

# Synthesis, Structure and Electrochemistry of isomeric Nickel(II) Complexes of a [9]ane fused Cyclam Macrotricyclic. Evidence for a Stable *trans-IV* and a Redox Induced Rearrangement in a *trans-I* Conformations.

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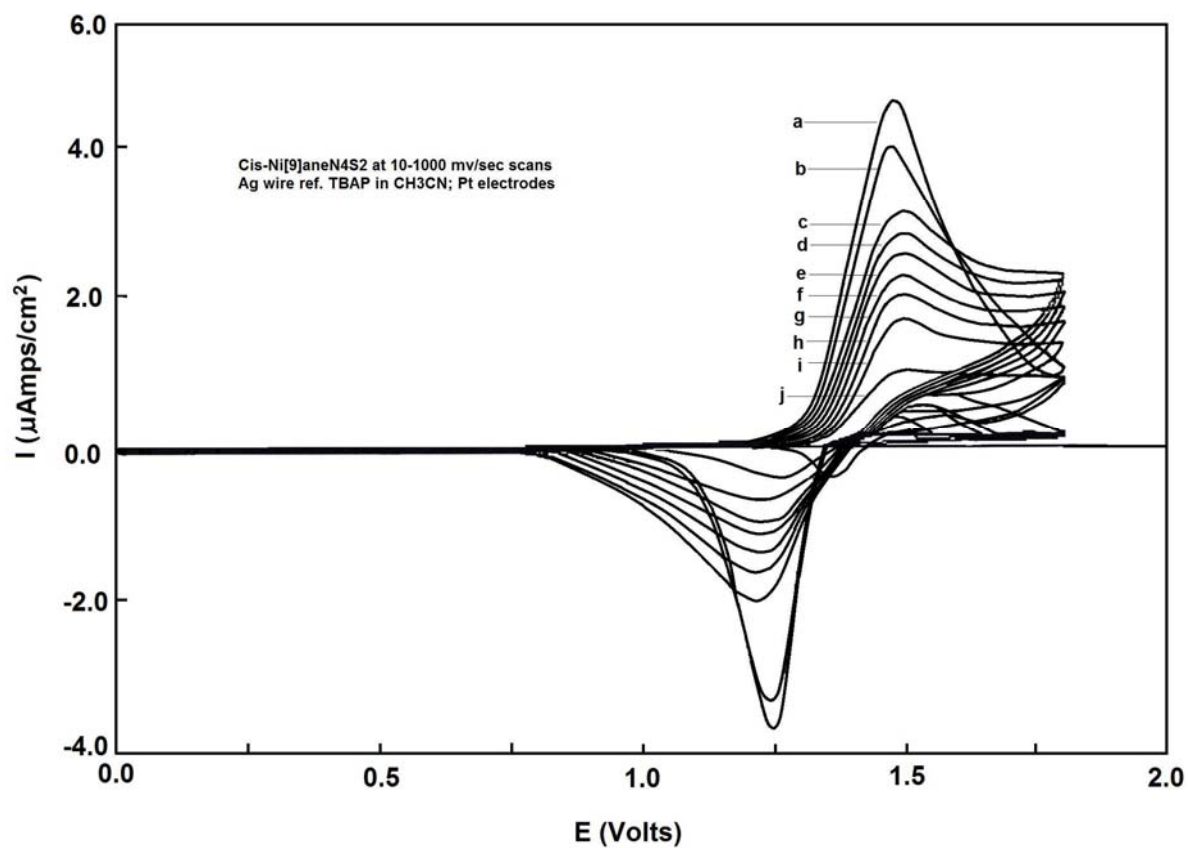
Figure S3. Scan rate dependent cyclic voltammogram of *cis*-[Ni(*trans-I*, *syn-L3*)] cation.

**Table S1. Crystallographic Data**

Molecular formula	cis-NiCl <sub>2</sub> S <sub>2</sub> O <sub>4</sub> N <sub>4</sub> C <sub>18</sub> H <sub>44</sub>	trans-NiCl <sub>2</sub> S <sub>2</sub> O <sub>8</sub> N <sub>4</sub> C <sub>18</sub> H <sub>36</sub>
Structural formula	[Ni(C <sub>18</sub> H <sub>36</sub> N <sub>4</sub> S <sub>2</sub> )]Cl <sub>2</sub> ·4H <sub>2</sub> O	[Ni(C <sub>18</sub> H <sub>36</sub> N <sub>4</sub> S <sub>2</sub> )](ClO <sub>4</sub> ) <sub>2</sub>
Formula weight	574.30	630.24
Crystal size, mm	0.29 × 0.33 × 0.42	0.17 × 0.21 × 0.45
Crystal color	dark lavender	pale pink
a, Å	17.450(3)	22.384(9)
b, Å	12.188(2)	10.118(2)
c, Å	11.897(2)	14.300(3)
V, Å <sup>3</sup>	2530.2(8)	2493.3(13)
Cell detn, refls	488	225
d(calcd), g cm <sup>-3</sup>	1.51	1.68
Space group	Pna2 <sub>1</sub>	C <sub>2/c</sub>
Z	4	4
F000	1224	1320
Linear abs coeff, mm <sup>-1</sup>	1.17	1.21
h,k,l ranges	-20, 20; -14, 8; -14, 14	-26, 26; -7, 11; -16, 16
Crystal decay, %	0.35	0.19
Absorption range	0.86-1.00	0.76-1.00
Reflections measured	12895	6350
Unique reflections	4440	2193
R for merge	0.027	0.026
Refls in refinement I>2.0σ(I)	3770	1713
Parameters refined	280	160
R1, wR2	0.032, 0.078	0.051, 0.142
R1 for I>0.0σ(I)	0.043	0.066
GOF	1.01	1.07
Final diff map, e Å <sup>-3</sup>	-0.24, +0.35	-0.49, +0.86

**Table S2. Important Bond Lengths (Å) and Angles (°).**

<i>cis</i> -[Ni( <i>trans-I</i> , <i>syn-L3</i> )] <sup>2+</sup>		<i>trans</i> -[Ni( <i>trans-IV</i> , <i>anti-L3</i> )] <sup>2+</sup>	
Ni(1)-N(4)	2.100(3)	Ni(1)- N(2)	2.124(4)
Ni(1)-N(2)	2.101(3)	Ni(1)- N(2)	2.124(4)
Ni(1)-N(1)	2.164(3)	Ni(1)- N(1)	2.127(4)
Ni(1)-N(3)	2.179(3)	Ni(1)- N(1)	2.127(4)
Ni(1)-S(2)	2.4265(11)	Ni(1)-S(1)	2.5321(13)
Ni(1)-S(1)	2.4512(11)	Ni(1)- S(1)	2.5321(13)
N(4)-Ni(1)-N(2)	177.20(13)	N(2)-Ni(1)-N(2)	180.0(3)
N(4)-Ni(1)-N(1)	94.12(12)	N(2)-Ni(1)-N(1)	83.54(15)
N(2)-Ni(1)-N(1)	84.30(13)	N(2)-Ni(1)-N(1)	96.46(15)
N(4)-Ni(1)-N(3)	84.50(13)	N(2)-Ni(1)-N(1)	96.46(15)
N(2)-Ni(1)-N(3)	93.68(13)	N(2)-Ni(1)-N(1)	83.54(15)
N(1)-Ni(1)-N(3)	105.32(11)	N(1)-Ni(1)-N(1)	180.0(2)
N(4)-Ni(1)-S(2)	83.29(9)	N(2)-Ni(1)-S(1)	98.60(11)
N(2)-Ni(1)-S(2)	98.64(9)	N(2)-Ni(1)- S(1)	81.40(11)
N(1)-Ni(1)-S(2)	170.43(9)	N(1)-Ni(1)-S(1)	98.88(11)
N(3)-Ni(1)-S(2)	83.66(8)	N(1)-Ni(1)-S(1)	81.12(11)
N(4)-Ni(1)-S(1)	98.73(9)	N(2)-Ni(1)-S(1)	81.40(11)
N(2)-Ni(1)-S(1)	83.42(10)	N(2)-Ni(1)-S(1)	98.60(11)
N(1)-Ni(1)-S(1)	83.60(9)	N(1)-Ni(1)-S(1)	81.12(11)
N(3)-Ni(1)-S(1)	170.35(8)	N(1)-Ni(1)-S(1)	98.88(11)
S(2)-Ni(1)-S(1)	87.67(4)	S(1)-Ni(1)-S(1)	180.00(5)



**Figure S3.** Scan rate dependent cyclic voltammogram of *cis*-[Ni(*trans*-1, *syn*-L3)] cation. Scan rates (mV/sec): a = 10; b = 25; c = 50; d = 100; e = 200; f = 300; g = 400; h = 500; i = 750 and j = 1000.