Electronic Supplementary Information for Dalton Transactions
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Non-trivial solution chemistry between amido-pyridylcalix[4]arenes and some metal salts

Supplementary Information

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Sample δ_H / ppm	Ar-<u>H</u>	OH	Ar-C<u>H</u>$_2$-Ar	*tert*-Bu	O<u>CH</u>$_2$	<u>NH</u>	N<u>CH</u>$_2$	Py-<u>H</u>
3[a]	7.06, 6.82	7.03	4.03, 3.34 (*J* 13.3)	1.27, 0.97	4.51	9.07	4.64 (*J* 5.2)	8.35 (*J* 4.9), 7.56 (*J* 7.7), 7.29 (*J* 7.7), 7.13 (br)
3 + $HgCl_2$[a]	7.02, 6.82	7.23	3.95, 3.33 (*J* 13.3)	1.27, 0.97	4.54	9.23	4.75 (*J* 5.6)	8.48 (*J* 4.8), 7.62 (*J* 7.7), 7.33 (*J* 4.9), 7.25 (br)
3 + $Hg(ClO_4)_2$[a]	Could not be carried out due to lack of solubility of $Hg(ClO_4)_2$ in $CDCl_3$							
3[b]	7.17	8.47	4.21, 3.47 (*J* 12.8)	1.19, 1.14	4.54	9.06	4.55 (br)	8.47 (br), 7.73 (*J* 7.8), 7.38 (*J* 7.8), 7.23 (br)
3 + $HgCl_2$[b]	7.16	8.45	4.21, 3.46 (*J* 12.8)	1.19,1.13	4.54	9.05	4.55 (br)	8.46 (br), 7.73 (*J* 7.8), 7.38 (*J* 7.9), 7.23 (br)
3 + $Hg(ClO_4)_2$[b]	7.15	8.36	4.18, 3.46 (*J* 12.8)	1.18, 1.12	4.56	9.24	4.72 (br)	8.55 (br), 7.92 (br), 7.54 (br), 7.42 (br)
3[c]	7.23, 7.19	8.05	4.15, 3.46 (*J* 13.0)	1.22, 1.14	4.55	9.06	4.68 (*J* 5.6)	8.44 (*J* 4.8), 7.68 (*J* 7.7), 7.40 (*J* 7.7), 7.17 (br)
3 + $HgCl_2$[c]	7.23, 7.19	7.97	4.14, 3.44 (*J* 13.0)	1.21, 1.14	4.53	8.76	4.83 (*J* 5.7)	8.60 (br), 7.79 (*J* 7.8), 7.52 (*J* 7.8), 7.33 (br)
3 + $Hg(ClO_4)_2$[c]	7.21, 7.15	8.04	4.09, 3.38 (*J* 13.0)	1.19, 1.13	4.65	9.03	5.16 (*J* 5.9)	8.82 (*J* 5.5), 8.33 (*J* 7.5), 7.87 (*J* 7.5), 7.86 (br)

^{1}H NMR of mercury complexes of **3**. (a = $CDCl_3$, b = d_6DMSO, c = CD_3CN)

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Sample δ_H / ppm	Ar-H	OH	Ar-CH_2-Ar	*tert*-Bu	OCH_2	NH	NCH_2	Py-H
3	7.17	8.47	4.21, 3.47	1.19, 1.14	4.54	9.06	4.55	8.47, 7.73, 7.38, 7.23
3 + $Hg(ClO_4)_2$ (0.2 Eq)	7.16	8.45	4.20, 3.46	1.18, 1.13	4.54	9.07	4.56	8.47, 7.76, 7.40, 7.25
3 + $Hg(ClO_4)_2$ (0.4 Eq)	7.16	8.42	4.20, 3.46	1.18, 1.13	4.55	9.12	4.60	8.49, 7.79, 7.43, 7.29
3 + $Hg(ClO_4)_2$ (0.6 Eq)	7.16	8.40	4.19, 3.46	1.18, 1.12	4.55	9.16	4.64	8.51, 7.83, 7.48, 7.33
3 + $Hg(ClO_4)_2$ (0.8 Eq)	7.15	8.38	4.18, 3.46	1.18, 1.12	4.55	9.20	4.64	8.53, 7.87, 7.50, 7.39
3 + $Hg(ClO_4)_2$ (1.0 Eq)	7.15	8.36	4.18, 3.46	1.18, 1.12	4.56	9.24	4.72	8.55, 7.92, 7.54, 7.42
3 + $Hg(ClO_4)_2$ (2.0 Eq)	7.15	8.31	4.15, N/O	1.17, 1.11	4.58	9.38	4.86	8.61, 8.05, 7.62, 7.59
3 + $Hg(ClO_4)_2$ (4.0 Eq)	7.14	8.25	4.13, N/O	1.17, 1.11	4.60	9.54	4.99	8.68, 8.21, 7.79, 7.72
3 + $Hg(ClO_4)_2$ (6.0 Eq)	7.14	8.22	4.11, N/O	1.16, 1.11	4.60	9.59	5.02	8.70, 8.26, 7.84, 7.77
3 + $Hg(ClO_4)_2$ (8.0 Eq)	7.13	8.20	4.10, N/O	1.16, 1.11	4.61	9.64	5.05	8.71, 8.27, 7.87,7.79
3 + $Hg(ClO_4)_2$ (10.0 Eq)	7.13	8.18	4.10, N/O	1.16, 1.10	4.61	9.65	5.06	8.72, 8.28, 7.89, 7.82

^{1}H NMR titrations of **3** and mercury(II) perchlorate in deuterated DMSO. (N/O:Peak masked by DMSO peak)

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Sample δ_H / ppm	Ar-H	OH	Ar-CH_2-Ar	*tert*-Bu	OCH_2	NH	NCH_2	Py-H
3	7.17	8.47	4.21, 3.47	1.19, 1.14	4.54	9.06	4.55	8.47, 7.73, 7.38, 7.23
3 + $HgCl_2$ (0.2 Eq)	7.16	8.45	4.21, 3.46	1.18,1.13	4.54	9.05	4.55	8.46, 7.73, 7.38, 7.22
3 + $HgCl_2$ (1.0 Eq)	7.16	8.45	4.21, 3.46	1.19,1.13	4.54	9.05	4.55	8.46, 7.73, 7.38, 7.23
3 + $HgCl_2$ (10.0 Eq)	7.16	8.45	4.21, 3.46	1.19, 1.13	4.54	9.06	4.55	8.46, 7.73, 7.38, 7.23

^{1}H NMR titrations of **3** and mercury(II) chloride in deuterated DMSO. No shifts in peak values were observed throughout these titrations, only the data for 0.2, 1.0 and 10.0 shown.

Sample δ_H / ppm	Ar-H	OH	Ar-CH_2-Ar	*tert*-Bu	OCH_2	NH	NCH_2	Py-H
3	7.17	8.47	4.21, 3.47	1.19, 1.14	4.54	9.06	4.55	8.47, 7.73, 7.38, 7.23
3 + $Hg(SCN)_2$ (0.2 Eq)	7.16	8.45	4.21, 3.46	1.18,1.13	4.54	9.05	4.55	8.46, 7.73, 7.38, 7.23
3 + $Hg(SCN)_2$ (1.0 Eq)	7.16	8.45	4.21, 3.46	1.18,1.13	4.54	9.05	4.55	8.46, 7.73, 7.37, 7.22
3 + $Hg(SCN)_2$ (10.0 Eq)	7.16	8.45	4.20, 3.46	1.18,1.13	4.53	9.05	4.55	8.46, 7.73, 7.37, 7.22

^{1}H NMR titrations of **3** and mercury(II) thiocyanate in deuterated DMSO. No shifts in peak values were observed throughout these titrations, only the data for 0.2, 1.0 and 10.0 shown.

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Sample δ_H / ppm (30 ºC)	Ar-H	OH	Ar-CH_2-Ar	*tert*-Bu	OCH_2	NH	NCH_2	Py-H
3	7.17	8.44	4.22, 3.47	1.20, 1.14	4.55	9.05	4.56	8.47, 7.74, 7.39, 7.24
3 + $Hg(ClO_4)_2$ (0.5 Eq)	7.17	8.44	4.22, 3.47	1.20, 1.14	4.55	9.06	4.56	8.48, 7.75, 7.40, 7.25
3 + $Hg(ClO_4)_2$ (1.0 Eq)	7.17	8.41	4.21, 3.47	1.20, 1.14	4.56	9.12	4.63	8.51, 7.81, 7.46, 7.31
3 + $Hg(ClO_4)_2$ (1.5 Eq)	7.16	8.38	4.20, 3.47	1.20, 1.14	4.57	9.18	4.68	8.54, 7.87, 7.51, 7.38
3 + $Hg(ClO_4)_2$ (2.0 Eq)	7.16	8.37	4.19, 3.47	1.20, 1.14	4.57	9.23	4.72	8.56, 7.92, 7.55, 7.42
3 + $Hg(ClO_4)_2$ (5.0 Eq)	7.15	8.28	4.17, 3.47	1.20, 1.14	4.60	9.41	4.89	8.63, 8.07, 7.70, 7.58
3 + $Hg(ClO_4)_2$ (10.0 Eq)	7.15	8.23	4.14, 3.47	1.19, 1.13	4.62	9.57	5.01	8.70, 8.23, 7.84, 7.75
3 + $Hg(ClO_4)_2$ (15.0 Eq)	7.15	8.21	4.13, 3.47	1.19, 1.12	4.62	9.63	5.06	8.73, 8.27, 7.87, 7.58

Variable temperature ^{1}H NMR spectroscopy of **3** and mercury(II) perchlorate at 30 ºC.

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Sample δ_H / ppm (40 ºC)	Ar-H	OH	Ar-CH_2-Ar	*tert*-Bu	OCH_2	NH	NCH_2	Py-H
3	7.15, 7.14	8.36	4.22, 3.47	1.20, 1.14	4.55	8.99	4.56	8.45, 7.71, 7.37, 7.21
3 + $Hg(ClO_4)_2$ (0.5 Eq)	7.16, 7.15	8.38	4.23, 3.47	1.21, 1.14	4.55	9.02	4.57	8.47, 7.74, 7.39, 7.24
3 + $Hg(ClO_4)_2$ (1.0 Eq)	7.17, 7.15	8.35	4.22, 3.47	1.20, 1.13	4.56	9.08	4.62	8.50, 7.80, 7.45, 7.30
3 + $Hg(ClO_4)_2$ (1.5 Eq)	7.16, 7.15	8.33	4.20, 3.47	1.20, 1.13	4.56	9.13	4.66	8.54, 7.84, 7.49, 7.35
3 + $Hg(ClO_4)_2$ (2.0 Eq)	7.16, 7.15	8.31	4.20, 3.47	1.20, 1.13	4.57	9.16	4.69	8.54, 7.87, 7.52, 7.38
3 + $Hg(ClO_4)_2$ (5.0 Eq)	7.15, 7.15	8.25	4.18, 3.46	1.20, 1.13	4.59	9.31	4.82	8.61, 8.02, 7.65, 7.54
3 + $Hg(ClO_4)_2$ (10.0 Eq)	7.15, 7.14	8.19	4.15, 3.46	1.19, 1.12	4.61	9.44	5.01	8.67, 8.13, 7.75, 7.67
3 + $Hg(ClO_4)_2$ (15.0 Eq)	7.15, 7.14	8.17	4.14, 3.46	1.19, 1.12	4.62	9.51	5.01	8.70, 8.15, 7.81, 7.73

Variable temperature ^{1}H NMR spectroscopy of **3** and mercury(II) perchlorate at 40 ºC.

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Sample δ_H / ppm (50 ºC)	Ar-<u>H</u>	OH	Ar-C<u>H</u>$_2$-Ar	*tert*-Bu	OC<u>H</u>$_2$	N<u>H</u>	NC<u>H</u>$_2$	Py-<u>H</u>
3	7.16	8.46	4.22, 3.47	1.20, 1.14	4.55	9.07	4.56	8.47, 7.73, 7.38, 7.23
3 + $Hg(ClO_4)_2$ (0.5 Eq)	7.16, 7.14	8.30	4.23, 3.46	1.21, 1.13	4.55	8.98	4.57	8.47, 7.73, 7.39, 7.23
3 + $Hg(ClO_4)_2$ (1.0 Eq)	7.16, 7.14	8.28	4.23, 3.46	1.21, 1.13	4.56	9.02	4.61	8.49, 7.77, 7.43, 7.28
3 + $Hg(ClO_4)_2$ (1.5 Eq)	7.15, 7.13	8.26	4.22, 3.46	1.21, 1.13	4.56	9.06	4.65	8.51, 7.81, 7.47, 7.32
3 + $Hg(ClO_4)_2$ (2.0 Eq)	7.15, 7.13	8.25	4.21, 3.46	1.21, 1.13	4.56	9.09	4.67	8.52, 7.84, 7.49, 7.35
3 + $Hg(ClO_4)_2$ (5.0 Eq)	7.15, 7.15	8.20	4.19, 3.46	1.21, 1.12	4.58	9.23	4.78	8.58, 7.96, 7.60, 7.48
3 + $Hg(ClO_4)_2$ (10.0 Eq)	7.14, 7.12	8.14	4.17, 3.46	1.21, 1.12	4.59	9.34	4.87	8.64, 8.06, 7.70, 7.58
3 + $Hg(ClO_4)_2$ (15.0 Eq)	7.14, 7.12	8.17	4.16, 3.46	1.20, 1.12	4.61	9.39	4.91	8.66, 8.12, 7.74, 7.64

Variable temperature ^{1}H NMR spectroscopy of **3** and mercury(II) perchlorate at 50 ºC.

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Sample δ_H / ppm (60 ºC)	Ar-<u>H</u>	OH	Ar-C<u>H</u>$_2$-Ar	*tert*-Bu	OC<u>H</u>$_2$	N<u>H</u>	NC<u>H</u>$_2$	Py-<u>H</u>
3	7.13, 7.09	8.18	4.22, 3.43 (*J* 13.0)	1.20, 1.10	4.53	8.91	4.55 (*J* 6.0)	8.44, 7.69(*J* 7.8), 7.36, 7.20
3 + $Hg(ClO_4)_2$ (0.5 Eq)	7.16, 7.12	8.21	4.24, 3.45	1.22, 1.12	4.55	8.93	4.57	8.47, 7.72, 7.39, 7.23
3 + $Hg(ClO_4)_2$ (1.0 Eq)	7.15, 7.11	8.19	4.23, 3.45	1.22, 1.12	4.55	8.97	4.60	8.48, 7.76, 7.42, 7.26
3 + $Hg(ClO_4)_2$ (1.5 Eq)	7.15, 7.11	8.17	4.23, 3.45	1.22, 1.12	4.56	9.00	4.63	8.50, 7.78, 7.45, 7.30
3 + $Hg(ClO_4)_2$ (2.0 Eq)	7.15, 7.11	8.17	4.22, 3.45	1.22, 1.12	4.56	9.02	4.65	8.51, 7.80, 7.47, 7.32
3 + $Hg(ClO_4)_2$ (5.0 Eq)	7.15, 7.11	8.12	4.20, 3.45	1.22, 1.12	4.57	9.13	4.73	8.56, 7.90, 7.55, 7.42
3 + $Hg(ClO_4)_2$ (10.0 Eq)	7.14, 7.10	8.07	4.18, 3.45	1.22, 1.11	4.59	9.24	4.83	8.61, 8.01, 7.64, 7.54
3 + $Hg(ClO_4)_2$ (15.0 Eq)	7.14, 7.10	8.06	4.17, 3.45	1.21, 1.11	4.60	9.28	4.86	8.63, 8.12, 7.68, 7.56

Variable temperature ^{1}H NMR spectroscopy of **3** and mercury(II) perchlorate at 60 ºC.

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Sample δ_H / ppm (70 ºC)	Ar-H	OH	Ar-CH_2-Ar	*tert*-Bu	OCH_2	NH	NCH_2	Py-H
3	7.15, 7.09	8.11	4.25, 3.45 (*J* 13.0)	1.23, 1.11	4.55	8.89	4.57 (*J* 5.9)	8.46, 7.71 (*J* 7.8), 7.38 (*J* 7.8), 7.22
3 + $Hg(ClO_4)_2$ (0.5 Eq)	7.15, 7.09	8.08	4.25, 3.45 (*J* 13.0)	1.23, 1.11	4.55	8.89	4.57 (*J* 5.9)	8.47, 7.71 (*J* 7.8), 7.39 (*J* 7.8), 7.22
3 + $Hg(ClO_4)_2$ (1.0 Eq)	7.15, 7.09	8.08	4.24, 3.45 (*J* 13.0)	1.23, 1.11	4.59	8.91	4.55 (*J* 5.4)	8.48, 7.74 (br), 7.41 (br), 7.25
3 + $Hg(ClO_4)_2$ (1.5 Eq)	7.15, 7.09	8.07	4.24, 3.45 (*J* 13.0)	1.23, 1.11	4.62	8.94	4.56 (*J* 5.9)	8.49, 7.77 (*J* 7.8), 7.44 (*J* 7.8), 7.28
3 + $Hg(ClO_4)_2$ (2.0 Eq)	7.15, 7.09	8.07	4.23, 3.45 (*J* 13.0)	1.23, 1.11	4.63	8.96	4.56 (br)	8.50, 7.78 (*J* 7.5), 7.45 (*J* 7.5), 7.29
3 + $Hg(ClO_4)_2$ (5.0 Eq)	7.15, 7.09	8.03	4.22, 3.45 (*J* 12.9)	1.23, 1.11	4.70	9.04	4.57 (br)	8.54, 7.86 (br), 7.53 (br), 7.38
3 + $Hg(ClO_4)_2$ (10.0 Eq)	7.14, 7.08	7.98	4.20, 3.45 (*J* 12.9)	1.22, 1.10	4.78	9.14	4.58 (br)	8.59, 7.94 (br), 7.60 (*J* 7.5), 7.47
3 + $Hg(ClO_4)_2$ (15.0 Eq)	7.14, 7.08	7.98	4.19, 3.45 (*J* 12.9)	1.22, 1.10	4.81	9.17	4.59 (br)	8.60, 7.97 (br), 7.63 (*br*), 7.50

Variable temperature ^{1}H NMR spectroscopy of **3** and mercury(II) perchlorate at 70 ºC.

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Sample δ_H / ppm (80 ºC)	Ar-H	OH	Ar-CH_2-Ar	*tert*-Bu	OCH_2	NH	NCH_2	Py-H
3	7.14, 7.07	7.99	4.25, 3.44 (*J* 13.0)	1.24, 1.10	4.55	8.84	4.57 (*J* 5.9)	8.46 (*J* 4.7), 7.70 (*J* 7.7), 7.38 (*J* 7.7), 7.21
3 + $Hg(ClO_4)_2$ (0.5 Eq)	7.14, 7.07	7.98	4.25, 3.44 (*J* 13.0)	1.24, 1.10	4.55	8.84	4.57 (*J* 5.8)	8.46 (br), 7.70 (*J* 7.8), 7.39 (*J* 7.8), 7.22
3 + $Hg(ClO_4)_2$ (1.0 Eq)	7.14, 7.06	7.95	4.25, 3.44 (*J* 13.0)	1.24, 1.10	4.55	8.85	4.59 (*J* 5.9)	8.48 (br), 7.73 (*J* 7.8), 7.41 (*J* 7.8), 7.24
3 + $Hg(ClO_4)_2$ (1.5 Eq)	7.14, 7.06	7.94	4.24, 3.44 (*J* 13.0)	1.24, 1.09	4.55	8.87	4.60 (*J* 5.7)	8.48 (br), 7.74 (*J* 7.7), 7.42 (*J* 7.7), 7.26
3 + $Hg(ClO_4)_2$ (2.0 Eq)	7.14, 7.06	7.94	4.23, 3.44 (*J* 13.0)	1.24, 1.09	4.56	8.89	4.62 (*J* 5.6)	8.49 (br), 7.75 (*J* 7.7), 7.43 (*J* 7.7), 7.27
3 + $Hg(ClO_4)_2$ (5.0 Eq)	7.15, 7.09	7.92	4.22, 3.45 (*J* 12.9)	1.23, 1.11	4,57	8.96	4.67 (br)	8.52 (br), 7.82 (br), 7.49 (br), 7.34
3 + $Hg(ClO_4)_2$ (10.0 Eq)	7.14, 7.06	7.88	4.21, 3.44 (*J* 12.9)	1.24, 1.08	4.57	9.04	4.74 (*J* 4.9)	8.56 (br), 7.90 (br), 7.56 (*J* 7.7), 7.41
3 + $Hg(ClO_4)_2$ (15.0 Eq)	7.14, 7.06	7.86	4.20, 3.44 (*J* 13.0)	1.24, 1.09	4.58	9.08	4.77 (br)	8.58 (br), 7.92 (br), 7.59 (br), 7.45

Variable temperature ^{1}H NMR spectroscopy of **3** and mercury(II) perchlorate at 80 ºC.

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Sample δ_H / ppm (90 ºC)	Ar-H	OH	Ar-CH_2-Ar	*tert*-Bu	OCH_2	NH	NCH_2	Py-H
3	7.14, 7.05	7.89	4.26, 3.43 (*J* 13.0)	1.25, 1.09	4.55	8.80	4.57 (*J* 5.6)	8.46 (*J* 4.4), 7.70 (*J* 7.6), 7.39 (*J* 7.6), 7.21
3 + $Hg(ClO_4)_2$ (0.5 Eq)	7.14, 7.04	7.85	4.25, 3.43 (*J* 13.0)	1.25, 1.08	4.55	8.79	4.57 (*J* 5.6)	8.46 (*J* 4.4), 7.70 (*J* 7.7), 7.38 (*J* 7.7), 7.21
3 + $Hg(ClO_4)_2$ (1.0 Eq)	7.14, 7.03	7.81	4.25, 3.43 (*J* 13.0)	1.25, 1.08	4.55	8.79	4.59 (*J* 5.3)	8.47 (br), 7.71 (*J* 7.7), 7.40 (*J* 7.7), 7.22
3 + $Hg(ClO_4)_2$ (1.5 Eq)	7.14, 7.03	7.81	4.25, 3.43 (*J* 13.0)	1.25, 1.08	4.55	8.81	4.60 (*J* 5.6)	8.48 (br), 7.73 (*J* 7.7), 7.41 (*J* 7.7), 7.24
3 + $Hg(ClO_4)_2$ (2.0 Eq)	7.14, 7.03	7.81	4.25, 3.43 (*J* 13.0)	1.25, 1.08	4.55	8.82	4.61 (br)	8.48 (br), 7.74 (*J* 7.5), 7.42 (*J* 7.5), 7.25
3 + $Hg(ClO_4)_2$ (5.0 Eq)	7.14, 7.03	7.79	4.23, 3.43 (*J* 12.8)	1.25, 1.08	4.56	8.88	4.65 (br)	8.51 (br), 7.79 (br), 7.47 (br), 7.31
3 + $Hg(ClO_4)_2$ (10.0 Eq)	7.13, 7.03	7.76	4.22, 3.43 (*J* 12.9)	1.25, 1.07	4.57	8.94	4.70 (br)	8.55 (br), 7.85 (br), 7.53 (*J* 7.5), 7.37
3 + $Hg(ClO_4)_2$ (15.0 Eq)	7.14, 7.08	7.76	4.21, 3.43 (*J* 12.9)	1.24, 1.07	4.58	8.99	4.73 (br)	8.56 (br), 7.88 (br), 7.55 (br), 7.41

Variable temperature ^{1}H NMR spectroscopy of **3** and mercury(II) perchlorate at 90 ºC.