

SUPPLEMENTARY MATERIAL

Conversion of tetrahedral to octahedral structures upon solvent coordination: Studies on the $M[(OPPh_2)(SePPh_2)N]_2$ ($M = Co, Ni$) and $[Ni\{(OPPh_2)(EPPh_2)N\}_2(dmf)_2]$ ($E = S, Se$) complexes

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X-ray crystallography

Table S1 Crystallographic data for complexes **1 – 4**

	1	2	3	4
Formula	C ₄₈ H ₄₀ CoN ₂ O ₂ P ₄	C ₄₈ H ₄₀ N ₂ NiO ₂ P ₄ Se ₂	C ₅₄ H ₅₄ N ₄ NiO ₄ P ₄ S ₂	C ₅₄ H ₅₄ N ₄ NiO ₄ P ₄ Se ₂
Fw	1017.55	1017.33	1069.72	1163.52
Space group	<i>P2</i> ₁ / <i>c</i>	<i>P2</i> ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>T</i> , °C	25	25	25	25
λ , Å	Mo K α	Mo K α	Mo K α	Mo K α
<i>a</i> , Å	12.593(3)	12.602(5)	9.3092(2)	9.326(4)
<i>b</i> , Å	18.466(5)	18.425(7)	10.3818(2)	10.505(5)
<i>c</i> , Å	19.534(5)	19.582(8)	13.2729(2)	13.500(6)
α , (°)			89.175(1)	88.89(1)
β , (°)	99.92(1)	100.140(10)	85.612(1)	86.33(1)
γ , (°)			84.502(1)	85.30(1)
<i>V</i> , Å ³	4475(2)	4476(3)	1273.10(4)	1315.3(10)
<i>Z</i>	4	4	1	1
ρ_{calcd} , g cm ⁻³	1.510	1.510	1.395	1.469
μ , mm ⁻¹	2.195 (Mo K α)	2.244 (Mo K α)	0.639 (Mo K α)	1.923 (Mo K α)
<i>R</i> 1 ^a	0.0495 ^b	0.0581 ^c	0.0240 ^d	0.0394 ^e
w <i>R</i> 2 ^a	0.1193 ^b	0.1360 ^c	0.06328 ^d	0.1033 ^e

$$^a w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP] \text{ and } P = (\max(F_o^2, 0) + 2F_c^2)/3;$$

$$R1 = \Sigma(|F_o| - |F_c|) / \Sigma(|F_o|) \text{ and } wR2 = D^{1/2}$$

^bfor 4828 reflections with $I > 2\sigma(I)$; ^cfor 4956 reflections with $I > 2\sigma(I)$; ^dfor 4753 reflections with $I > 2\sigma(I)$; ^efor 3931 reflections with $I > 2\sigma(I)$.

Further experimental crystallographic details

Co[(OPPh₂)(SePPh₂)N]₂ (1): $2\theta_{\max} = 46^\circ$; reflections collected/unique/used, 6433/6221 [$R_{\text{int}} = 0.0252$]/6221; 706 parameters refined; $(\Delta/\sigma)_{\max} = 0.001$; $(\Delta\rho)_{\max}/(\Delta\rho)_{\min} = 0.989/-0.600 \text{ e}/\text{\AA}^3$; $R1/wR2$ (for all data), 0.0712/0.1313. All hydrogen atoms were located by difference maps and were refined isotropically. All non-hydrogen atoms were refined anisotropically.

Ni[(OPPh₂)(SePPh₂)N]₂ (2): $2\theta_{\max} = 47^\circ$; reflections collected/unique/used, 6837/6616 [$R_{\text{int}} = 0.0238$]/6616; 706 parameters refined; $(\Delta/\sigma)_{\max} = 0.002$; $(\Delta\rho)_{\max}/(\Delta\rho)_{\min} = 0.699/-0.568 \text{ e}/\text{\AA}^3$; $R1/wR2$ (for all data), 0.0871/0.1537. All hydrogen atoms were either located by difference maps and were refined isotropically or were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically.

[Ni{(OPPh₂)(SPPPh₂)N}₂(dmf)₂] (3): $2\theta_{\max} = 52^\circ$; reflections collected/unique/used, 24276/4992 [$R_{\text{int}} = 0.0142$]/4992; 421 parameters refined; $(\Delta/\sigma)_{\max} = 0.007$; $(\Delta\rho)_{\max}/(\Delta\rho)_{\min} = 0.399/-0.227 \text{ e}/\text{\AA}^3$; $R1/wR2$ (for all data), 0.0251/0.0637. All hydrogen atoms were located by difference maps and were refined isotropically. All non-hydrogen atoms were refined anisotropically.

[Ni{(OPPh₂)(SePPh₂)N}₂(dmf)₂] (4): $2\theta_{\max} = 50^\circ$; reflections collected/unique/used, 4765/4453 [$R_{\text{int}} = 0.0083$]/4453; 401 parameters refined; $(\Delta/\sigma)_{\max} = 0.001$; $(\Delta\rho)_{\max}/(\Delta\rho)_{\min} = 0.633/-0.545 \text{ e}/\text{\AA}^3$; $R1/wR2$ (for all data), 0.0458/0.1088. All hydrogen atoms were either located by difference maps and were refined isotropically or were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically.

UV-vis spectroscopy

The electronic spectra in CH₂Cl₂ of complexes **1** (blue), as well as for Ni[(OPPh₂)(SPPPh₂)N]₂ (light blue) and **2** (green), exhibit characteristic d-d bands (bands 1-3, Table S2) of tetrahedral Co(II),^{1,2} and Ni(II) complexes, respectively.^{1,3,4} Band 4 in Table S2 reflects a charge transfer transition.⁴ When light yellow crystals of complexes **3** and **4** are dissolved in CH₂Cl₂, they turn to light blue and green, respectively. The spectra of **3** and **4** are identical to those of Ni[(OPPh₂)(SPPPh₂)N]₂ and **2**, respectively (Table S2), providing evidence that the dmf molecules are removed from the coordination sphere of **3** and **4**, which revert to the corresponding tetrahedral Ni[(OPPh₂)(SPPPh₂)N]₂ and **2** complexes.

Table S2 The main transition bands (cm⁻¹) of complexes **1** – **4** and Ni[(OPPh₂)(SPPPh₂)N]₂. In parenthesis, the corresponding extinction coefficients (ε, M⁻¹/cm⁻¹) are listed

Complex	Band 1	Band 2	Band 3	Band 4
1	13660 (232)	15700 (385)	17500 (416)	
Ni[(OPPh ₂)(SPPPh ₂)N] ₂	14470 (145)	16020 (88)	18010 (62)	30670 (2800)
2	14020 (166)	15570 (103)	17540 (90)	28570 (2450)
3	14490	16000	18180	30770
4	14020	15570	17540	28490

1. B. N. Figgis and M. A. Hitchman, *Ligand Field Theory and its Applications*, Wiley-VCH, 2000.
2. D. Maganas, S. S. Staniland, A. Grigoropoulos, F. White, S. Parsons, N. Robertson, P. Kyritsis and G. Pneumatikakis, *Dalton Trans.*, 2006, 2301.
3. A. Davison and E. S. Switkes, *Inorg. Chem.*, 1971, **10**, 837.
4. D. Maganas, A. Grigoropoulos, S. S. Staniland, S. D. Chatziefthimiou, A. Harrison, N. Robertson, P. Kyritsis and F. Neese, *Inorg. Chem.*, 2010, **49**, 5079.

Geometry optimization parameters

The BP86/def2-TZVP/DKH-optimized structures (the coordinates of which are listed in Table S4) provide Ni–X bond lengths (Table S3) and X–Ni–X angles, X = S, O, which are in very good agreement with the crystallographic ones (within ~ 0.03 Å and $\sim 1-5^\circ$, respectively).

Table S3 Calculated (BP86/TZVP/DKH-optimized) and crystallographic Ni–X bond lengths (Å) and X–Ni–X angles ($^\circ$), and relevant Löwdin bond orders.

		Crystallographic	Calculated	Löwdin Bond Order
		Ni[(OPPh₂)(SPMe₂)N]₂^a	Ni^{H,H}L₂	
Ni–X	Ni–S	2.306(4)	2.27	0.82
	Ni–O	1.959(7)	1.96	0.53
X–Ni–X	S–N–S'	107.2(1)	104.1	
	O–Ni–O'	101.8(3)	100.1	
	O–Ni–S	103.8(2)	105.0	
	O–Ni–S'	104.7(2)	106.5	
	O'–Ni–S	127.2(1)	132.1	
		[Ni{(OPPh₂)(SPPH₂)N}₂(dmf)₂]	Ni^{H,H}L₂(dmf)₂	
Ni–X	Ni–S	2.5181(4)	2.51	0.41
	Ni–O	2.0205(9)	2.07	0.37
	Ni–O(dm f)	2.0679(10)	2.09	0.40
X–Ni–X	S–Ni–S'	180	180	
	O–Ni–O'	180	180	
	O–Ni–S	93.88(3)	96.9	
	O–Ni–S'	86.12(3)	82.6	
	O(dm f)–Ni–O(dm f)	180	180	

^aThe corresponding Ni[(OPPh₂)(SPPH₂)N]₂ complex provide X–Ni–X angles strongly influenced by the bulky phenyl groups environment. Therefore, a better agreement was found for the less strained Ni[(OPPh₂)(SPMe₂)N]₂ complex, the structural parameters of which are listed.⁵

5. A. Silvestru, D. Bilc, R. Rosler, J. E. Drake and I. Haiduc, *Inorg. Chim. Acta*, 2000, **305**, 106.

Table S4 The Cartesian coordinates of the BP86/def2-TZVP-optimized structures $C_{2v}(I)$ and $^{Oh}C_i$, corresponding to the $Ni^{H,H}L_2$ and $Ni^{H,H}L_2(dmf)_2$ models, respectively.

$C_{2v}(I)$: BP86/def2-TZVP

Ni	2.470531000	3.398818000	1.791646000
S	1.598051000	1.383806000	2.363461000
S	2.692150000	4.485611000	3.794395000
P	-0.371581000	4.378180000	1.263526000
P	-0.287225000	1.980048000	2.809386000
P	5.009840000	5.050831000	1.119897000
P	3.334628000	6.276066000	3.067310000
O	1.088119000	4.360441000	0.784054000
O	4.061374000	3.899715000	0.760200000
N	-1.028470000	3.054053000	1.881042000
N	4.431562000	6.327615000	1.902573000
H	-1.190679000	4.740772000	0.169662000
H	-0.548262000	5.467839000	2.163474000
H	-1.107551000	0.827312000	2.832606000
H	-0.311660000	2.370805000	4.177422000
H	5.605156000	5.573283000	-0.052208000
H	6.123899000	4.503387000	1.813847000
H	3.784290000	7.023485000	4.187286000
H	2.217828000	7.050933000	2.658420000

*Oh*C_i: BP86/def2-TZVP

Ni	5.162303000	0.047189000	6.616704000
N	5.960947000	-1.474889000	9.929129000
O	5.625511000	0.852692000	8.466676000
S	3.994628000	-2.010501000	7.460580000
P	4.506622000	-2.050212000	9.433239000
P	6.402252000	0.056726000	9.560306000
H	4.482019000	-3.392240000	9.914391000
H	3.428419000	-1.481550000	10.201021000
H	7.803755000	-0.006986000	9.289141000
H	6.364488000	0.865872000	10.746537000
O	3.346446000	1.091401000	6.649759000
C	3.286951000	2.172735000	7.257920000
H	2.162309000	3.826159000	7.755092000
N	2.169945000	2.927629000	7.286540000
H	1.354189000	2.643025000	6.751086000
H	4.144283000	2.562917000	7.829846000
N	4.363757000	1.569196000	3.304226000
O	4.699061000	-0.758353000	4.766757000
S	6.330020000	2.104806000	5.772820000
P	5.818088000	2.144470000	3.800131000
P	3.922363000	0.037618000	3.673103000
H	5.842789000	3.486602000	3.318900000
H	6.896323000	1.575709000	3.032401000
H	2.520764000	0.101425000	3.944287000
H	3.960086000	-0.771624000	2.486813000

O	6.978157000	-0.997025000	6.583634000
C	7.037677000	-2.078389000	5.975537000
H	8.162318000	-3.731930000	5.478490000
N	8.154714000	-2.833245000	5.946919000
H	8.970468000	-2.548594000	6.482373000
H	6.180348000	-2.468632000	5.403643000

Figure S1 The most important BP86/def2-TZVP structures along the $C_{2v(I)} \rightarrow C_{2v(II)} \rightarrow {}^{Oh}C_i$ interconversion pathway



