

Supporting Data

Absorbance maxima and extinction coefficients utilized for equilibrium constant determination.

Species	Absorbance Max (nm)	Molar Absorbivity at Max (L/mole•cm)
$\text{Pt}(\text{CNC}_2\text{H}_5)_4^{2+}$	207	29,400
$\text{Pt}(\text{CN})_4^{2-}$	216	20,000
1:1	319	15,000
1:2	350	21,000
2:1	363	57,000
2:2	420	35,000

Table 1. Dilution of the double salt for the dinuclear association constant K_1 determination at 7°C. At low concentrations the only band in the visible region is the one at 319nm which is attributed to the dinuclear species $[\text{Pt}(\text{CNC}_2\text{H}_5)_4][\text{Pt}(\text{CN})_4]$. 209nm and 216nm are peak maxima for the anion and cation respectively and the 255nm band is a band where both the anion and cation absorb.

$\text{Pt}(\text{CN})_4^{2-}$ Initial [M]	$\text{Pt}(\text{CNC}_2\text{H}_5)_4^{2+}$ Initial [M]	A_{209}	A_{216}	A_{255}	A_{319}
7.059E-6	7.059E-6	0.155	0.167	0.091	0.03
7.84E-6	7.84E-6	0.174	0.181	0.095	0.036
8.62E-6	8.62E-6	0.181	0.193	0.101	0.037
9.41E-6	9.41E-6	0.208	0.212	0.111	0.046
1.02E-5	1.02E-5	0.217	0.230	0.117	0.051
1.09E-5	1.09E-5	0.248	0.252	0.129	0.06
1.17E-5	1.17E-5	0.275	0.281	0.140	0.070

Table 1A. Equilibrium concentration values for the dinuclear association species present at 7°C

Pt(CN) ₄ ²⁻ Initial [M]	Pt(CNC ₂ H ₅) ₄ ²⁺ Initial [M]	Pt(CN) ₄ ²⁻ Equilibrium [M]	Pt(CNC ₂ H ₅) ₄ ²⁺ Equilibrium [M]	[Pt(CN) ₄][Pt(CNC ₂ H ₅) ₄]
7.059E-6	7.059E-6	4.59 E-6	4.59 E-6	2.46 E-6
7.84E-6	7.84E-6	4.96 E-6	4.96 E-6	2.87 E-6
8.62E-6	8.62E-6	5.32 E-6	5.32 E-6	3.30 E-6
9.41E-6	9.41E-6	5.67 E-6	5.67 E-6	3.74 E-6
1.02E-5	1.02E-5	5.99 E-6	5.99 E-6	4.19 E-6
1.09E-5	1.09E-5	6.32 E-6	6.32 E-6	4.66 E-6
1.17E-5	1.17E-5	6.63 E-6	6.63 E-6	5.13 E-6

$$K_1 = \frac{[\text{Pt}_2][\text{Pt}^{2+}][\text{Pt}^{2+}]}{[\text{Pt}^{2+}]^2} = 112,000 (\log K = 5.05)$$

Table 2. Dilution of the double salt for K_1 determination at 17°C.

$\text{Pt}(\text{CN})_4^{2-}$ Initial [M]	$\text{Pt}(\text{CNC}_2\text{H}_5)_4^{2+}$ Initial [M]	A_{209}	A_{216}	A_{255}	A_{319}
7.45E-6	7.45E-6	0.185	0.203	0.112	0.031
8.28E-6	8.28E-6	0.205	0.219	0.121	0.035
9.11E-6	9.11E-6	0.219	0.236	0.129	0.037
9.94E-6	9.94E-6	0.239	0.254	0.138	0.043
1.08E-5	1.08E-5	0.257	0.281	0.147	0.045
1.49E-5	1.49E-5	0.351	0.372	0.193	0.082
2.07E-5	2.07E-5	0.464	0.492	0.251	0.129

Table 2A. Equilibrium concentration values for the dinuclear species present at 17°C

Pt(CN) ₄ ²⁻ Initial [M]	Pt(CNC ₂ H ₅) ₄ ²⁺ Initial [M]	Pt(CN) ₄ ²⁻ Equilibrium[M]	Pt(CNC ₂ H ₅) ₄ ²⁺ Equilibrium[M]	[Pt(CN) ₄][Pt(CNC ₂ H ₅) ₄]
7.45E-6	7.45E-6	5.43 E-6	5.43 E-6	2.0 E-6
8.28E-6	8.28E-6	5.90 E-6	5.90 E-6	2.38 E-6
9.11E-6	9.11E-6	6.35 E-6	6.35 E-6	2.73 E-6
9.94E-6	9.94E-6	6.79 E-6	6.79 E-6	3.11 E-6
1.08E-5	1.08E-5	7.21 E-6	7.21 E-6	3.52 E-6
1.49E-5	1.49E-5	9.16 E-6	9.16 E-6	5.70 E-6
2.07E-5	2.07E-5	1.16 E-5	1.16 E-5	9.10 E-6

$$K_1 = [\text{Pt}_2]/[\text{Pt}^{2+}][\text{Pt}^{2+}] = 67,608 (\log K = 4.83)$$

Table 3. Dilution of the double salt for K_1 determination at 22°C.

$\text{Pt}(\text{CN})_4^{2-}$ Initial [M]	$\text{Pt}(\text{CNC}_2\text{H}_5)_4^{2+}$ Initial [M]	A ₂₀₉	A ₂₁₆	A ₃₁₉
6.16E-6	6.16E-6	0.167	0.178	0.014
7.14E-6	7.14E-6	0.191	0.204	0.183
8.25E-6	8.25E-6	0.223	0.231	0.026
9.24E-6	9.24E-6	0.242	0.254	0.029
1.02E-5	1.02E-5	0.270	0.281	0.035
2.05E-5	2.05E-5	0.493	0.514	0.101

Table 3A. Equilibrium concentration values for the dinuclear association species present at 22°C

Pt(CN) ₄ ²⁻ Initial [M]	Pt(CNC ₂ H ₅) ₄ ²⁺ Initial [M]	Pt(CN) ₄ ²⁻ Equilibrium [M]	Pt(CNC ₂ H ₅) ₄ ²⁺ Equilibrium [M]	[Pt(CN) ₄] [Pt(CNC ₂ H ₅) ₄]
6.16E-6	6.16E-6	5.18 E-6	5.18 E-6	9.93 E-7
7.14E-6	7.14E-6	5.88 E-6	5.88 E-6	1.28 E-6
8.25E-6	8.25E-6	6.64 E-6	6.64 E-6	1.64 E-6
9.24E-6	9.24E-6	7.29 E-6	7.29 E-6	1.96 E-6
1.02E-5	1.02E-5	7.93 E-6	7.93 E-6	2.33 E-6
2.05E-5	2.05E-5	1.36 E-5	1.36 E-5	6.84 E-6

$$K_1 = [\text{Pt}_2]/[\text{Pt}^{2-}][\text{Pt}^{2+}] = 37,000(\log K = 4.57)$$

Table 4. Continuous Variations Method absorption data for the double salt at 7°C. The concentration is increased by a factor of 100 from the dilution data in tables 1-3. This resulted in additional bands arising in the visible region to lower energy than the 319nm band.

Ratio 2+/-	Pt(CNC ₂ H ₅) ₄ ²⁺ Initial [M]	Pt(CN) ₄ ²⁻ Initial [M]	A ₂₀₇	A ₂₁₆	A ₂₅₅	A ₃₁₉	A ₃₆₃	A ₄₂₀
0:10	0	9.94 E-4	0.644	1.99	1.154	0	0	0
1:9	9.86 E-5	8.95 E-4	0.625	1.804	0.909	0.092	0.091	0.047
2:8	1.97 E-4	7.96 E-4	0.599	1.549	0.698	0.147	0.153	0.136
3:7	2.96 E-4	6.96 E-4	0.579	1.219	0.479	0.188	0.202	0.253
4:6	3.95 E-4	5.97 E-4	0.555	0.927	0.312	0.211	0.232	0.344
5:5	4.93 E-4	4.97 E-4	0.571	0.695	0.191	0.216	0.269	0.418
6:4	5.92 E-4	3.98 E-4	0.716	0.605	0.174	0.189	0.349	0.399
7:3	6.91 E-4	2.98 E-4	0.961	0.593	0.251	0.140	0.430	0.274
8:2	7.89 E-4	1.99 E-4	1.302	0.620	0.378	0.096	0.401	0.127
9:1	8.88 E-4	9.94 E-5	1.688	0.659	0.541	0.044	0.243	0.030
10:0	9.86 E-4	0	2.016	0.696	0.723	0	0	0

Table 4A. Equilibrium concentration values for the tetranuclear association species present at 7°C.

Ratio	Pt(CNC ₂ H ₅) ₄ ²⁺ Initial [M]	Pt(CN) ₄ ²⁻ Initial [M]	Pt(CNC ₂ H ₅) ₄ ²⁺ Equilibrium [M]	Pt(CN) ₄ ²⁻ Equilibrium [M]	[1:1]	[1:2]	[2:1]	[2:2]
0:10	0	9.94 E-4	0	9.94 E-4	0	0	0	0
1:9	9.86 E-5	8.95 E-4	4.3 E-7	7.5 E-4	3.6 E-5	4.9 E-5	1.3 E-7	6.3 E-6
2:8	1.97 E-4	7.96 E-4	1.2 E-6	5.3 E-4	7.3 E-5	7.0 E-5	7.2 E-7	2.6 E-6
3:7	2.96 E-4	6.96 E-4	2.8 E-6	3.4 E-4	1.1 E-4	6.6 E-5	2.5 E-6	5.7 E-5
4:6	3.95 E-4	5.97 E-4	7.1 E-6	1.7 E-4	1.4 E-4	4.4 E-5	8.1 E-6	9.4 E-5
5:5	4.93 E-4	4.97 E-4	2.7 E-5	5.1 E-5	1.5 E-4	1.4 E-5	3.4 E-5	1.1 E-4
6:4	5.92 E-4	3.98 E-4	1.0 E-4	1.1 E-5	1.3 E-4	2.5 E-6	1.1 E-4	7.6 E-5
7:3	6.91 E-4	2.98 E-4	2.4 E-4	2.9 E-6	7.9 E-5	4.2 E-7	1.5 E-4	3.0 E-5
8:2	7.89 E-4	1.99 E-4	4.5 E-4	7.8 E-7	3.9 E-5	5.6 E-8	1.4 E-4	7.6 E-6
9:1	8.88 E-4	9.94 E-5	7.1 E-4	1.8 E-7	1.4 E-5	4.8 E-9	8.3 E-5	1.0 E-6
10:0	9.86 E-4	0	9.86 E-4	0	0	0	0	0

Table 5. Continuous Variations Method absorption data for the double salt at 17°C.

Ratio 2+/2-	Pt(CNC ₂ H ₅) ₄ ²⁺ Initial [M]	Pt(CN) ₄ ²⁻ Initial [M]	A ₂₀₇	A ₂₁₆	A ₂₅₅	A ₃₁₉	A ₃₆₃	A ₄₂₀
0:10	0	9.94 E-4	0.635	1.986	1.149	0	0	0
1:9	9.86 E-5	8.95 E-4	0.626	1.803	0.915	0.106	0.078	0.031
2:8	1.97 E-4	7.96 E-4	0.610	1.558	0.710	0.167	0.137	0.098
3:7	2.96 E-4	6.96 E-4	0.607	1.224	0.497	0.218	0.195	0.197
4:6	3.95 E-4	5.97 E-4	0.588	0.957	0.334	0.245	0.234	0.276
5:5	4.93 E-4	4.97 E-4	0.623	0.738	0.219	0.255	0.281	0.339
6:4	5.92 E-4	3.98 E-4	0.781	0.649	0.199	0.226	0.357	0.327
7:3	6.91 E-4	2.98 E-4	0.998	0.615	0.267	0.167	0.410	0.224
8:2	7.89 E-4	1.99 E-4	1.321	0.636	0.388	0.108	0.374	0.107
9:1	8.88 E-4	9.94 E-5	1.691	0.673	0.545	0.053	0.224	0.026
10:0	9.86 E-4	0	2.011	0.704	0.726	0	0	0

Table 5A. Equilibrium concentration values for the tetranuclear association species present at 17°C.

Ratio	Pt(CNC ₂ H ₅) ₄ ²⁺ Initial [M]	Pt(CN) ₄ ²⁻ Initial [M]	Pt(CNC ₂ H ₅) ₄ ²⁺ Equilibrium [M]	Pt(CN) ₄ ²⁻ Equilibrium [M]	[1:1]	[1:2]	[2:1]	[2:2]
0:10	0	9.94 E-4	0	9.94 E-4	0	0	0	0
1:9	9.86 E-5	8.95 E-4	7.1 E-7	7.4 E-4	3.6 E-5	5.2 E-5	1.4 E-7	4.8 E-6
2:8	1.97 E-4	7.96 E-4	2.1 E-6	5.2 E-4	7.4 E-5	7.7 E-5	8.6 E-7	2.1 E-5
3:7	2.96 E-4	6.96 E-4	5.0 E-6	3.3 E-4	1.1 E-4	7.4 E-5	3.1 E-6	4.8 E-5
4:6	3.95 E-4	5.97 E-4	1.2 E-6	1.7 E-4	1.5 E-4	5.0 E-5	1.0 E-5	8.2 E-5
5:5	4.93 E-4	4.97 E-4	3.9 E-5	6.0 E-5	1.6 E-4	1.9 E-5	3.5 E-5	1.0 E-4
6:4	5.92 E-4	3.98 E-4	1.2 E-4	1.6 E-5	1.4 E-4	4.4 E-6	9.2 E-5	7.1 E-5
7:3	6.91 E-4	2.98 E-4	2.6 E-4	5.2 E-6	9.2 E-5	9.3 E-7	1.3 E-4	3.2 E-5
8:2	7.89 E-4	1.99 E-4	4.6 E-4	1.6 E-6	5.0 E-5	1.6 E-7	1.3 E-4	9.5 E-6
9:1	8.88 E-4	9.94 E-5	7.1 E-4	4.1 E-7	1.9 E-5	1.6 E-8	7.6 E-5	1.4 E-6
10:0	9.86 E-4	0	9.86 E-4	0	0	0	0	0

Table 6. Continuous Variations Method absorption data for the double salt at 22°C

Ratio 2+/2-	Pt(CNC ₂ H ₅) ₄ ²⁺ Initial [M]	Pt(CN) ₄ ²⁻ Initial [M]	A ₂₀₇	A ₂₁₆	A ₂₅₅	A ₃₁₉	A ₃₆₃	A ₄₂₀
0:10	0	1.01 E-3						
1:9	9.81 E-5	9.09 E-4	0.543	1.624	0.804	0.083	0.044	0
2:8	1.97 E-4	8.08 E-4	0.551	1.377	0.618	0.157	0.098	0.068
3:7	2.96 E-4	7.07 E-4	0.566	1.098	0.438	0.215	0.159	0.148
4:6	3.94 E-4	6.06 E-4	0.601	0.871	0.306	0.247	0.211	0.215
5:5	4.92 E-4	5.05 E-4	0.659	0.683	0.217	0.253	0.264	0.255
6:4	5.91 E-4	4.04 E-4	0.857	0.640	0.214	0.222	0.316	0.236
7:3	6.89 E-4	3.03 E-4	1.056	0.594	0.283	0.160	0.341	0.160
8:2	8.01 E-4	2.02 E-4	1.350	0.618	0.393	0.104	0.292	0.081
9:1	8.86 E-4	1.01 E-4	1.678	0.653	0.53	0.044	0.169	0
10:0	9.95 E-4	0						

Table 6A. Equilibrium concentration values for the tetranuclear association species present at 22°C.

Ratio	Pt(CNC ₂ H ₅) ₄ ²⁺ Initial [M]	Pt(CN) ₄ ²⁻ Initial [M]	Pt(CNC ₂ H ₅) ₄ ²⁺ Equilibrium [M]	Pt(CN) ₄ ²⁻ Equilibrium [M]	[1:1]	[1:2]	[2:1]	[2:2]
0:10	0	1.01 E-3	0	9.94 E-4	0	0	0	0
1:9	9.81 E-5	9.09 E-4	1.3 E-7	7.6 E-4	3.7 E-5	5.1 E-5	1.4 E-7	3.9 E-6
2:8	1.97 E-4	8.08 E-4	3.9 E-6	5.4 E-4	7.9 E-5	7.7 E-5	9.3 E-7	1.8 E-5
3:7	2.96 E-4	7.07 E-4	9.2 E-6	3.5 E-4	1.2 E-4	7.6 E-5	3.4 E-6	4.1 E-5
4:6	3.94 E-4	6.06 E-4	2.2 E-6	1.9 E-4	1.6 E-4	5.4 E-5	1.0 E-5	6.9 E-5
5:5	4.92 E-4	5.05 E-4	5.9 E-5	7.8 E-5	1.7 E-4	2.4 E-5	3.1 E-5	8.6 E-4
6:4	5.91 E-4	4.04 E-4	1.5 E-4	2.7 E-5	1.5 E-4	7.6 E-6	7.1 E-5	6.8 E-5
7:3	6.89 E-4	3.03 E-4	2.9 E-4	1.0 E-5	1.1 E-4	2.1 E-6	1.0 E-4	3.6 E-5
8:2	8.01 E-4	2.02 E-4	5.0 E-4	3.6 E-6	6.8 E-5	4.4 E-7	1.0 E-4	1.3 E-5
9:1	8.86 E-4	1.01 E-4	7.2 E-4	1.1 E-6	2.9 E-5	5.8 E-8	6.5 E-5	2.4 E-6
10:0	9.95 E-4	0	9.86 E-4	0	0	0	0	0