Electronic Supplementary Information for Dalton Transactions

Syntheses, solid state and solution structures of the palladium(II) complexes of malonamide-derived open-chain and macrocyclic ligands

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Electronic Supplementary Information

Table S1

Selected interatomic distances (Å) and angles (°) for palladium(II) and nickel(II) complexes (corresponding values for nickel(II) complexes are presented in square brackets: NiL^{1}·(ref. [1]), NiL^{2}·(ref. [2]), *m* – N-*meso* (as a half of Ni_2L^4) (ref. [3]), *r* – N-*rac* NiL^{3}·(ref. [2]); for palladium complexes standard uncertainties (s.u.) are given in parentheses.

	ML^{1}	**ML^{2}**	**ML^{3}**
		Metal environment	
M-N(1)	2.048(3) [1.918]	2.047(1) [1.935]	2.012(2) [1.907*m*] [1.890*r*]
M-N(2)	1.983(3) [1.870]	1.983(1) [1.882]	1.963(2) [1.842*m*] [1.838*r*]
M-N(3)	1.979(3) [1.869]	1.987(1) [1.895]	1.952(2) [1.843*m*] [1.840*r*]
M-N(4)	2.053(3) [1.922]	2.044(1) [1.947]	2.008(2) [1.910*m*] [1.885*r*]
N(1)-M-N(2)	83.3(1) [85.2]	83.4(1) [84.8]	87.2(1) [88.1*m*] [87.4*r*]
N(2)-M-N(3)	94.5(1) [95.3]	94.9(1) [94.1]	97.1(1) [96.7*m*] [98.2*r*]
N(3)-M-N(4)	83.3(1) [85.6]	83.5(1) [85.0]	85.9(1) [86.5*m*] [87.1*r*]
N(1)-M-N(4)	99.0(1) [93.9]	98.2(1) [95.9]	88.4(1) [88.6*m*] [87.8*r*]
N(1)-M-N(3)	177.5(1) [177.2]	178.3(1) [176.2]	167.0(1) [166.5*m*] 173.1*r*]
N(2)-M-N(4)	177.2(1) [178.3]	178.1(1) [177.8]	172.4(1) [176.8*m*] [171.1*r*]
		Ligand	
O(1)-C(3)	1.273(4) [1.266]	1.279(2) [1.277]	1.276(3) [1.270*m*] [1.267*r*]
O(2)-C(5)	1.269(4) [1.274]	1.277(2) [1.294]	1.264(3) [1.259*m*] [1.266*r*]
N(2)-C(3)	1.314(5) [1.318]	1.310(2) [1.308]	1.313(3) [1.307*m*] [1.309*r*]
N(3)-C(5)	1.313(5) [1.314]	1.310(2) [1.302]	1.315(3) [1.314*m*] [1.304*r*]
O(1)-C(3)-N(2)	122.8(3) [123.6]	123.2(1) [124.3]	123.7(2) [124.1*m*] [124.1*r*]
O(1)-C(3)-C(4)	116.1(3) [115.8]	115.1(1) [115.3]	115.9(2) [117.0*m*] [116.1*r*]
N(2)-C(3)-C(4)	121.1(3) [120.6]	121.8(1) [120.4]	120.4(2) [118.9*m*] [119.8*r*]
O(2)-C(5)-N(3)	123.2(3) [123.6]	123.4(1) [123.2]	124.3(2) [124.3*m*] [124.0*r*]
O(2)-C(5)-C(4)	115.5(3) [116.4]	115.2(1) [115.2]	115.7(2) [116.5*m*] [116.1*r*]
N(3)-C(5)-C(4)	121.3(3) [120.0]	121.4(1) [121.6]	120.0(2) [119.1*m*] [119.9*r*]
N(1)-C(1)-C(2)-N(2)	47.1(4) [36.8]	43.8(1) [38.9]	45.6(3) [39.9*m*] [40.5*r*]
N(3)-C(6)-C(7)-N(4)	-40.4(4) [-43.0]	-44.7(1) [-40.8]	-48.2(3) [-40.8*m*] [37.7*r*]
N(1)-C(9)-C(8)-N(4)	-	-	-44.9(3) [-44.8*m*] [-49.1*r*]
N(1)-C(10)-C(9)-C(8)	-	-73.0(2) [-68.5]	-
N(4)-C(8)-C(9)-C(10)	-	74.8(2) [70.2]	-
		Deviations in chromophore	
R.m.s. deviation of N atoms from the mean N_4 plane	0.03 [0.04]	0.01 [0.01]	0.05 [0.10*m*] [0.10*r*]
Deviation of M from the mean N_4 plane	-0.01 [-0.01]	0.01 [-0.05]	0.16 [0.10*m*] [0.02*r*]

Table S2

Parameters of hydrogen bonds for palladium complexes of malonamide-derived ligands

D-H···A	**D-A**/ Å	**H···A**/ Å	**DHA**/°	Symmetry operation
		PdL^1·3H$_2$O		
O(3)-H(31)···O(1)	2.813(4)	2.02(6)	169(6)	1-x, -1-y, 1-z
O(3)-H(32)···O(1)	2.698(4)	2.11(6)	166(7)	
O(4)-H(41)···O(2)	2.723(4)	1.92(5)	174(4)	
O(4)-H(42)···O(5)	2.803(4)	2.10(5)	161(5)	0.5-x, -0.5+y, 1.5-z
O(5)-H(51)···O(2)	2.731(5)	1.98(5)	177(5)	
O(5)-H(52)···O(3)	2.778(5)	2.03(5)	172(4)	x, 1+y, z
N(1)-H(1A)···O(5)	3.018(4)	2.16	159	-0.5+x, 0.5-y, -0.5+z
N(1)-H(1B)···O(4)	2.982(4)	2.11	162	1-x, -y, 1-z
N(4)-H(4A)···O(3)	2.932(4)	2.08	157	1-x, -y, 1-z
N(4)-H(4B)···O(4)	2.978(4)	2.22	141	-0.5+x, 0.5-y, -0.5+z
		PdL^2·6H$_2$O		
O(3)···O(1)	2.772			
O(3)···O(2)	2.792			x, y, 1+z
O(4)···O(5)	2.750			
O(4)···O(5)	3.003			1-x, 1-y, -z
O(4)···O(7)	2.800			1-x, 1-y, 1-z
O(5)···O(2)	2.789			
O(5)···O(6)	2.782			
O(6)···O(7)	2.940			
O(6)···O(8)	2.768			1+x, y, z
O(7)···O(1)	2.721			
O(7)···O(8)	2.876			
O(8)···O(4)	2.837			
N(1)···O(2)	2.894			0.5+x, 0.5-y, 0.5+z
N(4)···O(1)	2.943			0.5+x, 0.5-y, -0.5+z
		PdL^3·5H$_2$O		
O(3)···O(1)	2.746			
O(3)···O(2)	2.670			-1+x, y, z
O(4)···O(3)	2.739			
O(4)···O(4)	2.818			-x, 1-y, 1-z
O(4)···O(6)	2.848			
O(5)···O(4)	2.859			-x, 1-y, 1-z
O(5)···O(6)	2.780			x, -1+y, z
O(5)···O(7)	2.840			
O(6)···O(7)	2.824			1-x, 1-y, 1-z
O(7)···O(1)	2.747			
O(7)···O(7)	2.776			1-x, 1-y, 1-z
N(1)···O(1)	2.889			1-x, 0.5+y, 1.5-z
N(4)···O(2)	2.777			2-x, 0.5+y, 1.5-z

Table S3

Chemical shifts δ and coupling constants J for PdL^2 and PdL^3 (data for corresponding nickel(II) analogues in parentheses, see ref. [2]).

H	δ / ppm	H-H	J / Hz	φ / °
			PdL^2	
			6-membered ring	
a	1.536 (1.299)	***a-c***	12.5 (12.9)	173.0 (171.3)
b	2.122 (1.876)	***a-d***	2.1 (2.9)	70.2 (69.5)
c	2.649 (2.555)	***b-c***	1.7 (2.3)	74.8 (69.2)
d	3.047 (2.502)	***b-d***	4.2 (3.6)	42.0 (49.9)
		a-b	-16.1 (-15.8)	gem
		c-d	-12.6 (-12.3)	gem
			5-membered rings	
e	2.721 (2.357)	***e-g***	13.5 (12.5)	167.2 (160.3)
f	3.061 (2.505)	***e-h***	5.7 (6.2)	47.6 (39.7)
g	2.972 (2.578)	***f-g***	4.4 (5.1)	48.0 (40.1)
h	3.545 (3.146)	***f-h***	1.2 (1.6)	71.7 (80.6)
		e-f	-11.7 (-11.4)	gem
		g-h	-13.8 (-13.6)	gem
			malonamide ring	
i	3.314 (2.988)	***i-j***	-20.2 (-20.4)	gem
j	3.572 (3.241)			
			PdL^3	
			5-membered rings (lateral)	
e	3.272 (3.147)	***e-g***	13.0 (12.8)	171.8 (161.2)
f	3.097 (2.694)	***e-h***	5.3 (6.2)	53.7 (40.5)
g	3.199 (2.749)	***f-g***	4.2 (5.5)	52.1 (40.6)
h	3.838 (3.366)	***f-h***	0.8 (0.4)	66.0 (80.1)
		e-f	-11.9 (-11.3)	gem
		g-h	-13.8 (-13.7)	gem
			malonamide ring	
i	3.195 (2.963)	***i-j***	-19.9 (-20.8)	gem
j	3.667 (3.243)	***g-j***	1.7	^5J
			5-membered ring (central)	
k	3.524 (3.276)	***k-k'***	5.3 (5.9)	53.9 (45.7)
l	3.337 (2.850)	***l-l'***	5.3 (5.9)	50.8 (45.1)
		k-l'	7.1 (6.8)	169.3 (165.7)
		l-k'	7.1 (6.8)	64.7 (75.0)
		k-l	-13.7 (-12.9)	gem

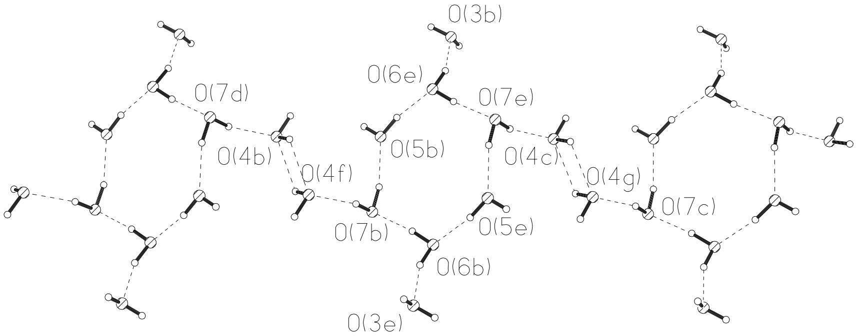
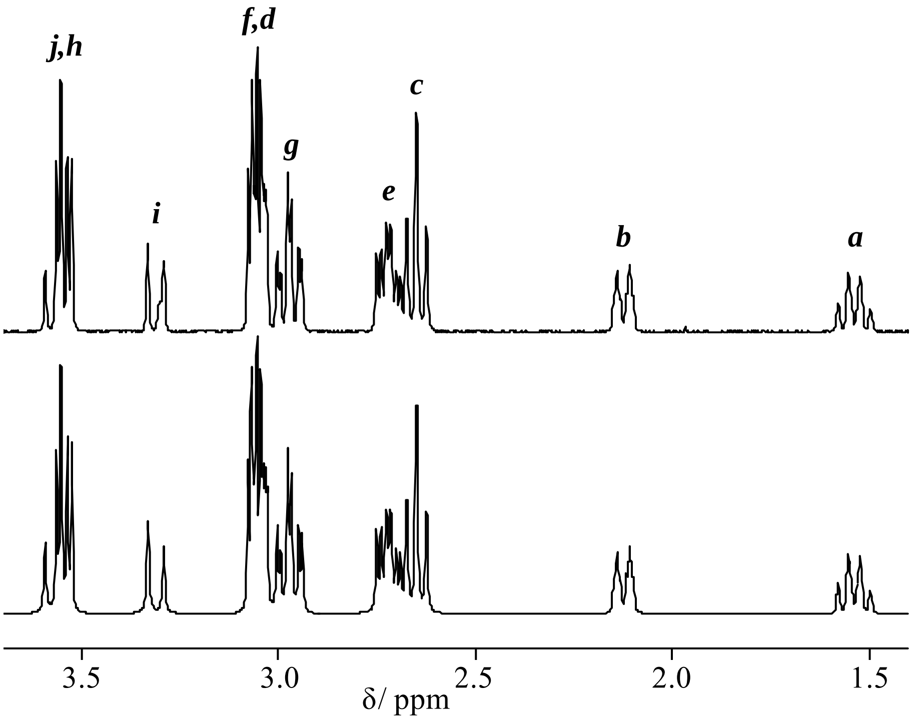
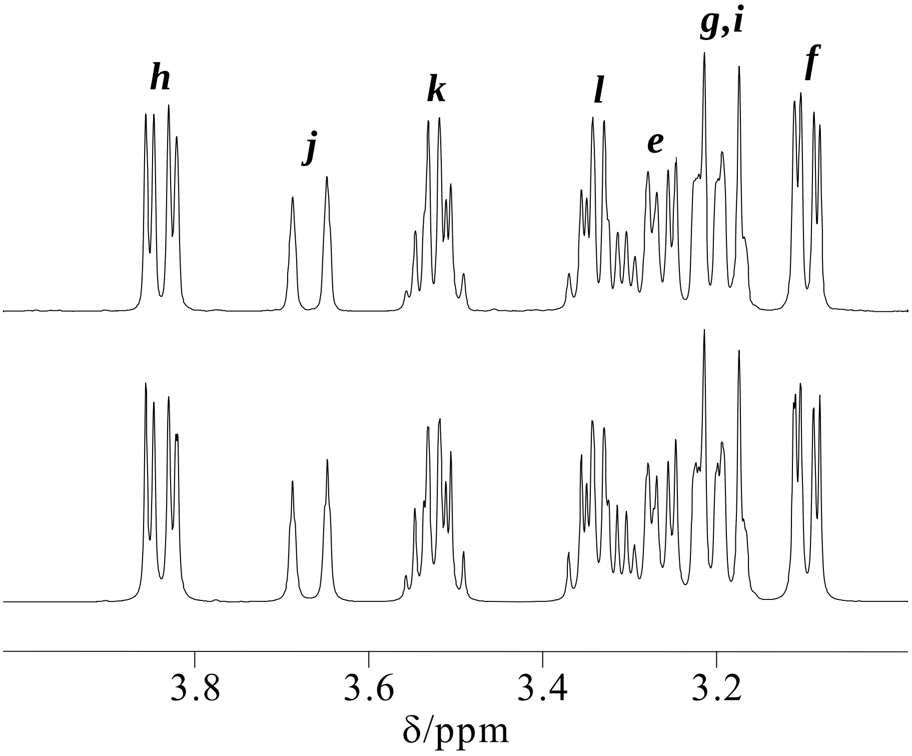


Fig. S1 Chain structure formed by the water molecules in the lattice of N-*rac*-NiL^3 (ref. ^{2})



(**a**)



(b)

Fig. S2 Experimental (top) and simulated (bottom) ^{1}H NMR spectra of PdL^2 (a) and PdL^3 (b).

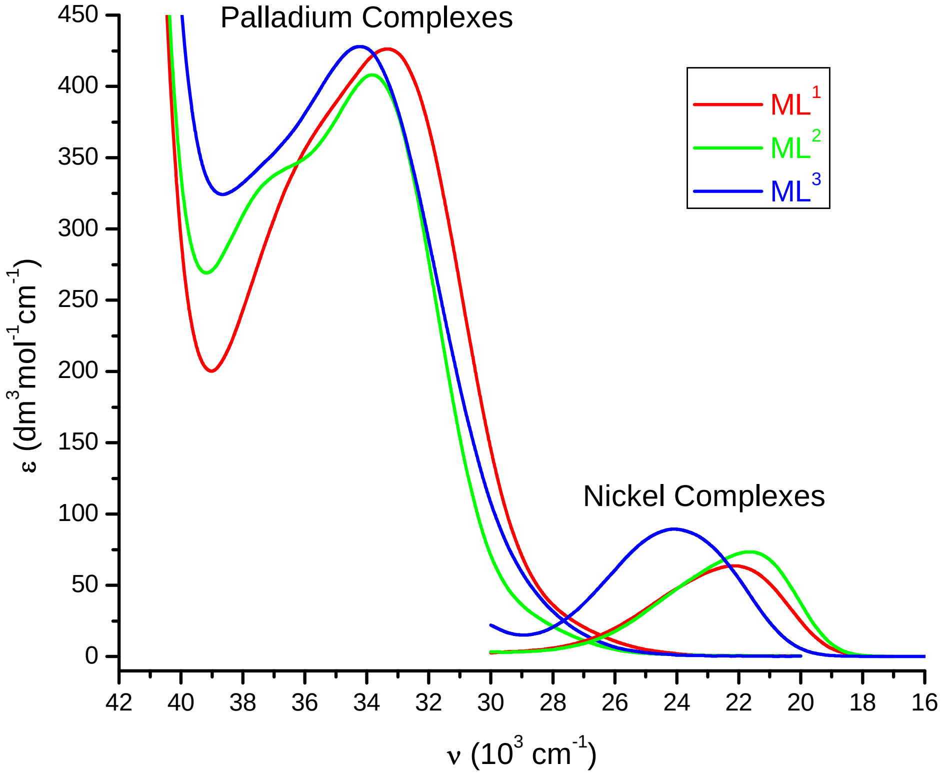


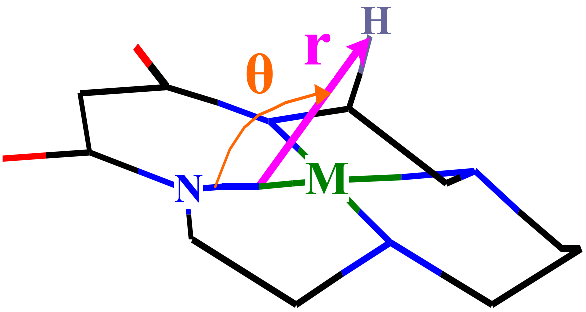
Fig. S3 Electronic absorption spectra of the palladium(II) and nickel(II) complexes ML^1, ML^2 and ML^3 in aqueous solution (only visible region is shown for the nickel complexes).

Calculation of the differences in magnetic anisotropy ($\Delta\Delta\chi$) of Pd-N *vs.* Ni-N bonds.

The shift δ of the proton signal induced by magnetically anisotropic group (bond) treated as a point dipole is described by McConnell equation [4]

$$\delta = -\sigma = \Delta\chi\cdot(3\cos^2\theta - 1)/3r^3$$

where $\Delta\chi$ is the difference of the magnetic susceptibilities for this bond along and perpendicular to the bond direction ($\chi_{\|} - \chi_{\perp}$), r - distance to a proton from the center of bond, and θ - the angle between this vector and bond direction.



For complexes under consideration magnetic anisotropy induced shift of the proton **p** signal should include the contributions from four (two M-N$_{\mathrm{amine}}$ and two M-N$_{\mathrm{amide}}$) bonds and can be expressed as

$$\delta(p) = 1/3\cdot\Delta\chi_{\mathrm{amine}}\cdot F_{\mathrm{amine}}(p) + 1/3\cdot\Delta\chi_{\mathrm{amide}}\cdot F_{\mathrm{amide}}(p)$$

where $\Delta\chi_{\mathrm{amine}}$ and $\Delta\chi_{\mathrm{amide}}$ are the differences of magnetic susceptibilities for M-N$_{\mathrm{amine}}$ and M-N$_{\mathrm{amine}}$ bonds, and F$_{\mathrm{amine}}$(p) and F$_{\mathrm{amide}}$(p) are the sums of the $(3\cos^2\theta - 1)/r^3$ factors from two amine and two amide groups, respectively.

These factors were calculated based on structural data. For N-*meso* isomer of the 13-membered nickel(II) complex NiL^3 the structure of this unit in bis(macrocyclic) complex Ni$_2$L^4 was used. The hydrogen atoms for these calculations were inserted in a single fashion by molecular mechanics program PC Model[5] at 1.09 Å distance in all structures and the values of F(p) were averaged for two halves of the molecule (for unsymmetrical central 5-membered ring in NiL^3 averaged values for hydrogen atoms ***k*** and ***k'*** and ***l*** and ***l'***, respectively, were taken). As can be seen from Table S4, geometric factors are not too different for nickel and palladium compounds. Neglecting this difference (averaged for Pd and Ni factors F(p) were used), the difference in chemical shifts of the proton **p** in palladium and nickel complexes $\Delta\delta^{\mathrm{calc}}$(p) can be expressed as

$$\Delta\delta^{calc}(p) = 1/3\cdot\Delta\Delta\chi_{amine}\cdot F_{amine}(p) + 1/3\cdot\Delta\Delta\chi_{amide}\cdot F_{amide}(p) + C$$

where $\Delta\Delta\chi_{amine} = \Delta\chi^{Pd}{}_{amine} - \Delta\chi^{Ni}{}_{amine}$ and $\Delta\Delta\chi_{amide} = \Delta\chi^{Pd}{}_{amide} - \Delta\chi^{Ni}{}_{amide}$. Constant term C was added to equation to account for other (not related to magnetic anisotropy of the bonds) possible effects. The values of $\Delta\Delta\chi_{amide}$, $\Delta\Delta\chi_{amine}$, and C were varied to fit the experimental chemical shift differences $\Delta\delta^{exp}$ (Table S5) by least-squares procedure.

Table S4

Geometric factors F (Å^{-3}) for macrocyclic complexes ML^2 and ML^3.

p	$10^3\times F_{amine}(p)$			$10^3\times F_{amide}(p)$		
	Ni	Pd	Averaged	Ni	Pd	Averaged
			ML^2			
a	-36.64	-47.22	-41.93	+20.24	+22.98	+21.61
b	-7.56	-10.54	-9.05	+12.06	+11.82	+11.94
c	-18.88	-20.64	-19.76	+16.12	+12.48	+14.30
d	+43.68	+40.08	+41.88	+9.08	+8.28	+8.68
e	-6.64	-6.98	-6.81	-22.82	-23.60	-23.21
f	+50.66	+49.58	+50.12	-4.36	-4.20	-4.28
g	-5.96	-7.12	-6.54	+34.46	+33.48	+33.97
h	-5.04	-5.24	-5.14	+47.60	+49.48	+48.54
i	+12.36	+12.98	+12.67	-17.78	-19.86	-18.82
j	+13.48	+12.46	+12.97	-7.78	-9.40	-8.59
			ML^3			
e	-20.72	-23.82	-22.27	-26.26	-28.48	-27.37
f	+46.94	+42.40	+44.67	-4.60	-5.30	-4.95
g	-9.82	-11.12	-10.47	+36.16	+31.32	+33.74
h	-8.44	-8.02	-8.23	+48.90	+49.34	+49.12
i	+20.30	+20.44	+20.37	-36.54	-28.54	-32.54
j	+15.52	+14.16	+14.84	-9.22	-10.64	-9.93
k	-26.90	-25.42	-26.16	+10.56	+7.82	+9.19
l	+6.62	+7.10	+6.86	+18.12	+16.44	+17.28

As a result the following values were obtained:

Complexes of 14-membered ligand ML^2:

$\Delta\Delta\chi_{amine} = (13.6 \pm 3.3)\times10^{-6}$ (Å^3/molecule) / $(13.6 \pm 3.3)\times10^{-30}$ (cm^3/molecule)
$\Delta\Delta\chi_{amide} = (4.5 \pm 4.0)\times10^{-6}$ (Å^3/molecule) / $(4.5 \pm 4.0)\times10^{-30}$ (cm^3/molecule)
$C = 0.324 \pm 0.03$

Complexes of 13-membered ligand ML^3:

$\Delta\Delta\chi_{amine} = (10.1 \pm 3.0)\times10^{-6}$ (Å^3/molecule) / $(10.1 \pm 3.0)\times10^{-30}$ (cm^3/molecule)

$\Delta\Delta\chi_{amide}$ = (12.8 ± 2.5)×10^{-6} (Å^3/molecule) / (12.8 ± 2.5)×10^{-30} (cm^3/molecule)

C = 0.329 ± 0.02)

Chemical shift differences calculated using these parameters along with the experimental values are presented in Table S5.

Table S5

Experimental and calculated chemical shift differences for ML^2 and ML^3.

	ML^2 (r.m.s. ($\Delta\delta^{calc}$-$\Delta\delta^{exp}$) = 0.071 ppm)			**ML^3** (r.m.s. ($\Delta\delta^{calc}$-$\Delta\delta^{exp}$) = 0.047 ppm)		
p	$\Delta\delta^{exp}$	$\Delta\delta^{calc}$	$\Delta\delta^{calc}$-$\Delta\delta^{exp}$	$\Delta\delta^{exp}$	$\Delta\delta^{calc}$	$\Delta\delta^{calc}$-$\Delta\delta^{exp}$
a	0.237	0.166	-0.071			
b	0.246	0.301	+0.055			
c	0.094	0.255	+0.161			
d	0.545	0.527	-0.018			
e	0.364	0.258	-0.106	0.125	0.137	+0.012
f	0.556	0.545	-0.011	0.403	0.458	+0.055
g	0.394	0.345	-0.049	0.450	0.437	-0.013
h	0.399	0.373	-0.026	0.472	0.510	+0.038
i	0.326	0.353	+0.027	0.232	0.259	+0.027
j	0.331	0.370	+0.039	0.424	0.336	-0.088
k				0.248	0.280	+0.032
l				0.487	0.425	-0.062

It should be noted that the assignment of lower-field signal of the central 5-membered ring to hydrogen atom ***k***(***k'***) and of higher-field one to hydrogen atom ***l***(***l'***) for N-*meso* isomer of ML^3 is rather arbitrary. However, the inversed order of these signals leads to worse fit (r.m.s. difference 0.092 ppm). This fact and the trends in variation of chemical shifts for other pairs (***e***, ***f***) and (***c***, ***d***) were the main reasons for choosing of such version of assignment (opposite to published for NiL^3).

References

1. R. M. Lewis, G. H. Nancollas and P. Coppens, *Inorg. Chem.*, 1972, **11**, 1371.

2. Ya. D. Lampeka, S. P.Gavrish, R. W. Hay, T. Eisenblätter and P. Lightfoot, *J. Chem. Soc., Dalton Trans*., 2000, 2023.

3. P. Comba, S. P. Gavrish, R. W. Hay, P. Hilfenhaus, Ya. D. Lampeka, P. Lightfoot and A. Peters, *Inorg. Chem*., 1999, **38**, 1416.

4. H. M. McConnell, *J. Chem. Phys.*, 1957, **27**, 226.

5. PC Model 7.0. Serena Software: Bloomington, IN, 1998.