Supplementary Material

Supplementary Material Concerning Solvent Exchange

Calculation of equilibrium constant

Definitions of integrals (from Figure 1):

$Ni(dmf)_6^{2+}$	I_1-I_3	I_4-I_2
$Ni(dmf)(\underline{dmf})_4Cl^+$	I_3	I_1-(I_4-I_2)
$Ni(\underline{dmf})(dmf)_4Cl^+$	I_2	I_4-(I_1-I_3)

Table S1: Integrals for the signals of bound DMF methyl-groups for solution 2.

$[Ni^{2+}] = 0.102$; $[Cl^-] = 0.1$

Experimental

T	I_1	I_2	I_3	I_4	K
193	0.47	0.06	0.29	0.19	140.65 ± 60.77
201	0.5	0.06	0.26	0.18	106.05 ± 72.59
215	0.46	0.05	0.3	0.2	140.65 ± 52.42
218	0.49	0.04	0.3	0.18	155.30 ± 109.35
			global fit of all	temperatures:	**134.27 ± 34.72**

Table S2: Integrals for the signals of bound DMF methyl-groups for solution 3.

$[Ni^{2+}] = 0.102$; $[Cl^-] = 0.3$

Experimental

T	I_1	I_2	I_3	I_4	K
193	0.44	0.09	0.35	0.13	46.97 ± 16.34
201	0.43	0.08	0.36	0.13	53.61 ± 15.34
215	0.42	0.08	0.37	0.12	76.72 ± 23.96
218	0.41	0.07	0.37	0.14	55.54 ± 14.75
			global fit of all	temperatures:	**56.54 ± 8.19**

global fit (all samples and all temperatures): **K = 116 ± 22**

Equations used for treatment of ^{13}C-NMR relaxation and chemical shift data:

Reduced transverse NMR relaxation time T_{2r} for the free or coalesced DMF signal:

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left(\frac{1}{T_2} - \frac{1}{T_{2A}^0}\right) = \frac{1}{\tau_m}\left[\frac{T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + \Delta\omega_m^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2}\right] + \frac{1}{T_{2os}} \qquad \text{(S1)}$$

Reduced chemical shift $\Delta\omega_r$ relative to pure DMF

$$\Delta\omega_r = \frac{\Delta\omega_s}{P_m} = \frac{\Delta\omega_m}{(\tau_m / T_{2m} + 1)^2 + \tau_m^2 \Delta\omega_m^2} + \Delta\omega_{os} \qquad \text{(S2)}$$

Inner- and outer-sphere relaxation,

$$1/T_{2m} = (1/T_{2m})^{298} \exp[(E_m / R)(1/T - 1/298.15K)] \qquad \text{(S3)}$$

$$1/T_{2os} = (1/T_{2os})^{298} \exp[(E_{os} / R)(1/T - 1/298.15K)] \qquad \text{(S4)}$$

Pseudo first order reaction rate constant for solvent exchange of a particular coordinated DMF molecule:

$$k = 1/\tau_m = \frac{k_B T}{h} \exp(\Delta S^{\ddagger} / R - \Delta H^{\ddagger} / RT) \qquad \text{(S5)}$$

Chemical shift between free and coordinated solvent in the absence of exchange

$$\Delta\omega_m = B_1 / T \qquad \text{(S6)}$$

Outer-sphere chemical shift

$$\Delta\omega_{os} = \Delta\omega_{os,0} + C/T \qquad \text{(S7)}$$

Fitting Results:

Parameter	Unit	Solution 1	Solution 2	Solution 3	Solution 4
k^{298}	$10^3 s^{-1}$	3.7 ± 0.4	529 ± 103		16.7 ± 1.9
$\Delta H^{\ddagger}$	kJ mol^{-1}	59.3 ± 4.6	42.36 ± 3.3		59.3*
$\Delta S^{\ddagger}$	J mol^{-1} K^{-1}	+22.3 ± 14	+6.7 ± 15		+34.8 ± 1
E_{os}	kJ mol^{-1}	5*	8*	8*	5*
$1/T_{2os}^{298}$	s^{-1}	454¨± 54	454*	454*	454*
E_m	kJ mol^{-1}	5*	5*	5*	5*
$1/T_{2m,cis}^{298}$	s^{-1}	435 ± 240	435*	435*	435*
$1/T_{2m,trans}^{298}$	s^{-1}	610 ± 490	610*	610*	610*
C_{cis}	10^6 rad K s^{-1}	-1.74 ± 0.17	0.22 ± 0.48	-1.3 ± 0.7	0*
C_{trans}	10^6 rad K s^{-1}	-1.45 ± 0.17	1.7 ± 0.5	0.3 ± 0.7	0*
$\Delta\omega_{os0}$	rad s^{-1}	5836 ± 700	¨-2160 ± 2220	6260 ± 3370	0*
$B_{1,cis}$	10^6 rad K s^{-1}	3.41 ± 0.12	7.2 ± 0.3	4.2 ± 0.3	4.3 ± 0.3
$B_{1,trans}$	10^6 rad K s^{-1}	7.26 ± 0.13	11.0 ± 0.3	5.5 ± 0.4	8.7 ± 0.4
$1/T_{2m,co}^{298}$ †	s^{-1}		135 ± 60		

* value fixed in the fitting procedure

† value for the coordinated DMF

cis/trans: Position of the methylgroup of DMF relative to the oxygen

Composition of solutions:

Solution 1: 0.102m in $[Ni(DMF)_6]^{2+}$ ($P_m = 4.3 \times 10^{-2}$) in DMF.

Solution 2: 0.026m in $[Ni(DMF)_6]^{2+}$, 0.076m in $[NiCl(DMF)_5]^{+}$ ($P_m = 2.76 \times 10^{-2}$) and 0.024m in Cl^- in DMF

Solution 3: 0.004m in $[Ni(DMF)_6]^{2+}$, 0.098m in $[NiCl(DMF)_5]^{+}$ ($P_m = 3.58 \times 10^{-2}$) and 0.202m in Cl^- in DMF

Solution 4: 0.1m in $[Ni(DMF)_6]^{2+}$, $<10^{-3}$m in $[NiBr(DMF)_5]^{+}$ and 0.11m in Br^- in DMF

Figure Captions:

Figure S1: Reduced transverse NMR relaxation rates, $1/T_{2r}$, (left) and reduced chemical shifts, $\Delta\omega_r$, (right) of solutions 1 to 4. (•) *trans*-CH_3 of free DMF, (■) *cis*-CH_3 of free DMF, Only filled symbols were used for the fitting procedure. Open symbols correspond to signals due to coordinated DMF or to high temperature free DMF signals not used in the fitting procedure.

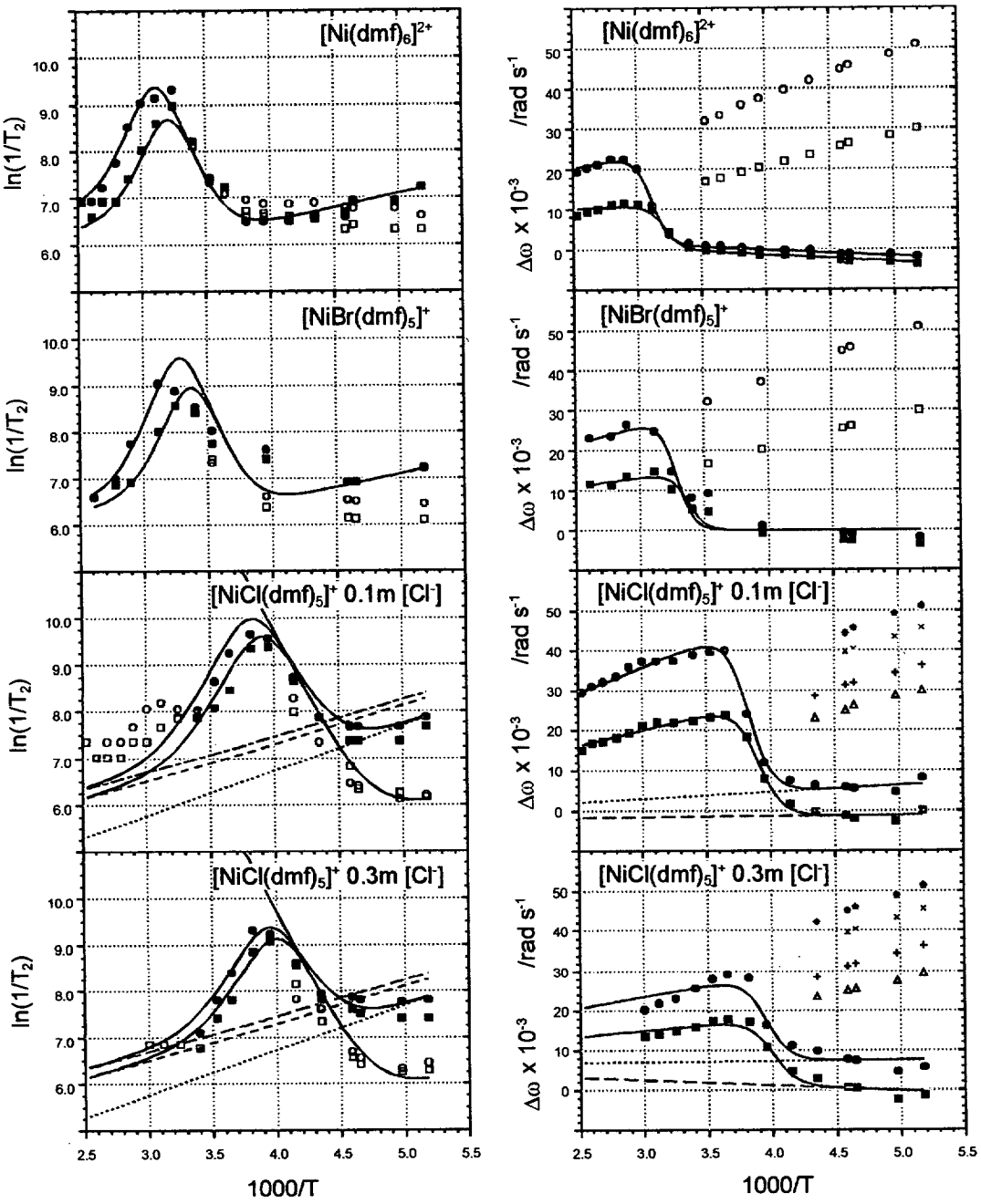

Table S3: Logarithms of reduced transverse ^{13}C-NMR relaxation rates $\ln(1/T_{2r})$ for the methyl-groups of free and bound DMF for a solution 0.102m in $[Ni(DMF)_6]^{2+}$ ($P_m = 4.3\times10^{-2}$) in DMF (Sol. 1).

1000K/T	$\ln(1/T_2)$ free/cis	$\ln(1/T_2)$ free/trans	$\ln(1/T_2)$ bound/cis	$\ln(1/T_2)$ bound/trans
5.18135	7.23572	7.23572	6.3198	6.6064
4.97512	6.93034	6.93034	6.32544	6.77382
4.65116	6.93034	6.93034	6.41557	6.77382
4.58716	6.68918	6.59387	6.33105	6.77741
4.34783	6.59387	6.59387	6.54614	6.89393
4.14938	6.59387	6.48851	6.50897	6.8653
3.95257	6.59387	6.48851	6.67102	6.86858
3.81679	6.59387	6.48851	6.71441	6.96035
3.64964	7.23572	7.23572	7.24112	7.08553
3.53357	7.42678	7.42678	7.43017	7.34113
3.40136	8.11993	8.22311		
3.24675	8.99176	9.30856		
3.11526	8.59535	9.1511		
3.003	8.02895	9.05346		
2.89855	7.42678	8.52539		
2.80112	6.93034	7.75702		
2.69542	6.93034	7.23572		
2.61097	6.59387	6.93034		
2.53165	6.93034	6.93034		

Table S4: Reduced chemical shift $\Delta\omega_r$ for the methyl-groups of free and bound DMF for a solution 0.102m in $[Ni(DMF)_6]^{2+}$ ($P_m = 4.3\times10^{-2}$) in DMF (Sol. 1).

1000K/T	$\Delta\omega_r$ free/cis $[10^3\ rad^{-1}\ s^{-1}]$	$\Delta\omega_r$ free/trans $[10^3\ rad^{-1}\ s^{-1}]$	$\Delta\omega_r$ bound/cis $[10^3\ rad^{-1}\ s^{-1}]$	$\Delta\omega_r$ bound/trans $[10^3\ rad^{-1}\ s^{-1}]$
5.18135	-3.6121	-1.75345	30.10667	50.96432
4.97512	-2.92942	-1.16896	28.35583	48.41051
4.65116	-2.79412	-1.16896	26.36469	45.62896
4.58716	-2.62944	-1.16896	25.59352	44.61749
4.34783	-1.53237	-0.14612	23.56468	41.85518
4.14938	-1.26949	-0.14612	21.88963	39.57937
3.95257	-1.19527	-0.14612	20.47372	37.55643
3.81679	-0.55511	0.43836	19.41827	36.07731
3.64964	-0.04252	0.87672	17.85708	33.46656
3.53357	-0.13297	0.87672	17.02269	32.07579
3.40136	0.71438	1.4612		
3.24675	4.21046	3.79913		
3.11526	9.94087	10.81291		
3.003	11.03794	20.16462		
2.89855	11.25829	22.50255		
2.80112	11.04028	22.50255		
2.69542	9.8605	21.18747		
2.61097	9.35025	20.45687		
2.53165	8.40163	19.43402		

Table S5: Logarithm reduced transverse ^{13}C-NMR relaxation rates $\ln(1/T_{2r})$ for the methyl-groups of free and bound DMF for a solution 0.026m in $[Ni(DMF)_6]^{2+}$, 0.076m in $[NiCl(DMF)_5]^{+}$ ($P_m = 2.8 \times 10^{-2}$) and 0.024m in Cl^- in DMF (Sol. 2).

1000K/T	$\ln(1/T_2)$ free/cis	$\ln(1/T_2)$ free/trans	$\ln(1/T_2)$ bound/cis	$\ln(1/T_2)$ bound/trans
5.18135	7.66472	7.85577	6.16201	6.20097
4.97512	7.35934	7.66472	6.25067	6.11454
4.65116	7.35934	7.66472	6.33211	6.39175
4.58716	7.35934	7.66472	6.81805	6.45794
4.34783	7.85577	7.85577		7.34524
4.14938	8.65211	8.72761	7.97884	8.28121
3.95257	9.37424	9.55656		
3.81679	9.34525	9.64753		
3.64964	8.45795	9.24207		
3.53357	8.05248	8.65211		
3.40136	7.85577	8.01612		
3.24675	7.85577	8.05248		
3.11526	7.66472	8.18602		
3.0030	7.35934	8.05248		
2.89855	7.35934	7.66472		
2.80112	7.02286	7.35934		
2.69542	7.02286	7.35934		
2.61097	7.02286	7.02286		
2.53165	7.35934	7.35934		

Table S6: Reduced chemical shift $\Delta\omega_r$ for the methyl-groups of free and bound DMF for a solution 0.026m in $[Ni(DMF)_6]^{2+}$, 0.076m in $[NiCl(DMF)_5]^+$ ($P_m = 2.8 \times 10^{-2}$) and 0.024m in Cl^- in DMF (Sol.2).

1000K/T	$\Delta\omega_r$ free/cis $[10^3\ rad^{-1}\ s^{-1}]$	$\Delta\omega_r$ free/trans $[10^3\ rad^{-1}\ s^{-1}]$	$\Delta\omega_r$ bound/cis $[10^3\ rad^{-1}\ s^{-1}]$	$\Delta\omega_r$ bound/trans $[10^3\ rad^{-1}\ s^{-1}]$
5.18135	0.06283	8.07837	36.39092	45.51542
4.97512	-2.47916	4.48799	34.45859	43.3121
4.65116	-1.82257	5.38558	32.15373	40.45369
4.58716	-1.12087	5.83438	31.3133	39.66697
4.34783	-0.33368	6.28318	28.75051	
4.14938	1.64081	7.40518		
3.95257	7.81358	11.89316		
3.81679	18.22145	23.78632		
3.64964	23.49662	39.71867		
3.53357	22.90892	39.26987		
3.40136	22.19062	38.59668		
3.24675	21.72522	37.02588		
3.11526	21.77391	37.02588		
3.003	20.99031	37.02588		
2.89855	19.30911	35.67949		
2.80112	18.07671	33.43549		
2.69542	17.16251	32.0891		
2.61097	16.8277	30.9671		
2.53165	15.1465	29.39631		

Table S7: Logarithm reduced transverse ^{13}C-NMR relaxation rates $\ln(1/T_{2r})$ for the methyl-groups of free and bound DMF for a solution 0.004m in $[Ni(DMF)_6]^{2+}$, 0.098m in $[NiCl(DMF)_5]^+$ ($P_m = 3.58 \times 10^{-2}$) and 0.202m in Cl^- in DMF (Sol. 3).

1000K/T	$\ln(1/T_2)$ free/cis	$\ln(1/T_2)$ free/trans	$\ln(1/T_2)$ bound/cis	$\ln(1/T_2)$ bound/trans
5.18135	7.50042	7.88818	6.29222	6.45794
4.97512	7.50042	7.85181	6.25672	6.33211
4.65116	7.6005	7.88818	6.41773	6.55638
4.58716	7.69147	7.95717	6.58281	6.68991
4.34783	7.88818	8.02171	7.34726	7.61553
4.14938	8.65032	8.71486	8.16403	7.82558
3.95257	9.16115	9.30957		
3.81679	8.938	9.38429		
3.64964	7.88818	8.4878		
3.53357	7.50042	7.88818		
3.40136	6.85856	7.19503		
3.24675	6.85856	6.85856		
3.11526	6.85856	6.85856		
3.003	6.85856	6.85856		

Table S8: Reduced chemical shift $\Delta\omega_r$ for the methyl-groups of free and bound DMF for a solution 0.004m in $[Ni(DMF)_6]^{2+}$, 0.098m in $[NiCl(DMF)_5]^+$ ($P_m = 3.58 \times 10^{-2}$) and 0.202m in Cl^- in DMF (Sol. 3).

1000K/T	$\Delta\omega_r$ free/cis $[10^3\ rad^{-1}\ s^{-1}]$	$\Delta\omega_r$ free/trans $[10^3\ rad^{-1}\ s^{-1}]$	$\Delta\omega_r$ bound/cis $[10^3\ rad^{-1}\ s^{-1}]$	$\Delta\omega_r$ bound/trans $[10^3\ rad^{-1}\ s^{-1}]$
5.18135	-1.27948	6.28318	36.34926	45.56292
4.97512	-2.48433	4.95038	34.45677	43.38881
4.65116	0.54797	7.99677	31.98453	40.39789
4.58716	0.76255	8.37757	31.32649	39.62544
4.34783	3.14407	10.66237	28.53726	
4.14938	5.20019	12.18556		
3.95257	11.77049	17.89754		
3.81679	18.69741	30.8447		
3.64964	19.36533	31.7967		
3.53357	18.86668	30.4639		
3.40136	17.30521	27.79831		
3.24675	16.14872	24.94232		
3.11526	15.42844	23.60952		
3.003	14.76357	21.89593		

Table S9: Logarithm reduced transverse ^{13}C-NMR relaxation rates $\ln(1/T_{2r})$ for the methyl-groups of free and bound DMF for a solution 0.1m in $[Ni(DMF)_6]^{2+}$, < 10^{-3}m in $[NiBr(DMF)_5]^{+}$ and 0.11m in Br^{-} in DMF (Sol. 4).

1000K/T	$\ln(1/T_2)$ free/cis	$\ln(1/T_2)$ free/trans	$\ln(1/T_2)$ bound/cis	$\ln(1/T_2)$ bound/trans
5.18135	7.23572	7.23572	6.10056	6.43803
4.65116	6.93034	6.93034	6.12146	6.50132
4.58716	6.93034	6.93034	6.14868	6.52922
3.95257	7.62349	7.42678	6.37584	6.60856
3.53357	8.02895	7.75702	7.41003	7.3513
3.40252	8.53275	8.4189		
3.24675	8.8864	8.56795		
3.11429	9.05576	8.01674		
2.89855	7.75702	6.93034		
2.77932	7	6.87377		
2.61097	6.59387	6.59387		

Table S10: Reduced chemical shift $\Delta\omega_r$ for the methyl-groups of free and bound DMF for a solution 0.1m in $[Ni(DMF)_6]^{2+}$, < 10^{-3}m in $[NiBr(DMF)_5]^{+}$ and 0.11m in Br^{-} in DMF (Sol. 4).

1000K/T	$\Delta\omega_r$ free/cis [10^3 rad^{-1} s^{-1}]	$\Delta\omega_r$ free/trans [10^3 rad^{-1} s^{-1}]	$\Delta\omega_r$ bound/cis [10^3 rad^{-1} s^{-1}]	$\Delta\omega_r$ bound/trans [10^3 rad^{-1} s^{-1}]
5.18135	-3.6121	-1.89957	29.96574	50.97456
4.65116	-2.648	-0.87672	26.10649	45.60759
4.58716	-2.3372	-0.58448	25.49953	44.74937
3.95257	-0.61078	1.02284	20.24164	37.225
3.53357	4.54289	9.05947	16.78671	32.23026
3.40252	5.24252	8.0264		
3.24675	10.05528	14.75817		
3.11429	14.78197	24.77765		
2.89855	13.4501	26.4478		
2.77932	11.3362	23.56777		
2.61097	11.54206	23.08703		

Supplementary Material Concerning Kinetics of Complex Formation

Table S11. Experimental Rate Constants for the System Nickel(II)/TMC/DMF with $[TMC]_o = 10^{-3}$ M and Variable Nickel Concentration at 298 K and I = 0.6 M ($TBAClO_4$)

$[Ni^{2+}]_o$ [M]	$[Ni^{2+}]_o$:$[TMC]_o$	$k_{obsd,1}$ [s^{-1}]	$k_{obsd,2}$ [s^{-1}]	$k_{obsd,3}$ [s^{-1}]
$1 \cdot 10^{-2}$	10:1	2,3 ± 0.2	0,9 ± 0.1	$(1.5 \pm 0.1) \cdot 10^{-3}$
$2 \cdot 10^{-2}$	20:1	4,9 ± 0.5	1,8 ± 0.1	$(1.8 \pm 0.1) \cdot 10^{-3}$
$5 \cdot 10^{-2}$	50:1	12 ± 1	4,6 ± 0.2	$(1.5 \pm 0.2) \cdot 10^{-3}$
$7 \cdot 10^{-2}$	70:1	17 ± 2	7 ± 1	$(1.6 \pm 0.2) \cdot 10^{-3}$
0.1	100:1	23 ± 2	10 ± 1	$(1.1 \pm 0.1) \cdot 10^{-3}$

Table S12 Experimental Rate Constants for the System Nickel(II)/TMC/4iBuM/DMF with $[TMC]_o = [nickel]_o = 10^{-3}$ M and Variable Concentration of the Base 4iBuM at 298 K and I = 0.6 M ($TBAClO_4$)

[4iBuM] [M]	$k_{obsd,1}$ [s^{-1}]	$k_{obsd,2}$ [s^{-1}]
$8 \cdot 10^{-3}$	$(9.8 \pm 0.5) \cdot 10^{-2}$	$(5.4 \pm 0.1) \cdot 10^{-4}$
$2 \cdot 10^{-2}$	$(1.01 \pm 0.07) \cdot 10^{-1}$	$(5.0 \pm 0.1) \cdot 10^{-4}$
$4 \cdot 10^{-2}$	$(1.02 \pm 0.07) \cdot 10^{-1}$	$(4.7 \pm 0.2) \cdot 10^{-4}$
$1.2 \cdot 10^{-1}$	$(9.9 \pm 0.5) \cdot 10^{-2}$	$(1.85 \pm 0.1) \cdot 10^{-4}$

Table S13 Experimental Rate Constants for the System Nickel(II)/TMC/TBACl/DMF with $[TMC]_o = [nickel]_o = 10^{-3}$ M and Variable Concentration of Chloride at 298 K and I = 0.6 M ($TBAClO_4$)

$[TBACl]_o$ [M]	% of monochloro nickel species	z[a]	$k_{obsd,1}$,[b] s^{-1}	$10^4 k_{obsd,2}$, s^{-1}
$1 \cdot 10^{-4}$	4.3	23	0.3 ± 0.1	10 ± 1
$2 \cdot 10^{-4}$	8.3	12	1.7 ± 0.1	11 ± 2
$1 \cdot 10^{-3}$	34	3.0	2.4 ± 0.2	9.5 ± 0.5
$2 \cdot 10^{-3}$	53	1.9	3.9 ± 0.1	13 ± 3
$3 \cdot 10^{-3}$	64	1.6	7.2 ± 0.2	11 ± 2
$5 \cdot 10^{-3}$	75	1.3	11 ± 0.3	9.8 ± 0.9
$7 \cdot 10^{-3}$	80	1.3	24 ± 1	11 ± 2
$1 \cdot 10^{-2}$	83	1.2	18 ± 1	12 ± 3
$2 \cdot 10^{-2}$	83	1.2	26 ± 1	9.1 ± 0.8
$5 \cdot 10^{-2}$	73	1.4	25 ± 0.8	12 ± 2
$1 \cdot 10^{-1}$	58	1.7	24 ± 2	8.5 ± 0.7

[a]Calculated according to $z = [TMC]_o/[Ni(DMF)_5Cl^+]$ on the basis of $\beta_1 = 708$ M^{-1} and $\beta_2 = 5754$ M^{-1} (see ref 9). [b]Calculated with eq 7a.

Table S14. Experimental Rate Constants for the System Nickel(II)/TEC/DMF with $[TEC]_o = 10^{-3}$ M and Variable Nickel Concentration at 298 K and I = 0.6 M ($TBAClO_4$)

$[Ni^{2+}]_o$ [M]	$[Ni^{2+}]_o$:$[TEC]_o$	$k_{obsd,1}$ [s^{-1}]	$k_{obsd,2}$ [s^{-1}]	$k_{obsd,3}$ [s^{-1}]
$5 \cdot 10^{-3}$	5 : 1	1.2 ± 0.1	$(3.7 \pm 0.1) \cdot 10^{-2}$	$(5.7 \pm 0.1) \cdot 10^{-3}$
$1 \cdot 10^{-2}$	10 : 1	2.5 ± 0.3	$(4.0 \pm 0.4) \cdot 10^{-2}$	$(6.1 \pm 0.1) \cdot 10^{-3}$
$2 \cdot 10^{-2}$	20 : 1	4.9 ± 0.3	$(4.7 \pm 0.7) \cdot 10^{-2}$	$(6.5 \pm 0.9) \cdot 10^{-3}$
$5 \cdot 10^{-2}$	50 : 1	12 ± 1	$(4.4 \pm 0.3) \cdot 10^{-2}$	$(6.5 \pm 0.3) \cdot 10^{-3}$

Table S15. Experimental Rate Constants for the System Nickel(II)/TEC/DMF with $[nickel]_o = 10^{-3}$ M and Variable Concentration of TEC at 298 K and I = 0.6 M ($TBAClO_4$)

$[TEC]_o$ [M]	$[TEC]_o$:$[Ni^{2+}]_o$	$k_{obsd,1}$ [s^{-1}]	$k_{obsd,2}$ [s^{-1}]	$k_{obsd,3}$ [s^{-1}]
$5 \cdot 10^{-3}$	5 : 1	1.2 ± 0.1	$(4.2 \pm 0.4) \cdot 10^{-2}$	$(6.2 \pm 0.6) \cdot 10^{-3}$
$1 \cdot 10^{-2}$	10 : 1	2.5 ± 0.3	$(5.4 \pm 1.1) \cdot 10^{-2}$	$(6.3 \pm 0.3) \cdot 10^{-3}$
$2 \cdot 10^{-2}$	20 : 1	4.7 ± 0.5	$(4.6 \pm 0.7) \cdot 10^{-2}$	$(6.1 \pm 0.9) \cdot 10^{-3}$
$3 \cdot 10^{-2}$	50 : 1	7.1 ± 0.5	$(5.0 \pm 04) \cdot 10^{-2}$	$(6.6 \pm 0.5) \cdot 10^{-3}$

Table S16. Experimental Rate Constants for the System Nickel(II)/TEC/TBACl/DMF with $[TEC]_o = [nickel]_o = 10^{-3}$ M and Variable Concentration of Chloride at 298 K and I = 0.6 M ($TBAClO_4$)

$[TBACl]_o$, [M]	% of monochloro nickel species	z[a]	$k_{obsd,1}$,[b] s^{-1}	$10^2 k_{obsd,2}$, s^{-1}	$10^3 k_{obsd,3}$, s^{-1}
$1 \cdot 10^{-4}$	4.3	23	0.10 ± 0.01	4.2 ± 0.5	5.9 ± 0.2
$2 \cdot 10^{-4}$	8.3	12	0.14 ± 0.01	3.5 ± 0.2	6.6 ± 0.5
$1 \cdot 10^{-3}$	33.9	3.0	0.35 ± 0.01	4.3 ± 0.3	6.0 ± 0.3
$2 \cdot 10^{-3}$	53.0	1.9	0.61 ± 0.05	4.0 ± 0.4	6.6 ± 0.2
$3 \cdot 10^{-3}$	63.9	1.6	1.02 ± 0.09	3.8 ± 0.4	6.7 ± 0.1
$5 \cdot 10^{-3}$	74.9	1.3	2.0 ± 0.07	3.9 ± 0.3	6.1 ± 0.2
$1 \cdot 10^{-2}$	82.9	1.2	5.4 ± 0.2	4.4 ± 0.2	6.2 ± 0.3
$2 \cdot 10^{-2}$	83.0	1.2	10.6 ± 0.4	4.1 ± 0.5	6.3 ± 0.1
$3.5 \cdot 10^{-2}$	78.9	1.3	10.8 ± 0.4	4.2 ± 0.2	5.7 ± 0.2
$5 \cdot 10^{-2}$	72.6	1.4	11.7 ± 0.5	4.1 ± 0.1	6.9 ± 0.4

[a]Calculated according to $z = [TEC]_o/[Ni(DMF)_5Cl^+]$ on the basis of $\beta_1 = 708$ M^{-1} and $\beta_2 = 5754$ M^{-1} (see ref 9). [b]Calculated with eq 7a.

Table S17. Vis Absorption Data of the Various Complexes

Complex	solvent	method[a]	λ_{max}, nm (ε_{max}, $M^{-1}cm^{-1}$)
trans I-Ni(TMC)$^{2+}$	nitromethane	B	513 (219)
trans I-Ni(TMC)(DMF)$^{2+}$ [b]	nitromethane	A	398 (137), 506 (17), 658 (41)
trans I-Ni(TMC)Cl^{+} [c]	DMF	A	426 (135), 715 (44)
trans I-Ni(TMC)Br^{+} [d]	DMF	A	433 (170), 723 (53)
trans III-Ni(TMC)$^{2+}$	nitromethane	B	494 (80)
trans III-Ni(TMC)$^{2+}$	DMF	B	374 (22), 500 (23), 603 sh, 766 (6), 851 (5)
trans III-Ni(TMC)Cl^{+} [c]	DMF	A	400 (111), 641 (38)
trans III-Ni(TMC)Br^{+} [d]	DMF	A	405 (256), 642 (73)
Ni(TEC)$^{2+}$ (violet form)	nitromethane	B	543 (185)
Ni(TEC)(DMF)$^{2+}$ (violet form)[b]	nitromethane	A	406 (100), 545 (92), 680 (33)
Ni(TEC)Cl^{+} [c]	DMF	A	435 (134), 740 (41)
Ni(TEC)Br^{+} [d]	DMF	A	442 (167), 749 (48)
Ni(TMC)$_{int}^{2+}$ [e]	DMF	C	394 (56), 504 (62)
Ni(TMC)$^{2+}$ [f]	DMF	C	398 (133)
Ni(TMC)Cl$_{int}^{2+}$ [g]	DMF	C	416 (137)
Ni(TMC)Cl^{+} [h]	DMF	C	423 (150)
Ni(TEC)$_{int,1}^{2+}$	DMF	C	408 (80), 531 (83)
Ni(TEC)$_{int,2}^{2+}$	DMF	C	407 (97), 542 (81)
Ni(TEC)$^{2+}$ [f]	DMF	C	407 (95), 542 (80)
Ni(TEC)Cl$_{int,1}^{2+}$ [g]	DMF	C	427 (137)
Ni(TEC)Cl$_{int,2}^{2+}$ [g]	DMF	C	438 (170)
Ni(TEC)Cl^{+} [h]	DMF	C	435 (175)

[a]Absorption data obtained by conventional spectrophotometry (B) and from either spectrophotometric titration studies in the range 350-1000 nm (A) or from kinetic studies in the range 320-620 nm (C). [b]Titration with DMF in nitromethane. [c]Titration with TBACl. [d]Titration with TBABr. [e]Data obtained in the presence of the base 4iBuM. [f]Final spectrum of the reaction of Ni(DMF)$_6^{2+}$ with the ligand. [g]Intermediate NiL$_{int}^{2+}$ in the presence of TBACl. [h]Final spectrum in the presence of TBACl.