SUPPLEMENTAL INFORMATION

Selective Generation of Aldimine and Ketimine Tautomers of the Schiff Base Condensates of Amino Acids with Imidazole Aldehydes or of Imidazole Methanamines with Pyruvates—Isomeric Control with 2- vs 4- substituted Imidazoles

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Table S1 Crystallographic Data for new Nickel Ketimine and Aldimine complexes

Table S2. Selected structural parameters, distances in Å and trans angles in °, involving the nickel(II) for the aldimine and ketimine forms of a) R=Me Ni(A_{Ald}-5Me4Im)$_2$ and Ni(A_{Ket}-5Me4Im)$_2$ b) R=iPr Ni(V_{Ald}-5Me4Im)$_2$ and and c) R=iBu Ni(L_{Ald}-5Me4Im)$_2$ and Ni(L_{Ket}-5Me4Im)$_2$.

Table S3 Selected structural parameters, distances in Å and angles in °, for the aldimine and ketimine forms of a) R=Me Ni(A_{Ald}-5Me4Im)$_2$ and Ni(A_{Ket}-5Me4Im)$_2$ (in text) b) R=iPr Ni(V_{Ald}-5Me4Im)$_2$ and Ni(V_{Ket}-5Me4Im)$_2$ and c) R=iBu Ni(L_{Ald}-5Me4Im)$_2$ and Ni(L_{Ket}-5Me4Im)$_2$(b) and c) in Supplemental.

ORTEP drawing of each complex

IR spectra for each complex

ESI MS for each complex

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Compound	**$Ni(A_{Ket}$-2Im)$_2$ ·3H_2 O**	**$Ni(A_{Ket}$-NMe2Im)$_2$ ·2H_2O**	**[$Ni(L_{Ket}$-NMe2Im)$_2$ ·1.5 H_2O**	**$Ni(A_{Ald}$-5Me4Im)$_2$ ·H_2O**	**$Ni(A_{Ket}$-5Me4Im)$_2$ ·2H_2O**
CSD number	2015580	2285095	2323328	2285097	2285098
Empirical formula	$C_{14}H_{16}N_6NiO_4$ ·3H_2O	$C_{16}H_{20}N_6NiO_4$ · 2 H_2O	$C_{44}H_{64}N_{12}Ni_2O_8$ ··3H_2O	$C_{16}H_{20}N_6NiO_4$ · H_2O	$C_{16}H_{20}N_6NiO_4$ ·2H_2O
M/ g mol^{-1}	443.07	455.12	1060.54	437.10	455.12
Temperature /K	150(2)	293(2)	100(2)	293(2)	297(2)
λ/ Å	0.71073	1.54184	1.54184	1.54178	1.54178
Crystal System	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	P21/n	P21/n	P-1	P21/n	Pbca
Unit cell dimensions	a=11.2052(5) Å, b=15.4495(7) Å, c=11.4742(5) Å, α= 90° β=106.8057(7)° γ= 90°	a=9.3926(2) Å, b=18.7718(3) Å, c=11.6171(2) Å, α= 90° β=105.188(2)° γ= 90°	a=10.6058(6) Å, b=12.2664(7) Å, c=12.4833(7) Å, α= 61.850(6)° β=83.338(5)° γ= 66.723(6)°	a=14.2064(8) Å, b=9.0827(4) Å, c=16.1368(10) Å, α= 90° β=112.662(7)° γ= 90°	a=9.5290(9) Å, b=16.1523(4) Å, c=27.4249(6) Å, α= 90° β=90° γ= 90°
Volume/ Å^3	1901.52(15)	1976.74(7)	1310.39(15)	1921.4(2)	4221.11(17)
Z	4	4	1	4	8
Abs. Coeff./mm^{-1}	1.070	1.837	1.445	1.826	1.720
F(000)	920.0	952	562	912	1904
Crystal size/ mm^3	0.41x0.37x0.35		0.415x0.084x0.066		0.240x0.186x0.170
Theta range/°	4.476 to 62.498	4.594 to 78.875	4.032 to 76.487	3.531 to 75.066	3.223 to 76.260
Index ranges	-16≤h≤16 -22≤k≤22 -16≤l≤16	-11≤h≤11 -22≤k≤23 -13≤l≤14	-13≤h≤13 -7≤k≤15 -15≤l≤15	-16≤h≤17 -10≤k≤11 -20≤l≤18	-12≤h≤10 -20≤k≤20 -33≤l≤34
Reflections Collected	33439	35489	14315	30655	52407
Independent Reflections	6168	4064	5163	3859	4383
R1	0.0365	0.0715	0.0762	0.0726	0.0410
wR2	0.0757	0.2016	0.1930	0.1906	0.1105
GOF on F^2	1.000	1.065	1.069	1.067	1.053

Table S1 cont.

Compound	**Ni(V_{Ald}-5Me4Im)$_2$**	**Ni(V_{Ket}-5Me4Im)$_2$**	**Ni(L_{Ald}-5Me4Im)$_2$**	**Ni(L_{ket}-5Me4Im)$_2$**
CSD number	2206541	2285096	2323329	2323331
Empirical formula	$C_{20}H_{28}N_6NiO_4$	$C_{20}H_{28}N_6NiO_4$	$C_{22}H_{32}N_6NiO_4$	$C_{22}H_{32}N_6NiO_4$
M/ g mol^{-1}	475.19	475.19	503.24	503.24
Temperature/ K	102(2)	263(2)	100(2)	170(2)
λ/ Å	0.71073	1.54178	1.54184	0.71073
Crystal System	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	C2/c	Pbcn	C2/c	C2/c
Unit cell dimensions	a=25.658(4) Å, b=29.909(4) Å, c=12.8720(19) Å, α= 90° β=110.693(7)° γ= 90°	a=11.59070(10) Å, b=13.91300(10) Å, c=13.92430(10) Å, α= 90° β=90° γ= 90°	a=14.7896(4) Å, b=14.4214(4) Å, c=12.5723(3) Å, α= 90° β=110.891(2)° γ= 90°	a=15.7370(7) Å, b=13.8295(6) Å, c=12.6156(5) Å, α= 90° β=115.467(2)° γ= 90°
Volume/ Å^3	9241(2)	2245.45(3)	2506.75(12)	2478.81(19)
Z	16	4	4	4
Abs. Coeff./mm^{-1}	0.877	1.573	1.438	0.821
F(000)	4000	1000	1064	1064.0
Crystal size/ mm^3		0.287x0.226x0.105	0.245x0.139x0.127	0.19x0.03x0.025
Theta range/°	2.171 to 25.259	4.966 to 76.310	4.430 to 76.217	4.568to 60.204
Index ranges	-30≤h≤30 -35≤k≤35 -15≤l≤15	-12≤h≤14 -17≤k≤17 -17≤l≤17	-18≤h≤18 -15≤k≤18 -15≤l≤15	-22≤h≤22 -19≤k≤19 -17≤l≤17
Reflections Collected	87793	117086	22899	47084
Independent Reflections	8372	2344	2581	3639
R1	0.0871	0.0325	0.0788	0.0321
wR2	0.1901	0.0900	0.2091	0.0730
GOF on F^2	1.065	1.051	1.127	1.052

Table S2. Selected structural parameters, distances in Å and trans angles in °, involving the nickel(II) for the aldimine and ketimine forms of a) R=Me Ni(A_{Ald}-5Me4Im)$_2$ and Ni(A_{Ket}-5Me4Im)$_2$ b) R=iPr Ni(V_{Ald}-5Me4Im)$_2$ and and c) R=iBu Ni(L_{Ald}-5Me4Im)$_2$ and Ni(L_{Ket}-5Me4Im)$_2$.

Parameter\cpd.	Ni(A_{Ald}-5Me4Im)$_2$	Ni(A_{Ket}-5Me4Im)$_2$	Ni(V_{Ald}-5Me4Im)$_2$	Ni(V_{Ket}-5Me4Im)$_2$	Ni(L_{Ald}-5Me4Im)$_2$	Ni(L_{Ket}-5Me4Im)$_2$
Ni-N_{Im}	2.089(4) 2.087(4)	2.0550(19) 2.0563(18)	2.106(6) 2.117(6)	2.0628(14) 2.0628(13)	2.095(2)	2.0663(11)
Ni-N_{AA}	2.010(4) 2.012(4)	2.0259(17) 2.0212(17)	2.028(5) 2.012(5)	2.0288(12) 2.0288(12)	2.024(3)	2.0221(10)
Ni-O	2.074(13) 2.088(4)	2.1105(18) 2.1109(16)	2.080(5) 2.069(5)	2.0848(11) 2.0848(11)	2.077(2)	2.0974(10)
N_{AA}-Ni-N_{AA}	174.38(17)	178.60(7)	170.1(3)	177.58(7)	177.83(14)	178.57(7)
N_{Im}-Ni-O	159.60(13) 159.8(3)	157.34(7) 157.14(7)	158.9(2) 158.8(2)	158.86(5) 158.87(5)	158.31(9) 158.31(9)	157.97(4) 157.97(4)

Table S3 Selected structural parameters, distances in Å and angles in °, for the aldimine and ketimine forms of a) R=Me Ni(A_{Ald}-5Me4Im)$_2$ and Ni(A_{Ket}-5Me4Im)$_2$ (in text) b) R=iPr Ni(V_{Ald}-5Me4Im)$_2$ and Ni(V_{Ket}-5Me4Im)$_2$ and c) R=iBu Ni(L_{Ald}-5Me4Im)$_2$ and Ni(L_{Ket}-5Me4Im)$_2$ (in supplemental).

b) Valine, R= i-Pr

Distance	Aldimine	Ketimine	Angle	Aldimine	Ketimine
C_{Ald}-C_{Im}	1.451(9) 1.432(10)	1.495(2)	C_{Im} –C_{Ald} –N_{AA}	116.0(6) 116.1(6)	108.56(12)
C_{Ald}-N_{AA}	1.275(9) 1.276(9)	1.4645(19)	C_{Im} –C_{Ald} –H	122.0 121.9	110.0
C_{Ald}-H	0.9500 0.9500	0.9700	C_{Im} –C_{Ald} –H’	xxxx	110.0
C_{Ald}-H’	xxxxxx	0.9700	N_{AA} –C_{Ald} –H	122.0 121.9	110.0
			N_{AA} –C_{Ald} –H’	xxxxx	110.0
			H –C_{Ald} –H’	xxxxx	108.4
N_{AA}-C_{Ald}	1.275(9) 1.276(9)	1.4645(19)	Ni–N_{AA}–C_{Ald}	116.5(4) 116.9(5)	116.89(9)
N_{AA}-C_{α}	1.454(8) 1.48(2)	1.2683(19)	Ni–N_{AA}–C_{α}	117.0(4) 115.8(8)	117.53(10)
N_{AA}-Ni	2.028(5) 2.012(5)	2.0288(12)	C_{α}–N_{AA}–C_{Ald}	124.5(6) 126.9(9)	124.81(13)
C_{α}-N_{AA}	1.454(8) 1.48(2)	1.2683(19)	N_{AA}–C_{α}–C_{β}	113.1(6) 114.9(15)	125.03(13)
C_{α}-C_{β}	1.555(9) 1.552(11)	1.516(2)	N_{AA}–C_{α}–C_{CA}	107.5(9) 108.9(10)	113.01(13)
C_{α}-C_{CA}	1.536(10) 1.48(2)	1.554(2)	N_{AA}–C_{α}–H	108.6 107.7	xxxxx
C_{α}-H	1.000 1.000	xxxxxx	C_{β}–C_{α}–C_{CA}	110.0(6) 109.7(15)	121.94(15)
			C_{β}–C_{α}–H	108.6 107.7	xxxxx
			C_{CA}–C_{α}–H	108.6 107.7	xxxxx

c) Leucine, R=iBu

Distance	Aldimine	Ketimine	Angle	Aldimine	Ketimine
C_{Ald}-C_{Im}	1.450(4)	1.4966(19)	C_{Im} –C_{Ald} –N_{AA}	115.6(3)	107.39(11)
C_{Ald}-N_{AA}	1.280(4)	1.4638(16)	C_{Im} –C_{Ald} –H	122.2	110
C_{Ald}-H	0.9500	0.990	C_{Im} –C_{Ald} –H’	xxxxx	110
C_{Ald}-H’	xxxxxx	0.990	N_{AA} –C_{Ald} –H	122.2	110
			N_{AA} –C_{Ald} –H’	xxxxx	110
			H –C_{Ald} –H’	xxxxx	109
N_{AA}-C_{Ald}	1.280(4)	1.4638(16)	Ni–N_{AA}–C_{Ald}	117.2(2)	118.41(8)
N_{AA}-C_{α}	1.458(4)	1.2732(16)	Ni–N_{AA}–C_{α}	117.36(19)	118.05(9)
N_{AA}-Ni	2.024(3)	2.0221(10)	C_{α}–N_{AA}–C_{Ald}	124.9(3)	123.52(11)
C_{α}-N_{AA}	1.458(4)	1.2732(16)	N_{AA}–C_{α}–C_{β}	112.1(3)	126.68(12)
C_{α}-C_{β}	1.516(4)	1.4989(19)	N_{AA}–C_{α}–C_{CA}	107.1(2)	113.07(12)
C_{α}-C_{CA}	1.553(4)	1.5453(18)	N_{AA}–C_{α}–H	109.9	xxxxx
C_{α}-H	1.000	xxxxxx	C_{β}–C_{α}–C_{CA}	107.8(3)	120.25(12)
			C_{β}–C_{α}–H	109.9	xxxxx
			C_{CA}–C_{α}–H	109.9	xxxxx