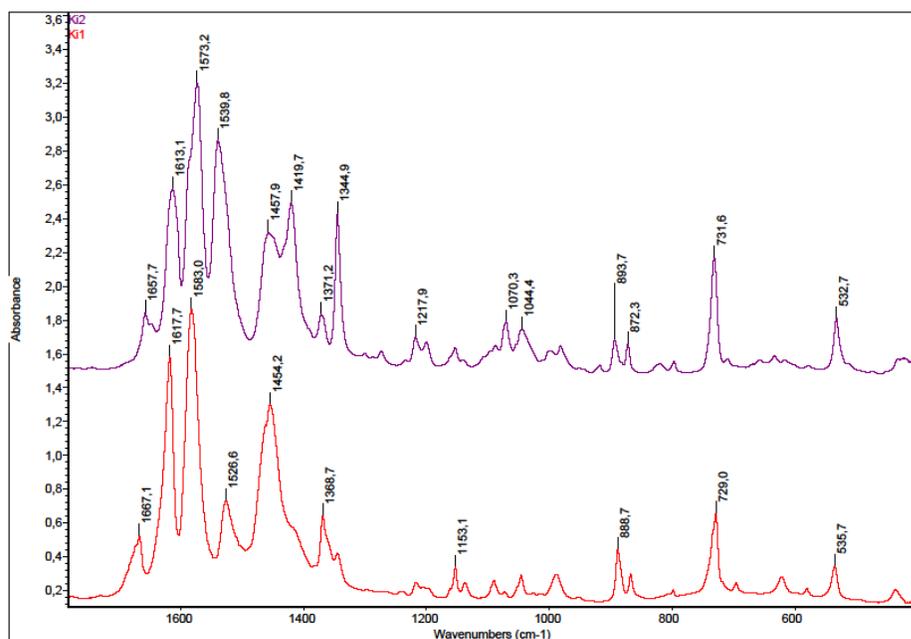


Figure S5 IR spectra of complex **1** (Ki1, bottom in red) and complex **2** (Ki2, top in violet) in the region of 400 – 1800 cm⁻¹, obtained from KBr pellets.

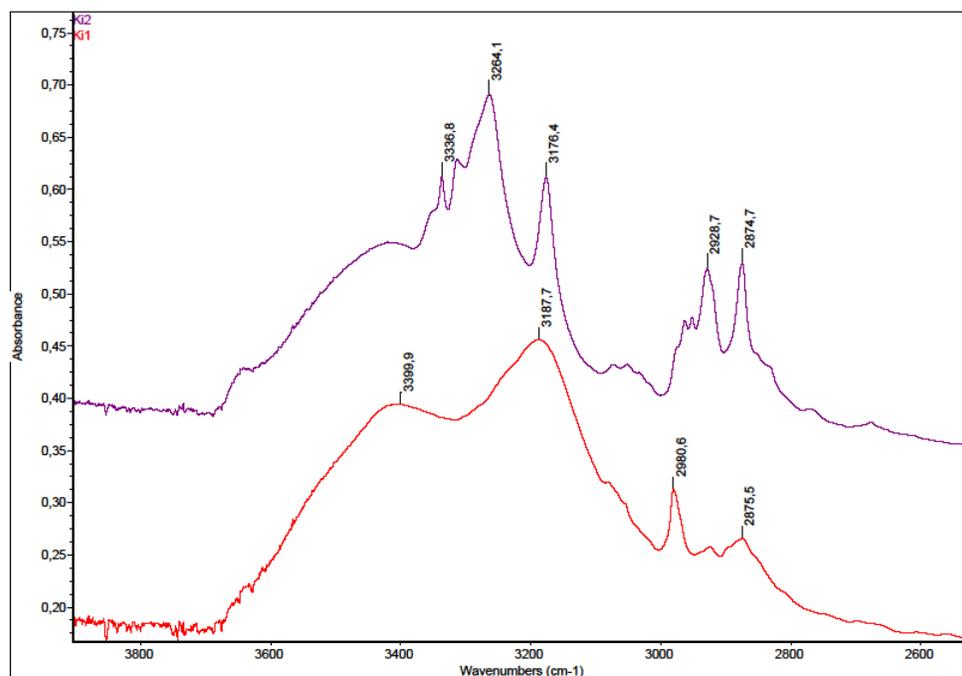


Figure S6 IR spectra of complex **1** (Ki1, bottom in red) and complex **2** (Ki2, top in violet) in the region of 2500 – 3900 cm⁻¹, obtained from KBr pellets.

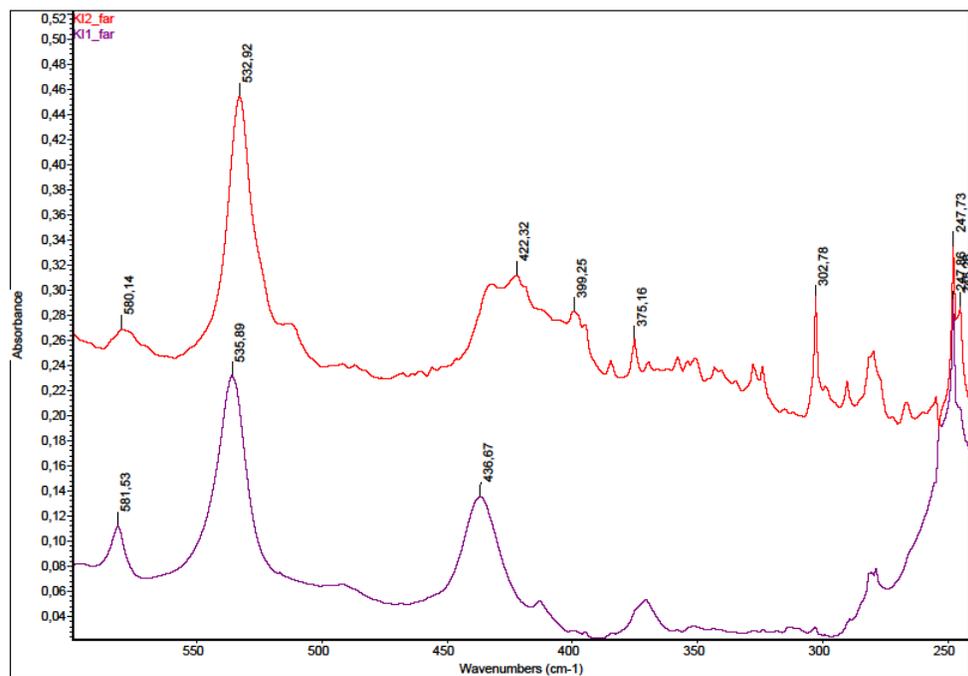


Figure S7 IR spectra of complex **1** (Ki1, bottom in red) and complex **2** (Ki2, top in violet) in the region of 240 – 600 cm⁻¹, obtained from CsI pellets.