Dependence of Magnetic Coupling on Ligands at Axial Positions of Ni^{II} in Phenoxido Bridged Dimers: Experimental Observations and DFT Studies

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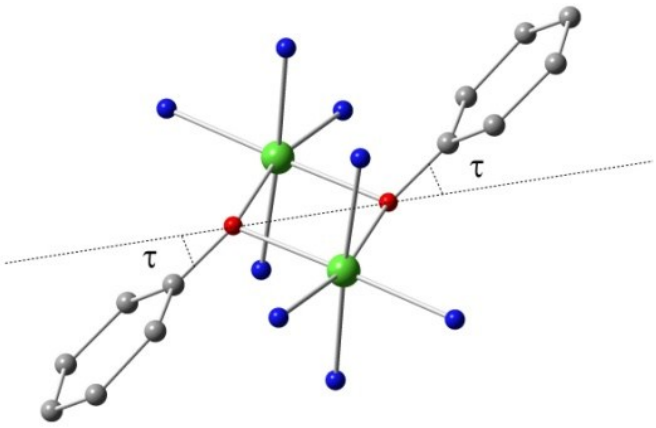

Scheme S1: Schematic representation for out-of-plane shift of phenyl rings is shown by τ angle. Colour codes: Ni green, O red, N blue and C gray.

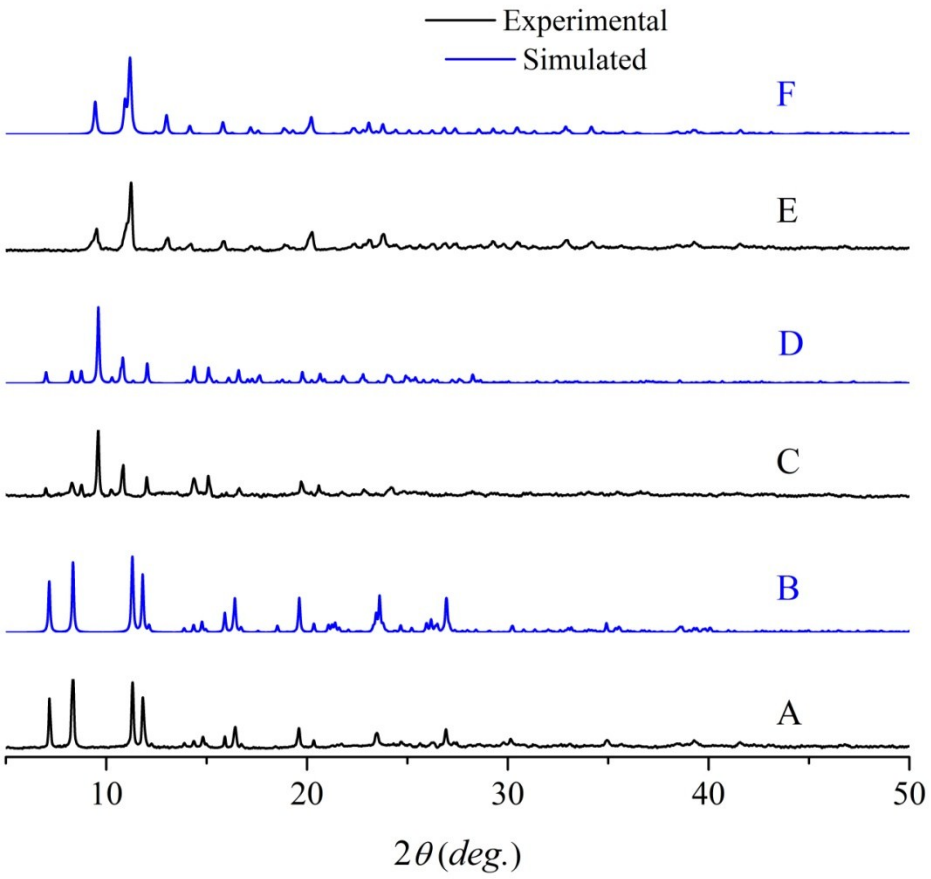

Figure S1: Intensity normalized PXRD patterns for complexes **1-3** are shown by A, C and E along with their respective simulated plots B, D and F.

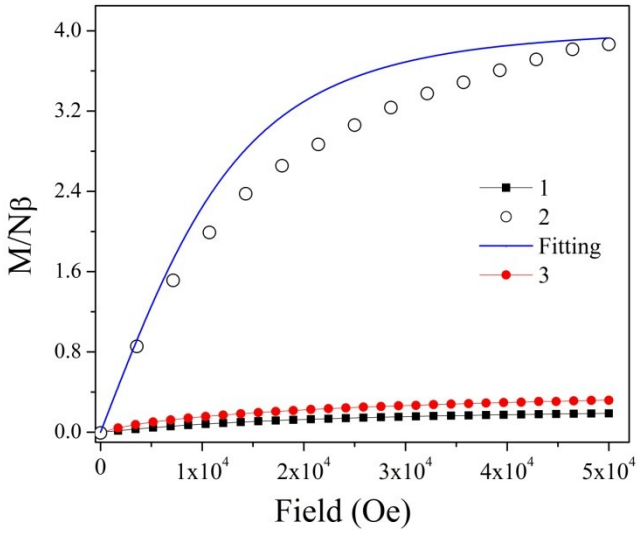

Figure S2: Field dependence of molar magnetizations for compounds **1-3** at 2 K. Solid blue line indicate the fitted curve for compound **2**, using Brillouin function, g = 2 with S = 2.

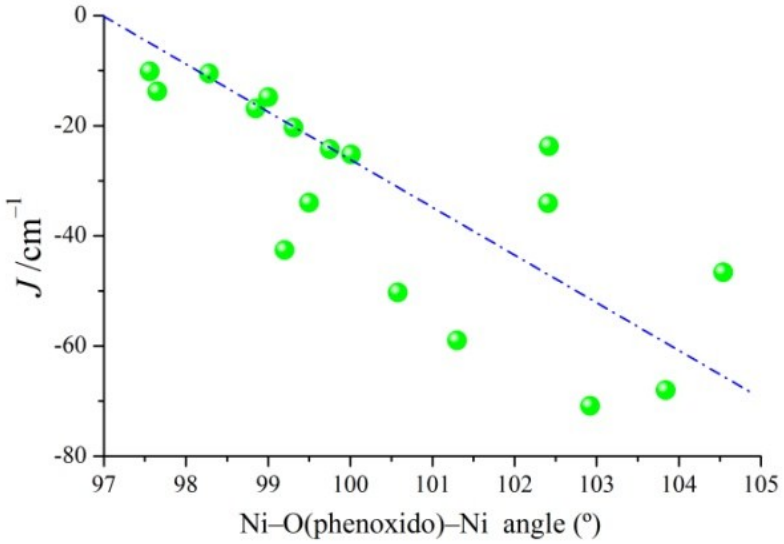

Figure S3: Plot of experimental *J* value vs. ∠Ni–O–Ni angle for earlier reported diphenoxido bridged dinuclear Ni^{II} complexes.

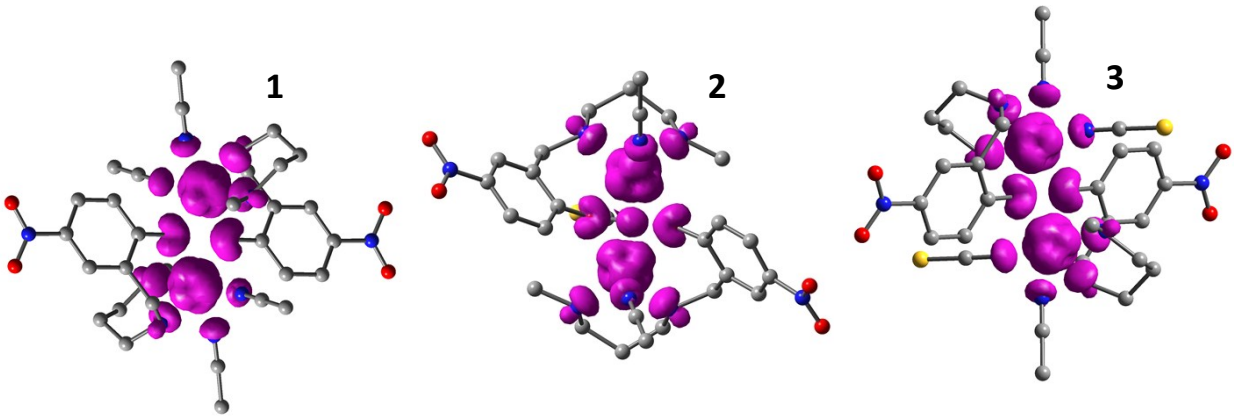

Figure S4: Spin density plots for triplet state of complexes **1**–**3** with surface cutoff value 0.004 e/Å^3.

Table S1: 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
$[Ni_2L_2(NO_2)_2]\cdot CH_2Cl_2\cdot C_2H_5OH, 2H_2O$	–10.52	98.28	**1**
$[Ni_2L_2(NO_3)_2]$	–20.34	99.31	**2**
$[Ni_2L_2(NO_2)_2]$	–25.25	100.01	**2**
$[Ni_2(L_1)_2(NCS)_2]$	−46.64	104.54	**3**
$[Ni_2(L_2)_2(NCS)_2]$	−70.9	102.92	**3**
$[Ni_2(L_3)_2(NCS)_2]$	−68.04	103.84	**3**
$[Ni_2L_2(NO_3)_2]$	–24.27	99.75	**4**
$[Ni_2(L)_2(OAc)_2]$	–50.28	100.58	**5**
$\{Ni(Hsalhyph)Cl(H_2O)\}_2$	–14.80	99	**6**
$[Ni_2L(H_2O)_4(ClO_4)_2.\ 4NH_2CONH_2$	−34	99.5	**7**
$[\ Ni_2L(NCS)_2(H_2O)_2].\ 2Me_2NCHO$	−42.6	99.2	**7**
$[Ni2L(MeOH)_2(ClO_4)_2].2NHEt$	−59	101.3	**7**
$[NiL_2(o\text{-}HSal)]\cdot 2H_2O$	–13.78	97.65	**8**
$[Ni_2L_2(o\text{-}Hap)_2]$	–16.87	98.85	**8**
$[Ni_2L_2(o\text{-}Hnap)_2]$	–10.14	97.56	**8**
$[Ni_2L^R{}_2(CH_3CN)_4](ClO_4)_2\cdot 2CH_3CN$	−34.10	102.41	This work
$[Ni_2L^R{}_2(NCS)_2\,(CH_3CN)_2]$	−23.72	102.42	This work

Table S2: Mulliken's atomic spin populations computed for triplet state of compounds **1**−**3**.

Selected atoms	Complex **1**	Complex **3**
Ni(1)	1.66548	1.68023
Ni(1)[a]	1.66543	1.68021
O(10) *phenoxido1*	0.09881	0.09201
O(10)[a] *phenoxido2*	0.09881	0.09202
N(1) *coordinating*	0.03721	0.05325
N(1)[a] *coordinating*	0.03720	0.05326
N(2) *coordinating*	0.04403	0.04085
N(2)[a] *coordinating*	0.04403	0.04085
N(22) *coordinating*	0.08961	0.07550
N(22)[a] *coordinating*	0.08961	0.07551
N(18) *coordinating*	0.08084	0.07455
N(18)[a] *coordinating*	0.08084	0.07455

Selected atoms	Complex **2**
Ni(1)	1.66779
Ni(2)	1.67502
O(10) *phenoxido1*	0.08364
O(24) *phenoxido2*	0.08124
N(2) *coordinating*	0.04705
N(3) *coordinating*	0.04041
N(18) *coordinating*	0.08335
N(22) *coordinating*	0.07269
N(32) *coordinating*	0.08037
N(36) *coordinating*	0.07093
N(1) *isocyanate*	0.02348
C(1) *isocyanate*	0.01065
S(1) *isocyanate*	0.04985

Table S3: A series of model complex (**3b-3d**) are created by changing only one Ni−N bond distance in complex **3a** to a value as it is in complex **1a**, keeping rest of the parameters unaltered. Changes are highlighted by bold font.

Bond length (Å)	Complex **1a**	Complex **3a**	Model **3b**	Model **3c**	Model **3d**	Model **3e**
Ni(1)−N(1)	2.171	2.068	**2.171**	2.068	2.068	2.068
Ni(1)−N(2)	2.104	2.126	2.126	**2.104**	2.126	2.126
Ni(1)−N(18)	2.081	2.101	2.101	2.101	**2.081**	2.101
Ni(1)−N(22)	2.098	2.103	2.103	2.103	2.103	**2.098**
Ni(1)−O(10)	2.077	2.097	2.097	2.097	2.097	2.097
Ni(1)−O(10)[a]	2.085	2.094	2.094	2.094	2.094	2.094
J value / cm^{-1}	−36.50	−24.8	−25.809	−25.28	−25.374	−24.704

Table S4: A series of model complex (**3f-3k**) are created by changing two random Ni−N bond distances in complex **3a** to as it is in complex **1a**, keeping rest of the parameters unaltered. Model complex (**3l**) is created by changing all the Ni−N bond distances in complex **3a** to as it is in complex **1a**, keeping rest of the parameters unaltered. Model complex (**3m**) is created by changing all the Ni−N bond distances and Ni−O bond distances in complex **3a** to as it is in complex **1a**, keeping rest of the parameters unaltered. Changes are highlighted by bold font.

Bond length (Å)	Model **3f**	Model **3g**	Model **3h**	Model **3i**	Model **3j**	Model **3k**	Model **3l**	Model **3m**
Ni(1)−N(1)	**2.171**	2.068	2.068	**2.171**	**2.171**	2.068	**2.171**	**2.171**
Ni(1)−N(2)	**2.104**	**2.104**	2.126	2.126	2.126	**2.104**	**2.104**	**2.104**
Ni(1)−N(18)	2.101	**2.081**	**2.081**	2.101	**2.081**	2.101	**2.081**	**2.081**
Ni(1)−N(22)	2.103	2.103	**2.098**	**2.098**	2.103	**2.098**	**2.098**	**2.098**
Ni(1)−O(10)	2.097	2.097	2.097	2.097	2.097	2.097	2.097	**2.077**
Ni(1)−O(10)[a]	2.094	2.094	2.094	2.094	2.094	2.094	2.094	**2.085**
J value / cm^{-1}	−26.229	−25.907	−25.315	−25.771	−26.455	−25.223	−26.639	−26.929

Table S5: Model complex (**1b**) is created by changing all the Ni−N bond distances in complex **1** to as it is in complex **3**, keeping rest of the parameters unaltered. Model complex (**1c**) is created by changing all the Ni−N bond distances and Ni−O bond distances in complex **1a** to as it is in complex **3a**, keeping rest of the parameters unaltered. Changes are highlighted by bold font.

Bond length (Å)	Model **1b**	Model **1c**
Ni(1)−N(1)	**2.068**	**2.068**
Ni(1)−N(2)	**2.126**	**2.126**
Ni(1)−N(18)	**2.101**	**2.101**
Ni(1)−N(22)	**2.103**	**2.103**
Ni(1)−O(10)	2.077	**2.097**
Ni(1)−O(10)[a]	2.085	**2.094**
J value / cm^{-1}	−34.967	−34.944

Table S6. Model **1d** is obtained through replacement of axially coordinated ACN group by NCS ion in complex **1**, keeping rest of bond parameter fixed. Model **3n** is obtained by means of replacement of axially coordinated NCS group by ACN molecule in complex **3** and kept the other structural parameter constant. ΔJ represents the change of calculated J value between the model structure and their respective parent structure (**1** or **3**).

Bond length (Å)	Model **1d**	Model **3n**
Ni(1)−N(1)	2.171	2.068
Ni(1)−N(2)	2.104	2.126
Ni(1)−N(18)	2.081	2.101
Ni(1)−N(22)	2.098	2.103
Ni(1)−O(10)	2.077	2.097
Ni(1)−O(10)[a]	2.085	2.094
J value / cm^{-1}	−29.3	−34.87
ΔJ / cm^{-1}	8.89	−8.63

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