## Supporting Information

# *In situ* transformation of a tridentate to a tetradentate unsymmetric Schiff base ligand *via* deaminative coupling in Ni(II) complexes: crystal structures, magnetic properties and catecholase activity study

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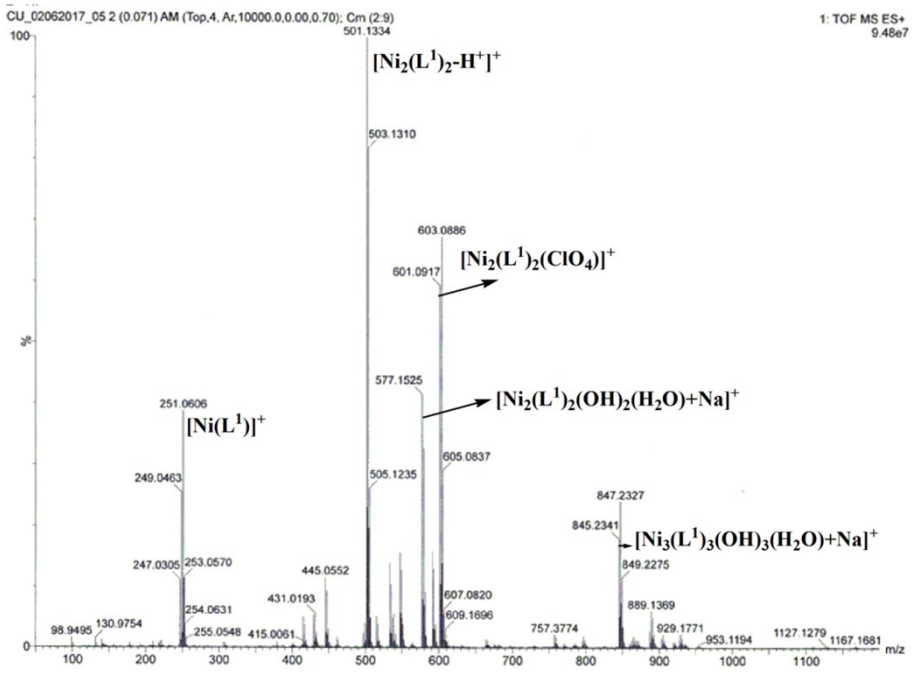


**Fig. S1** ESI-MS spectrum of **1** in methanol.

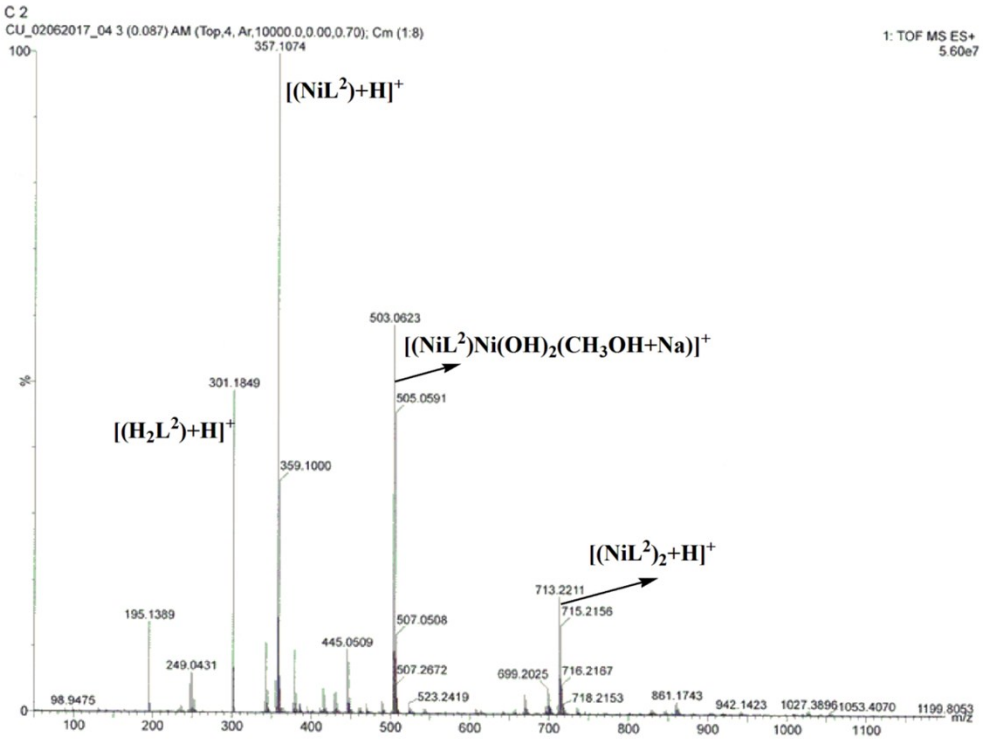


**Fig. S2** ESI-MS spectrum of **2** in methanol.

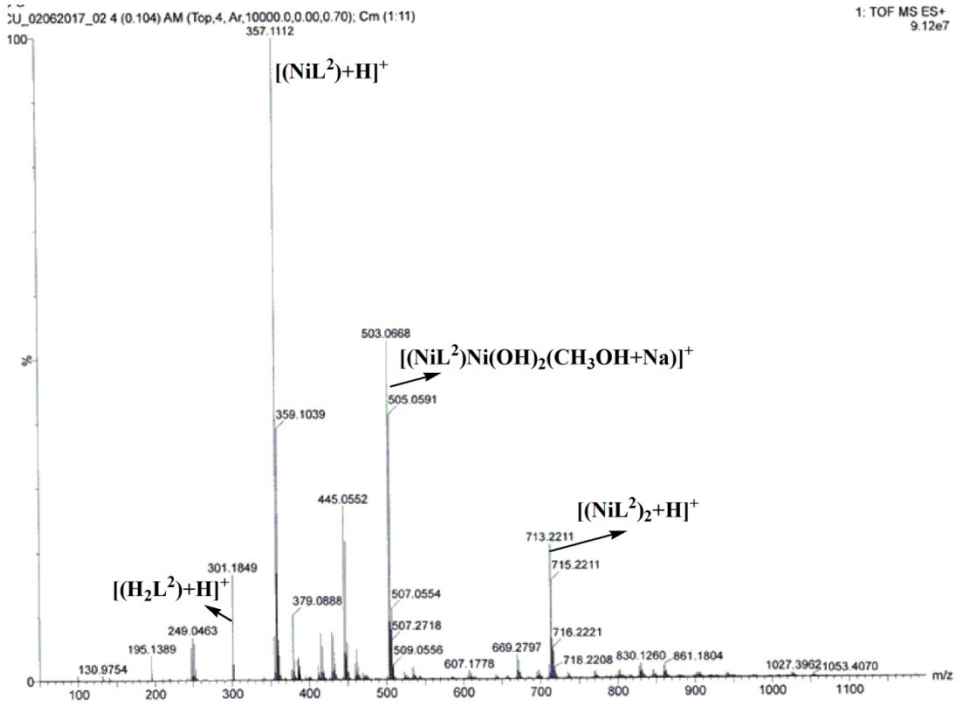


**Fig. S3** ESI-MS spectrum of **3** in methanol.

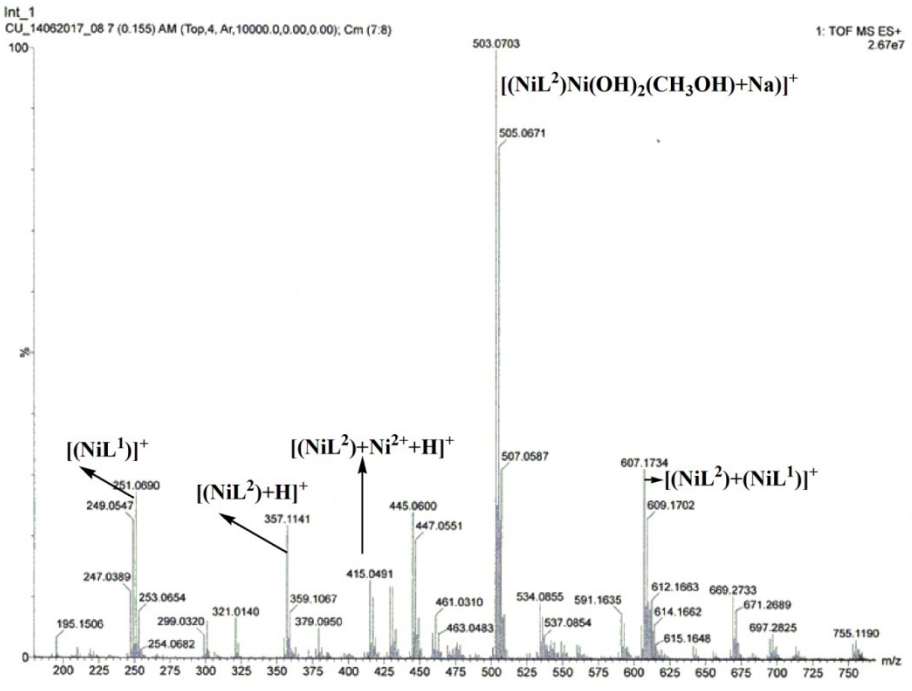


**Fig. S4** ESI-MS spectrum of reaction mixture from which metal complex **2** is isolated after one week in methanol.

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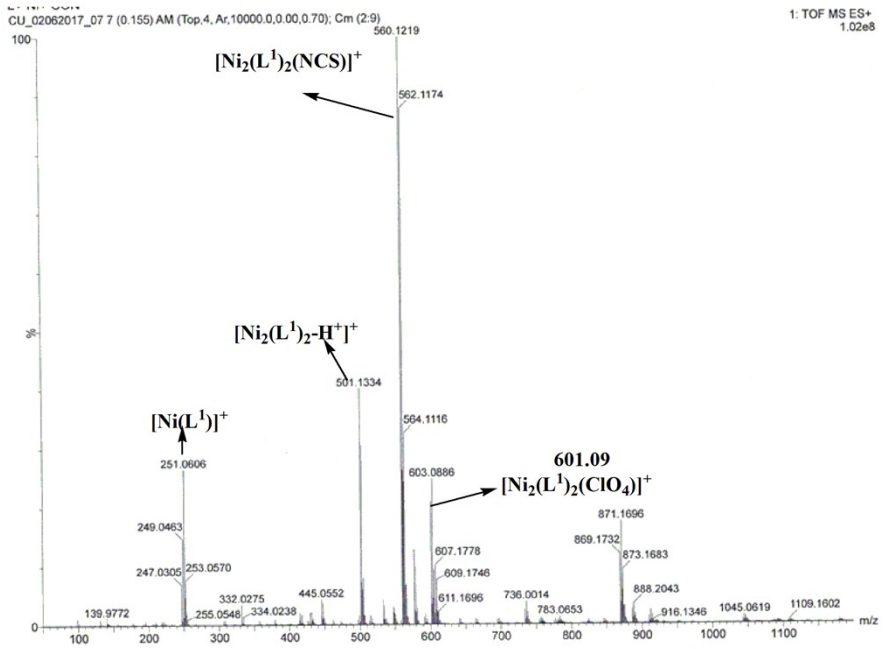


**Fig. S5** ESI-MS spectrum of reaction mixture in methanol taken immediately after mixing *in situ* generated **1** and $NH_4SCN$ in 1:2 ratios.

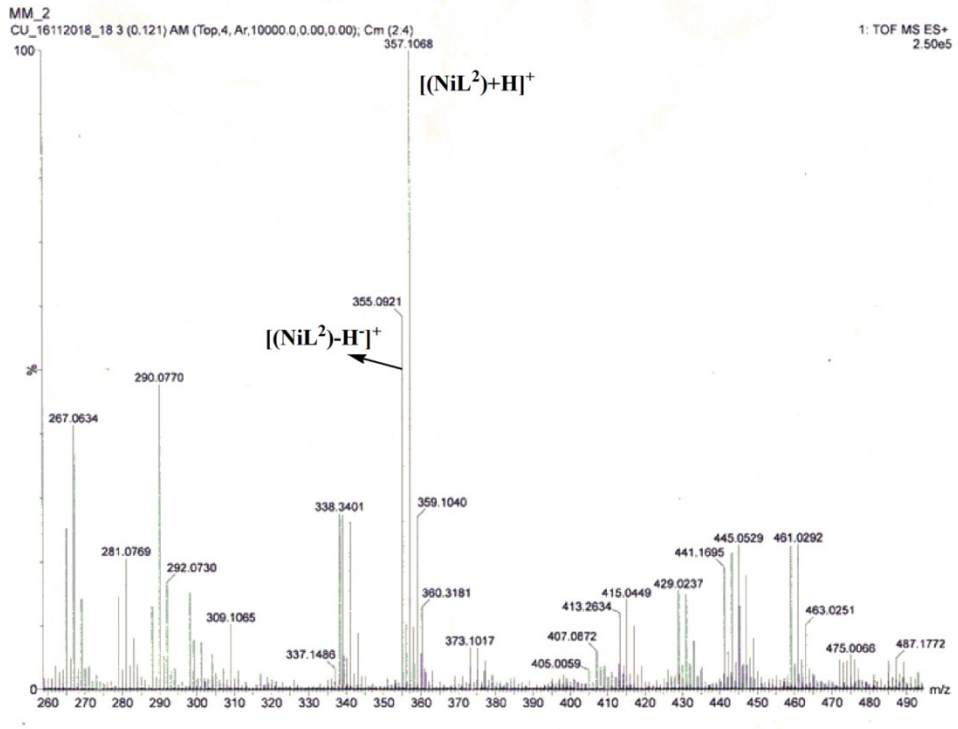


**Fig. S6** ESI-MS spectrum of the 1:1 molar mixture of **1** and purified nickel perchlorate complex of the unreduced ligand taken after one week in methanol.

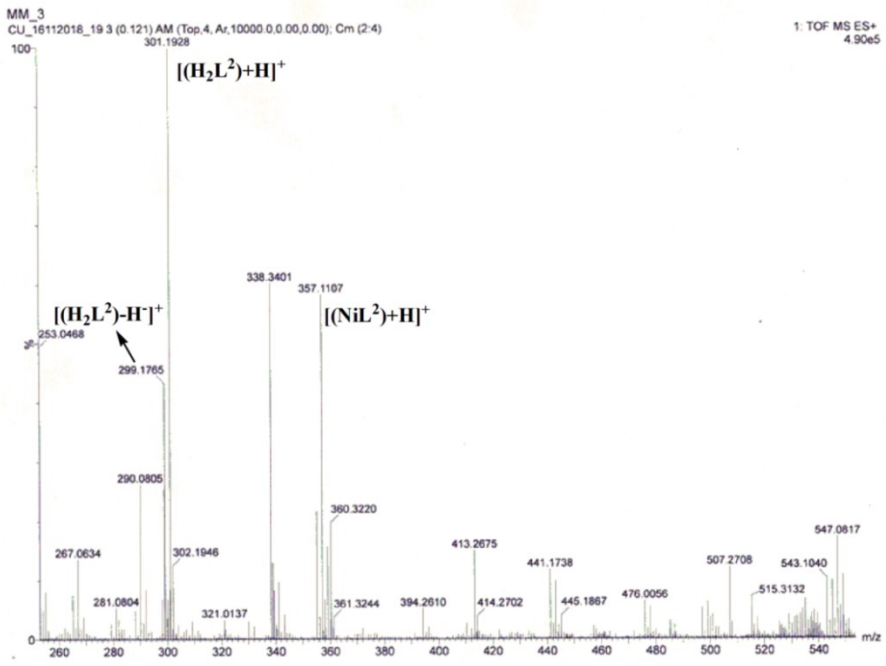


**Fig. S7** ESI-MS spectrum of the 1:1:4 molar mixture of **1,** purified nickel perchlorate complex of the unreduced ligand and $NH_4SCN$ taken after one week in methanol.

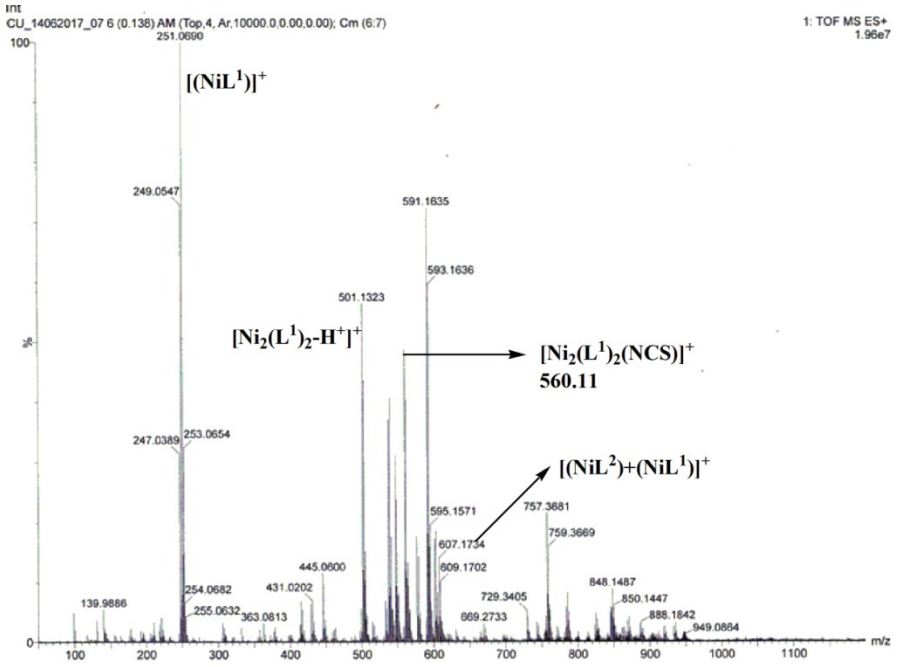

**Fig. S8** ESI-MS spectrum of the 1:2 molar mixture of **1** and $NH_4SCN$ taken after one week in methanol.

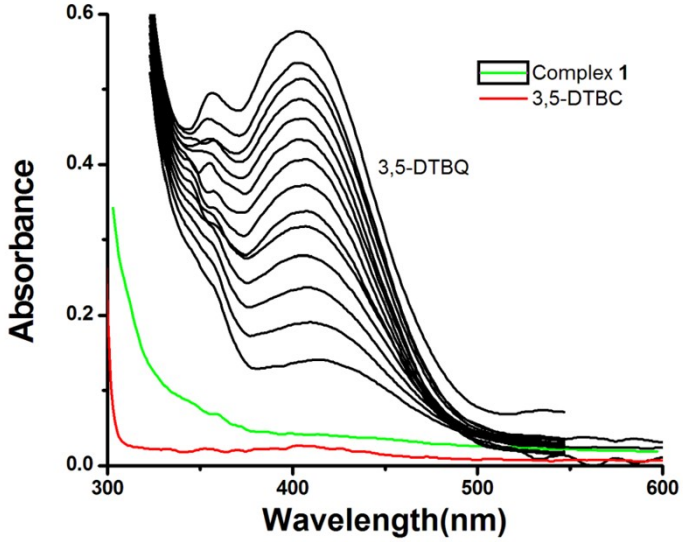


**Fig. S9** Increase in absorbance around 401 nm, after addition of equal volumes $1\times10^{-2}$(M) of 3,5-DTBC to a $1\times10^{-4}$ M methanol solution of **1**. The spectra were recorded in every 5 min interval.

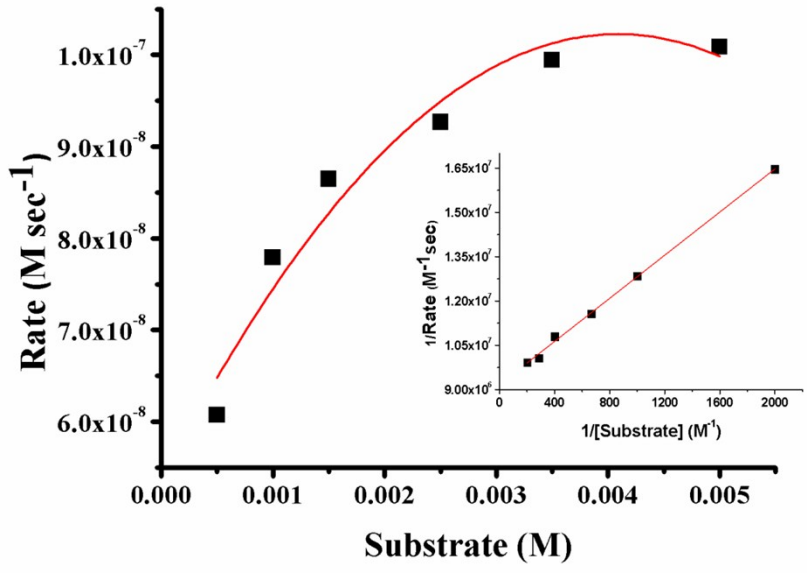


**Fig. S10** Plot of the initial rates *vs* substrate concentration for the oxidation of 3,5-DTBC catalyzed by **1**. The inset shows Lineweaver–Burk plot.

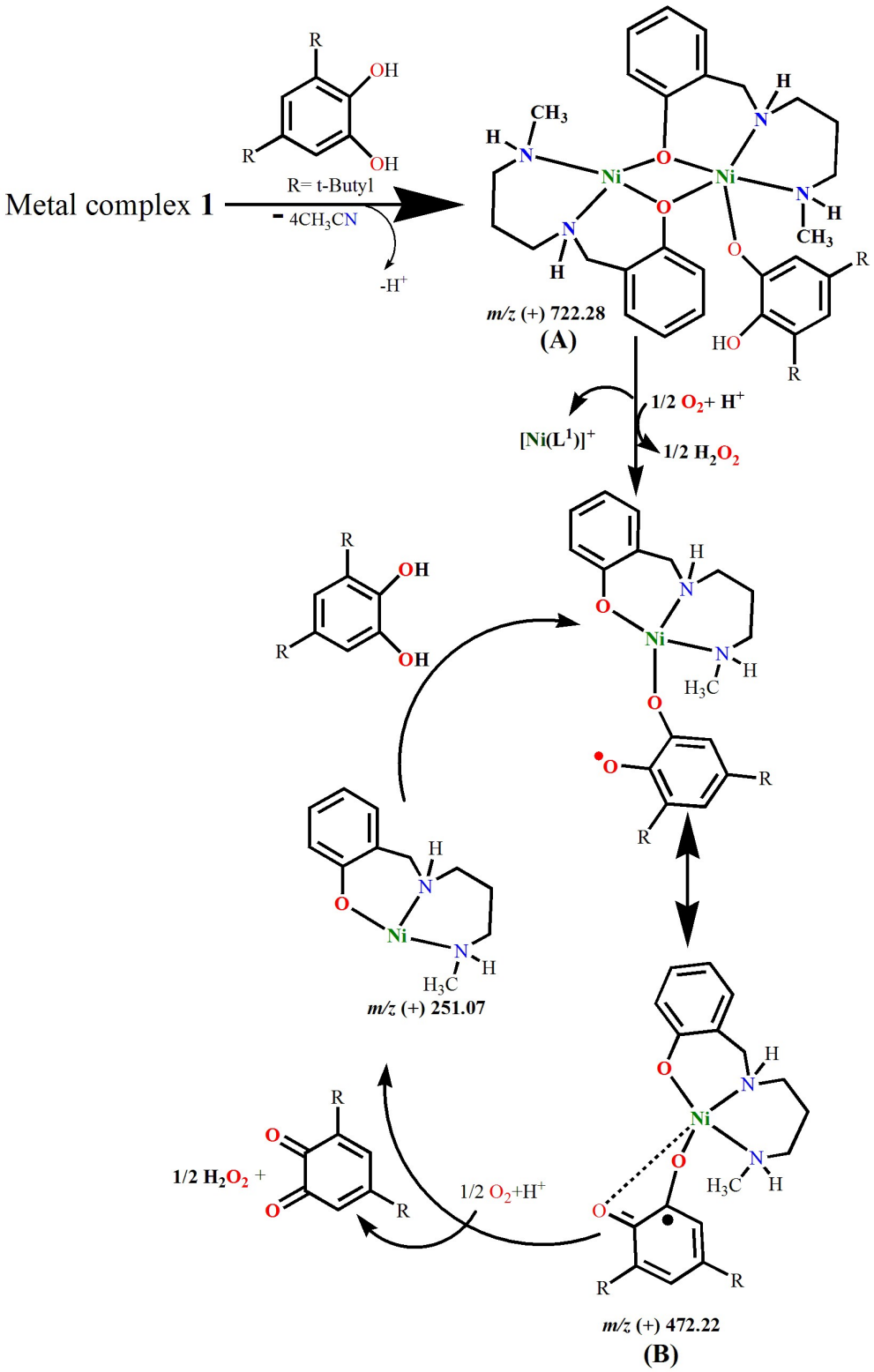


**Fig. S11** Proposed mechanism for catalytic oxidation of 3,5-DTBC to 3,5-DTBQ by **1**.

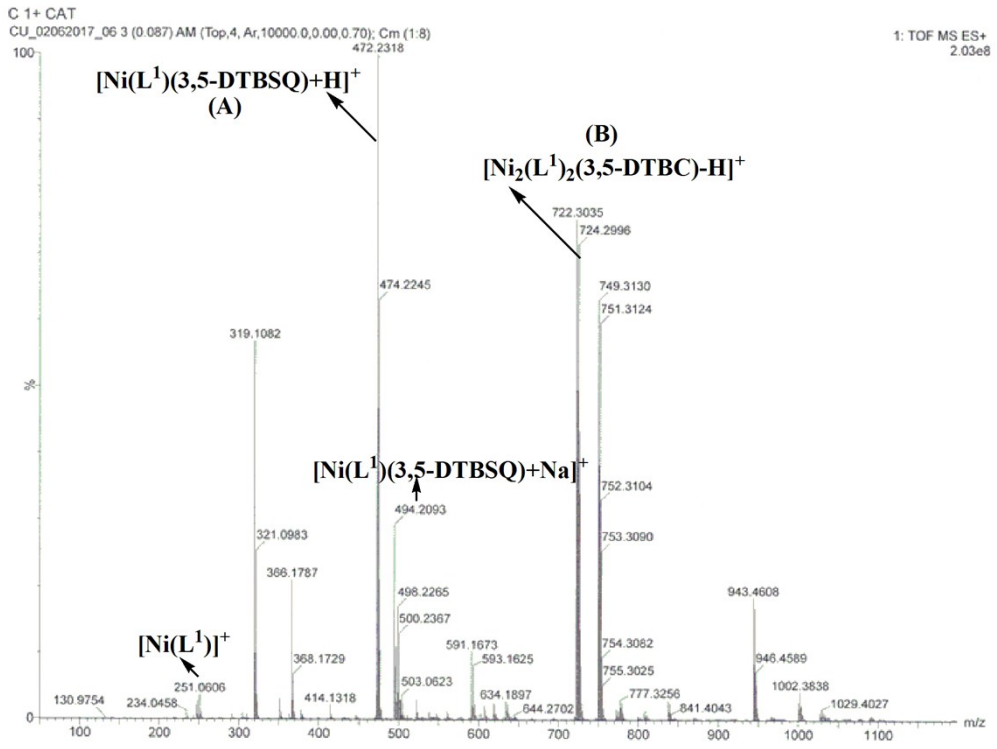


**Fig. S12** ESI-MS spectrum of **1** with 3,5-DTBC in methanol.

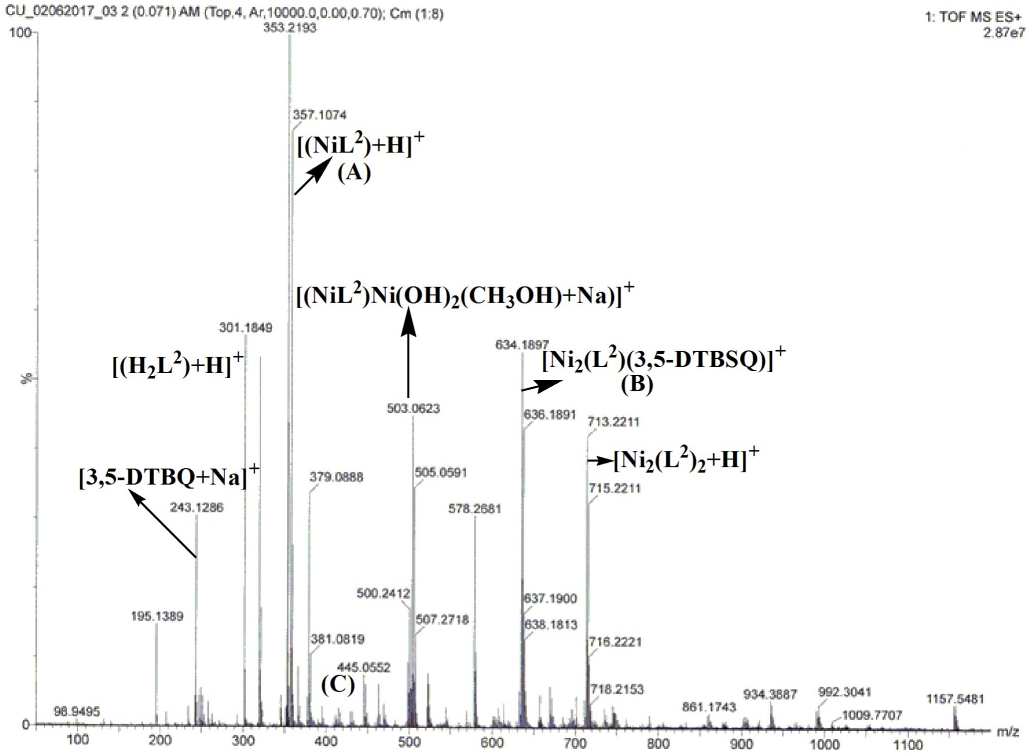


**Fig. S13** ESI-MS spectrum of **3** with 3,5-DTBC in methanol.

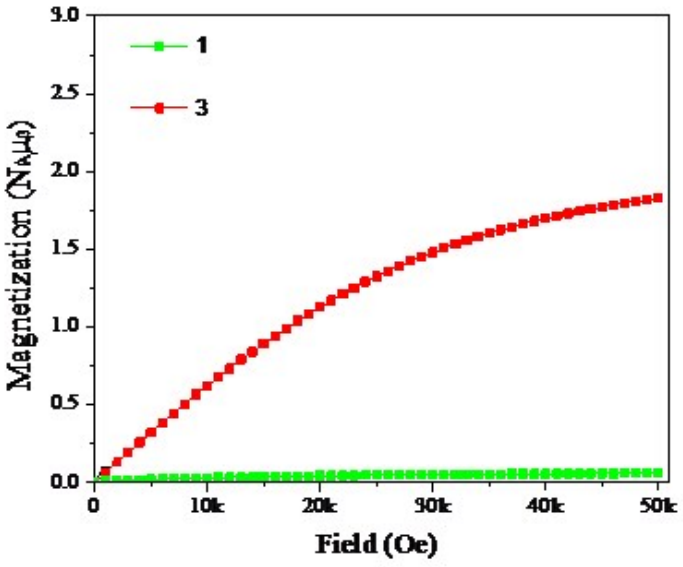


**Fig. S14** Field dependent molar magnetization for **1** and **3.**

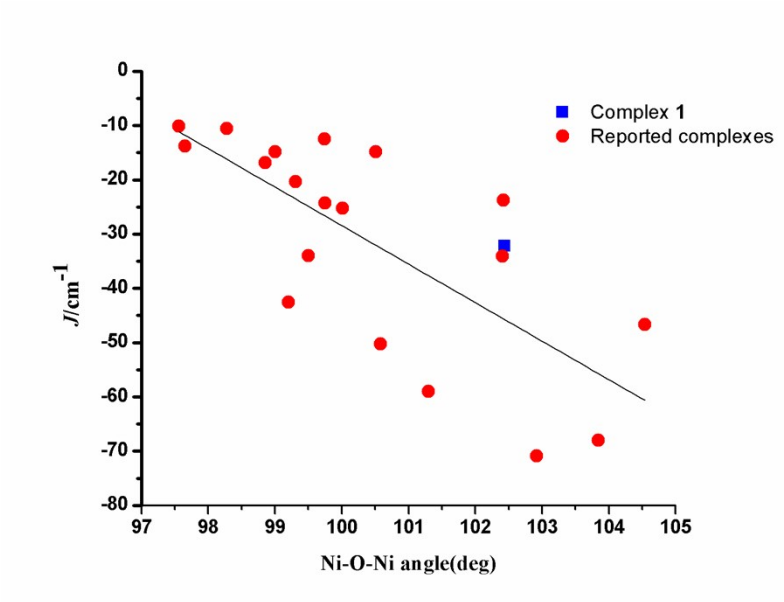


**Fig. S15** Plot of experimental *J* values in $cm^{-1}$ with Ni-O(phenoxido)-Ni angles.

**Table S1** Selected bond lengths (Å) for **1–3.**

| Bonds length | **1** | **2** | **3** |
|---|---|---|---|
| Ni(1)−O(10) | 2.060(2) | 2.044(4) | 2.100(2) |
| Ni(1)−O(1) | | | 2.134(4) |

| | | | |
|---|---|---|---|
| Ni(1)−O(2) | | | 2.132(3) |
| Ni(1)−N(1) | 2.208(3) | 2.029(6) | |
| Ni(1)−O(10)[a] | 2.055(2) | | |
| Ni(1)−N(2) | 2.097(4) | 2.155(6) | |
| Ni(1)−N(18) | 2.096(3) | 2.128(6) | 2.092(3) |
| Ni(1)−N(22) | 2.097(3) | 2.117(6) | 2.133(3) |
| Ni(1)−O(31) | | 2.067(5) | 2.051(2) |
| Ni(2)−O(10) | | | 2.181(2) |
| Ni(2)−O(31) | | | 2.053(2) |
| Ni(2)−N(1) | | | 2.063(3) |
| Ni(2)−O(10)[a] | | | 2.181(2) |
| Ni(2)−O(31)[a] | | | 2.053(2) |
| Ni(2)−N(1)[a] | | | 2.063(3) |

[a]*=1-x, 1-y, 1-z* for complex **1**, [a]*= -x, y, 1/2-z* for complex **3**

**Table S2**. Selected bond angles (°) for **1**.

| | **1** |
|---|---|
| O(10)–Ni(1)–N(1) | 88.40(9) |
| O(10)–Ni(1)–N(2) | 101.89(11) |
| O(10)–Ni(1)–O(10)[a] | 77.56(8) |
| O(10)–Ni(1)–N(18) | 167.26(9) |
| O(10)–Ni(1)–N(22) | 90.74(9) |
| N(1)–Ni(1)–N(2) | 86.62(12) |
| O(10)[a]–Ni(1)–N(1) | 94.39(9) |
| N(1)–Ni(1)–N(18) | 85.63(11) |
| N(1)–Ni(1)–N(22) | 176.14(11) |
| O(10)[a]–Ni(1)–N(2) | 178.84(11) |
| N(2)–Ni(1)–N(18) | 89.01(12) |

| | |
|---|---|
| N(2)–Ni(1)–N(22) | 89.88(12) |
| O(10)[a]–Ni(1)–N(18) | 91.66(9) |
| O(10)[a]–Ni(1)–N(22) | 89.10(9) |
| N(18)–Ni(1)–N(22) | 95.94(10) |
| Ni(1)–O(10)–Ni(1)[a] | 102.44(8) |

[a]=*1-x, 1-y, 1-z*

**Table S3** Selected bond angles (°) for **2–3.**

| | **2** | **3** |
|---|---|---|
| O(1)-Ni(1)-O(2) | | 171.10(12) |
| O(1)-Ni(1)-O(10) | | 88.13(11) |
| O(1)-Ni(1)-O(31) | | 86.97(12) |
| O(1)-Ni(1)-N(18) | | 93.30(14) |
| O(1)–Ni(1)–N(22) | | 97.31(13) |
| O(2)–Ni(1)–O(10) | | 84.52(10) |
| O(2)–Ni(1)–O(31) | | 86.97(9) |
| O(2)–Ni(1)–N(18) | | 92.07(11) |
| O(2)–Ni(1)–N(22) | | 89.54(11) |
| N(1)–Ni(1)–N(2) | 173.2(2) | |
| N(1)–Ni(1)–N(18) | 92.8(2) | |
| N(1)–Ni(1)–N(22) | 92.3(2) | |
| N(2)–Ni(1)–N(18) | 91.0(2) | |
| N(2)–Ni(1)–N(22) | 93.3(2) | |

| | | |
|---|---|---|
| O(10)–Ni(1)–N(1) | 89.8(2) | |
| O(10)–Ni(1)–N(2) | 84.49(19) | |
| O(31)–Ni(1)–N(1) | 92.1(2) | |
| O(31)–Ni(1)–N(2) | 83.8(2) | |
| O(10)–Ni(1)–O(31) | 86.39(17) | 81.18(9) |
| O(10)–Ni(1)–N(18) | 91.0(2) | 92.90(11) |
| O(10)–Ni(1)–N(22) | 176.7(2) | 172.45(10) |
| O(31)–Ni(1)–N(18) | 174.4(2) | 174.06(11) |
| O(31)–Ni(1)–N(22) | 90.96(19) | 93.90(11) |
| N(18)–Ni(1)–N(22) | 91.5(2) | 91.95(13) |
| O(10)–Ni(2)–O(31) | | 79.22(9) |
| O(10)–Ni(2)–N(1) | | 91.18(11) |
| O(10)–Ni(2)O(10)[a] | | 87.27(8) |
| O(10)–Ni(2)–O(31)[a] | | 86.85(9) |
| O(10)–Ni(2)–N(1)[a] | | 177.60(11) |
| O(31)–Ni(2)–N(1) | | 94.67(11) |
| O(10)[a] –Ni(2)–O(31) | | 86.85(9) |
| O(31)–Ni(2)–O(31)[a] | | 160.76(9) |
| O(31)–Ni(2)–N(1)[a] | | 98.87(11) |
| O(10)[a]–Ni(2)–N(1) | | 177.60(11) |
| O(31)[a]–Ni(2)–N(1) | | 98.87(11) |
| N(1)–Ni(2)–N(1)[a] | | 90.42(13) |
| O(10)[a]–Ni(2)–O(31)[a] | | 79.22(9) |
| O(10)[a]–Ni(2)–N(1)[a] | | 91.19(11) |
| O(31)[a]–Ni(2)–N(1)[a] | | 94.67(11) |

[a]= *-x, y, 1/2-z*

**Table S4** Different concentrations of substrate (3,5-DTBC) in methanol for kinetic measurement.

| Metal complex and its concentration (M) | 3,5-DTBC (M) |
|---|---|
| **1**($5\times10^{-5}$) | 0.005, 0.0035, 0.0025, 0.0015, 0.001, 0.0005 |
| **3**($5\times10^{-5}$) | 0.0075, 0.0065, 0.005, 0.0035, 0.0025, 0.0015, 0.001, 0.0005 |

| | $V_{max}$(M $sec^{-1}$) | Std. error | $K_M$ (M) | Std. error | $k_{cat}$ ($h^{-1}$) |
|---|---|---|---|---|---|
| **1** | $1.09\times10^{-7}$ | $8.83\times10^{-8}$ | $0.39\times10^{-3}$ | $8.32\times10^{-6}$ | 7.9 |
| **3** | $2.01\times10^{-7}$ | $1.22\times10^{-8}$ | $2.30\times10^{-3}$ | $6.82\times10^{-5}$ | 14.5 |

**Table S5** Kinetic parameters for the oxidation of 3,5-DTBC catalyzed by **1** and **3** in methanol.

**Table S6** Experimental *J* value vs. ∠Ni–O–Ni angle for earlier reported diphenoxido bridged dinuclear $Ni^{II}$ complexes.

| Compounds | *J* / $cm^{-1}$ | Ni-O-Ni angle (°) | References |
|---|---|---|---|
| $[Ni_2L^1{}_2(NO_2)_2]\cdot CH_2Cl_2\cdot C_2H_5OH$, $2H_2O$ | –10.52 | 98.28 | 45a |
| $[Ni_2L^2{}_2(NO_3)_2]$ | –20.34 | 99.31 | 42a |
| $[Ni_2L^2{}_2(NO_2)_2]$ | –25.25 | 100.01 | 42a |
| $[Ni_2(L^3)_2(NCS)_2]$ | −46.64 | 104.54 | 26a |
| $[Ni_2(L^4)_2(NCS)_2]$ | −70.9 | 102.92 | 26a |
| $[Ni_2(L^5)_2(NCS)_2]$ | −68.04 | 103.84 | 26a |
| $[Ni_2(L^6)_2(NO_3)_2]$ | –24.27 | 99.75 | 38 |
| $[Ni_2(L^7)_2(OAc)_2]$ | –50.28 | 100.58 | 45b |
| $\{Ni(Hsalhyph)Cl(H_2O)\}_2$ | –14.80 | 99 | 45c |
| $[Ni_2L^8(H_2O)_4(ClO_4)_2.\ 4NH_2CONH_2$ | −34 | 99.5 | 45d |

| | | | |
|---|---|---|---|
| [ $Ni_2L^8(NCS)_2(H_2O)_2$]. $2Me_2NCHO$ | −42.6 | 99.2 | 45d |
| $[Ni_2L^8(MeOH)_2(ClO_4)_2]$.2NHEt | −59 | 101.3 | 45d |
| $[NiL^9{}_2(o\text{-}HSal)]\cdot 2H_2O$ | –13.78 | 97.65 | 45e |
| $[Ni_2L^9{}_2(o\text{-}Hap)_2]$ | –16.87 | 98.85 | 45e |
| $[Ni_2L^9{}_2(o\text{-}Hnap)_2]$ | –10.14 | 97.56 | 45e |
| $[Ni_2L^{10}{}_2(CH_3CN)_4](ClO_4)_2\cdot 2CH_3CN$ | −34.10 | 102.41 | 42c |
| $[Ni_2L^{10}{}_2(NCS)_2\,(CH_3CN)_2]$ | −23.72 | 102.42 | 42c |
| $[Ni_2(L^{11})_2(OAc)_2(H_2O)_2]\cdot CH_3CN$ | −12.48 | 99.74 | 45f |
| $[Ni_2(L^{12})_2(SCN)_2(CH_3OH)_2]\cdot CH_3OH$ | −14.87 | 100.51 | 45f |
| $[Ni_2L_2(CH_3CN)_4](ClO_4)_2\cdot CH_3CN$ | −32.22 | 102.44 | This work |

$HL^1$= 2-[(3-amino-propylimino)-methyl]-phenol

$HL^2$= 2-({[3-(dimethylamino)propyl]imino}methyl)phenol

$HL^3$= 2-[1-(3-methylamino-propylamino)-ethyl]-phenol

$HL^4$= 2-[1-(2-dimethylamino-ethylamino)-ethyl]-phenol

$HL^5$=2-[1-(3-dimethylamino-propylamino)-ethyl]-phenol

$HL^6$= 2-[(3-Methylamino-propylimino)-methyl]-phenol

$HL^7$= 2-[(3-methylamino-propylimino)-methyl]-phenol)

$HL^9$= 2-((E)-(3-aminopentylimino)methyl)phenol

$HL^{10}$= 2-[(3-methylamino-propylamino)-methyl]-4-nitrophenol

$HL^{11}$= 4-bromo-2-[(2-hydroxy-1,1-dimethyl-ethylimino)-methyl]-phenol

$HL^{12}$= 4-bromo-2-[(2-hydroxy-1,1-dimethyl-ethylamino)-methyl]-phenol

**Table S7** Selected Ni(II) complexes showing catecholase activity with $K_{cat}$ values.

| Ni complexes | Solvent | $K_{cat}(h^{-1})$ | Ref. |
|---|---|---|---|
| $[Ni_2(L_1)(SCN)_2(AcO)\text{-}(H_2O)]$ | $CH_3OH$ | 863.9 | 41 |
| $[Ni_2(L_2)(SCN)_3(CH_3OH)_2]$ | $CH_3OH$ | 161.1 | 41 |

| | | | |
|---|---|---|---|
| $[Ni_2(L_1)(SCN)_3(H_2O)(CH_3OH)]$ | $CH_3OH$ | 154.0 | 41 |
| $[Ni_2(L_2)(SCN)(AcO)_2]$ | $CH_3OH$ | 303.7 | 41 |
| $[Ni_2(L_1)(N_3)3(H_2O)_2]$ | $CH_3OH$ | 172.8 | 41 |
| $[Ni_2(L_2)(N_3)_3(H_2O)_2]$ | $CH_3OH$ | 264.1 | 41 |
| $[Ni_2(L_3)(AcO)_2\text{-}(N(CN)_2)]_n$ | $CH_3OH$ | 128.6 | 41 |
| $[Ni_2(L_4)(AcO)_2(N(CN)_2)]$ | $CH_3OH$ | 275.0 | 41 |
| $[Ni_2(L_5)_2(NCS)_2]$ | $CH_3CN$ | 64.1 | 26a |
| $[Ni_2(L_6)_2(NCS)_2]$ | $CH_3CN$ | 51.1 | 26a |
| $[Ni_2(L_7)_2(NCS)_2]$ | $CH_3CN$ | 81.7 | 26a |
| $[NiL_8(H_2O)_3]I_2\cdot H_2O$ | $CH_3OH$ | 92.6 | 40a |
| $[NiL_8(H_2O)_3]Br_2\cdot H_2O$ | $CH_3OH$ | 84.8 | 40a |
| $[Ni_2(L_9)_2(H_2O)_4](NO_3)_2$ | $CH_3OH$ | 474 | 40a |
| $[Ni_5(L_{10})_2(OAc)_6(OH)_2]\cdot 5.5\ H_2O$ | $CH_3OH$ | 477 | 40a |
| $[NiL_8(H_2O)_3](NO_3)_2$ | $CH_3OH$ | 52.6 | 40a |
| $[NiL_{11}(H_2O)_3](NO_3)_2$ | $CH_3OH$ | 129 | 40a |
| $[Ni_4(L_{12})_2(H_2O)_8(\mu_2H_2O)_2](NO_3)_6(H_2O)_6$ | DMF | 12 | 39e |
| $[Ni_2L_{13}(PhCOO)(H_2O)_2]ClO_4$ | $CH_3OH$ | 167.4 | 26b |
| $[Ni_2L^1{}_2(CH_3CN)_4](ClO_4)_2\cdot 2CH_3CN$ | $CH_3OH$ | 7.9 | Present work |
| $[Ni_3(L^2)_2(NCS)_2(H_2O)_4]\cdot H_2O$ | $CH_3OH$ | 14.5 | Present work |

1. $HL_1$=2,6-bis($R_2$-iminomethyl)-4-$R_1$-phenol ; R1 = tert-butyl, R2 = N,N-dimethylethylene
2. $HL_2$=2,6-bis($R_2$-iminomethyl)-4-$R_1$-phenol; R1 = tert-butyl, $R_2$ = 2-(N-ethyl) pyridine
3. $HL_3$=2,6-bis($R_2$-iminomethyl)-4-$R_1$-phenol ; R1 = methyl, R2 = N,N-dimethylethylene
4. $HL_4$=2,6-bis($R_2$-iminomethyl)-4-$R_1$-phenol ; R1 = methyl, R2 = 2-(N-ethyl) pyridine
   deen = 2-(diethylamino) ethylamine, dmpn = 3-(dimethylamino)-1-propylamine, and modaH = diacetyl monoxime
5. $HL_5$=2-[1-(3-methylamino-propylamino)-ethyl]-phenol
6. $HL_6$=2-[1-(2-dimethylamino-ethylamino)-ethyl]-phenol
7. $HL_7$=2-[1-(3-dimethylamino-propylamino)-ethyl]-phenol
8. $HL_8$ = 2-[(2-piperazin-1-ylethylimino)methyl]phenol
9. $HL_9$= 2-formyl-4-methyl-6-(1-(2-aminomethyl)piperidine)-iminomethylphenol
10. $HL_{10}$= 4-methyl-2,6-bis(1-(2-aminomethyl)piperidine)-iminomethylphenol
11. $HL_{11}$=2-[(2-piperazin-1-ylethylimino)methyl]-4-chlorophenol
12. $HL_{12=}$ 2,6 diformyl-4-isopropyl phenol
13. $HL_{13=}$ 2-[(3-methylamino-propylamino)-methyl]-4-nitrophenol