Anion Exchange in [Ni(η^5-C_5H_4R)(Cl)(NHC)]. Counterion Effect on the Structure and Catalytic Activity

W. Buchowicz,[1] Ł. Banach, J. Conder, P. A. Guńka, D. Kubicki, and P. Buchalski
Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland

Supporting Information

VT ^{1}H measurements of complex **3c**

In order to estimate the thermodynamic parameters of complex **3c** a series of variable-temperature ^{1}H NMR experiments was performed in the temperature range from -55 to 100 ºC (Table S1). The function δ=f(1/T) used to fit the experimental data has the following form:

$$\delta = \delta_{ls} + \frac{C}{T[1 + e^{(\Delta H^\circ - T\Delta S^\circ)/RT}]}$$

where δ is the observed chemical shift, δ_{ls} is the chemical shift fitted for diamagnetic species, ΔHº and ΔSº are the enthalpy and entropy, respectively, of the transition between low-spin and high-spin states, T is the absolute temperature in Kelvin, and *C* is a constant related to the molar susceptibility of the high-spin species. The experimental data and the fitting curve are shown in Figure S1.
Final set of parameters with asymptotic standard errors is as follows:

RMSD of residuals: 0.0226991

δ_{ls}	= 4.72 ± 0.038	(0.81 %)
C	= 48000 ± 30600	(63.51 %)
ΔHº	= 15151 ± 430	(2.82 %)
ΔSº	= 16.7 ± 3.9	(23.14 %)

Table S1. Set of parameters used for fitting chemical shifts in **3c**

t [ºC]	T [K]	1/T [1/K]	Chemical shift of Cp [ppm]
-55	218.15	0.00458	4.30
-50	223.15	0.00448	4.26
-40	233.15	0.00429	4.10
-30	243.15	0.00411	3.90
-10	263.15	0.00380	3.39
10	283.15	0.00353	2.70
25	298.15	0.00335	2.00
30	303.15	0.00330	1.74
40	313.15	0.00319	1.22
50	323.15	0.00309	0.64
60	333.15	0.00300	0.00
70	343.15	0.00291	-0.68
80	353.15	0.00283	-1.42
90	363.15	0.00275	-2.20
100	373.15	0.00268	-3.00

[1] Corresponding autor:

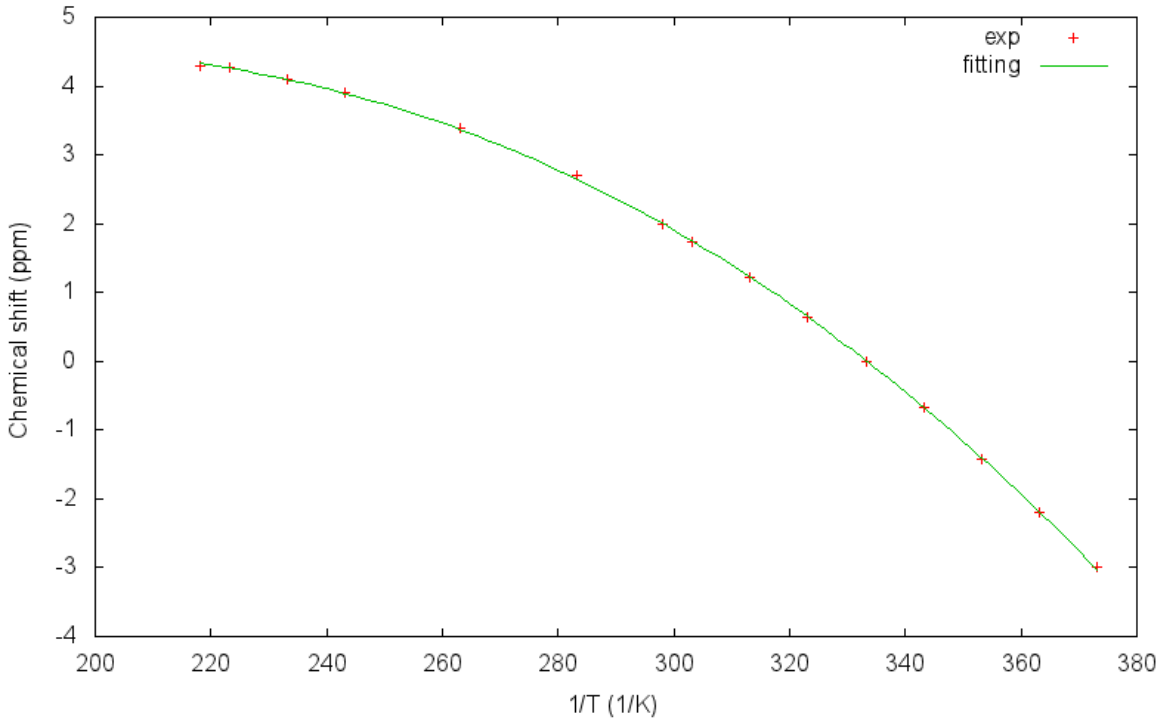
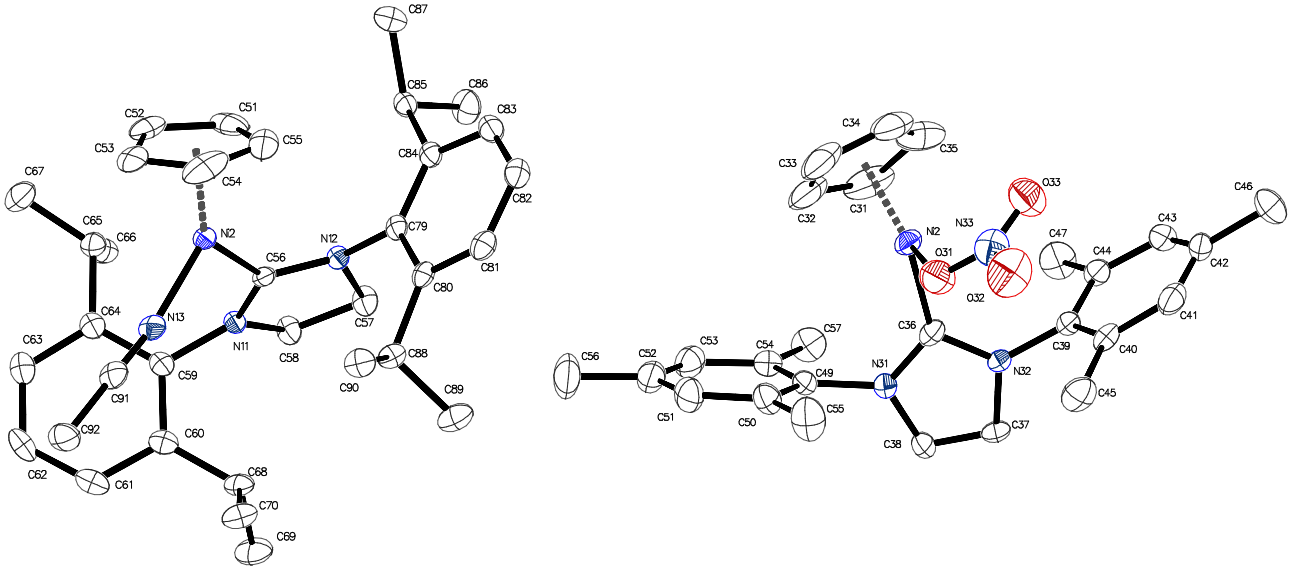


Figure S1. Experimental data and fitted curve for **3c**.

Table S2. Angles around nickel atoms and their sum in complexes **2c**, **3a**, **2j** and **3c**

angle / º	**2c**	**3a**	**2j**	**3c**
X(N3,O1)−Ni1−C6	102.23(8)	91.75(6)	94.61(7)	93.72(19)
C6−Ni1−Cg	132.57(6)	133.15(5)	132.50(5)	133.60(14)
Cg−Ni1−X(N3,O1)[a]	125.13(6)	135.03(4)	132.85(6)	131.95(15)
Σ	359.93(12)	359.93(9)	359.96(10)	359.3(3)
N13−Ni2−C56	102.83(8)		O31−Ni2−C36	94.2(2)
C56−Ni2−Cg	131.09(6)		C36−Ni2−Cg	133.81(19)
Cg−Ni1−N13	126.05(6)		Cg−Ni1−O31	131.31(15)
Σ	359.97(12)			359.3(3)

[a] N3 denotes the nitrogen atom of the coordinated acetonitrile for **2c** and **2j**; O1 denotes the oxygen atom of the trifluoroacetate or nitrate anions for complexes **3a** and **3c**, respectively. (See Figure 2 for the atom numbering scheme).



2c **3c**

Figure S3. The molecular structure of complexes **2c** and **3c** (second molecules from the asymmetric unit). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

Table S3. Selected bond lengths involving nickel in complexes **2c** and **3c** (the second molecules from the asymmetric unit)

d /Å	**2c**	*d* /Å	**3c**
Ni2−C51	2.023(2)	Ni2−C31	2.033(8)
Ni2−C52	2.135(2)	Ni2−C32	2.150(7)
Ni2−C53	2.125(2)	Ni2−C33	2.178(7)
Ni2−C54	2.149(3)	Ni2−C34	2.136(7)
Ni2−C55	2.123(3)	Ni2−C35	2.133(7)
Ni2−C56	1.907(2)	Ni2−C36	1.893(6)
Ni2−N13	1.8719(18)	Ni2−O31	1.905(4)

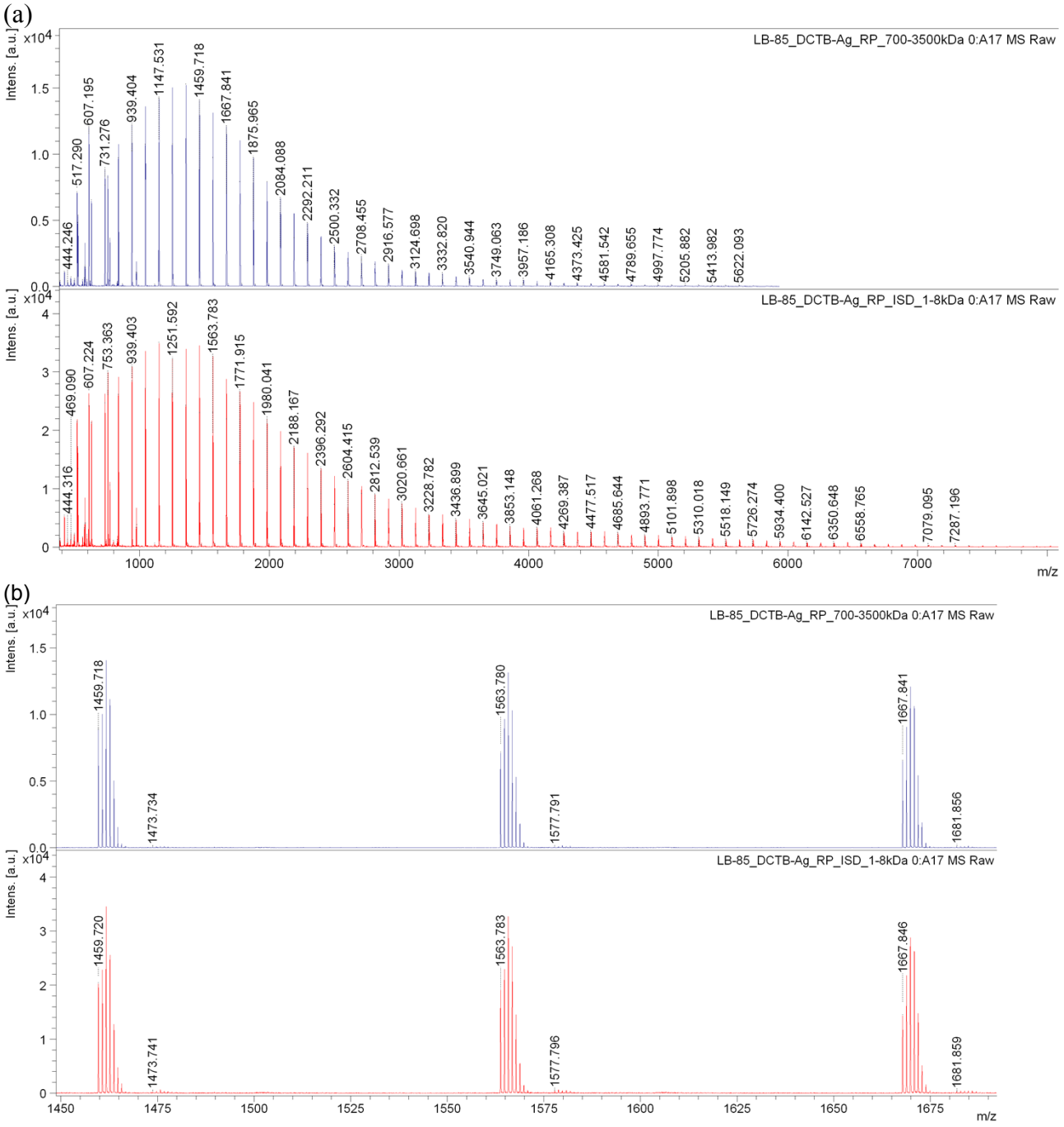


Figure S3. MALDI-TOF MS of polystyrene obtained with complex **2f** (DCTB matrix with added CF_3COOAg): (a) full spectrum; (b) expanded.