TABLE I: SUPPLEMENTARY INFORMATION: The individual contributions to the spin-spin coupling constants [Hz] for the formamide-formic acid and formamide-formamidine complexes calculated at the B3LYP/HuzIIIsu3 level

	FM···FA				FM···FA (TS)				FMA···FA			
	FC	DSO	PSO	SD	FC	DSO	PSO	SD	FC	DSO	PSO	SD
$^{1}J_{O1-C2}$	20.87	-0.08	13.54	-0.91	21.30	-0.10	10.24	0.53	22.06	-0.10	8.14	0.68
$^{1}J_{O7-C8}$	29.98	-0.11	9.22	0.30	25.14	-0.10	13.10	-0.50	23.50	-0.09	14.09	-1.50
$^{1}J_{N3-C2}$	-18.60	-0.09	4.41	-0.16	-16.85	-0.08	6.29	-0.92	-13.21	-0.07	6.91	-1.34
$^{1}J_{O9-C8}$	23.42	-0.08	14.10	-1.74	27.07	-0.11	11.92	0.01	29.26	-0.11	9.75	0.29
$^{2}J_{O1-N3}$	0.41	-0.02	-3.14	1.08	-0.74	-0.02	-2.80	1.16	0.28	-0.02	-2.38	1.17
$^{2}J_{O9-O7}$	-0.86	-0.04	-8.89	1.27	-0.93	-0.04	-9.30	1.41	-0.88	-0.04	-9.09	1.27
$^{1(h)}J_{O1-H10}$	7.97	-0.76	1.12	-0.54	-60.37	-0.57	-2.70	0.15	-73.60	-0.45	-5.50	0.18
$^{1(h)}J_{O7-H10}$	-71.79	-0.46	-5.03	0.20	3.41	-0.82	1.10	-0.50	7.95	-0.76	1.09	-0.57
$^{1(h)}J_{N3-H6}$	-98.69	-0.36	-1.12	-0.13	-47.09	-0.56	0.29	-0.37	-0.19	-0.58	0.61	-0.43
$^{1(h)}J_{O9-H6}$	5.84	-0.59	0.93	-0.46	-12.26	-0.67	0.41	-0.12	-65.33	-0.46	-4.01	0.21
$^{2h}J_{O7-O1}$	6.80	0.02	-0.48	0.26	13.82	0.02	-0.89	0.36	6.10	0.02	-0.49	0.26
$^{2h}J_{O9-N3}$	5.13	0.01	-0.13	0.08	19.33	0.02	-0.22	0.22	11.36	0.01	-0.16	0.16
$^{2h}J_{C2-H10}$	-0.42	0.12	-0.38	-0.12	-3.71	-0.35	-1.13	-0.14	-4.43	-0.46	-1.13	-0.10
$^{2h}J_{C8-H6}$	-0.09	0.07	-0.24	-0.11	-2.33	-0.06	-0.87	-0.18	-4.98	-0.38	-1.23	-0.17
$^{3h}J_{O7-C2}$	-0.02	0.02	-0.03	0.00	0.47	0.01	0.03	0.02	0.38	0.00	0.04	0.01
$^{3h}J_{O9-C2}$	0.25	0.00	0.04	0.01	-0.12	0.01	-0.03	0.01	-0.16	0.02	-0.03	0.00
$^{3h}J_{O1-C8}$	0.49	0.01	0.03	0.01	0.30	0.02	-0.01	0.02	0.11	0.02	-0.03	0.01
$^{3h}J_{N3-C8}$	0.16	0.01	0.01	0.01	1.07	0.00	0.03	0.02	0.72	0.00	0.03	0.01
$^{6h}J_{H11-H4}$	0.75	-1.30	1.27	0.00	1.49	-1.45	1.41	0.00	0.93	-1.35	1.31	0.00
	FM···FI				FM···FI (TS)				FMA···FI			
	FC	DSO	PSO	SD	FC	DSO	PSO	SD	FC	DSO	PSO	SD
$^{1}J_{O8-C9}$	21.34	-0.08	13.59	-1.00	22.02	-0.10	10.90	0.56	21.62	-0.10	8.10	0.74
$^{1}J_{N1-C2}$	-22.93	-0.08	3.75	0.14	-19.33	-0.08	5.56	-0.52	-13.03	-0.07	6.45	-1.03
$^{1}J_{N10-C9}$	-18.39	-0.09	4.35	-0.13	-10.57	-0.08	6.19	-0.72	-10.94	-0.07	6.97	-1.33
$^{1}J_{N3-C2}$	-11.46	-0.06	6.57	-1.08	-21.15	-0.08	4.93	-0.23	-22.48	-0.08	3.90	0.11
$^{2}J_{O8-N10}$	0.91	-0.02	-3.24	1.09	1.43	-0.02	-3.03	1.25	0.90	-0.02	-2.46	1.19
$^{2}J_{N3-N1}$	5.84	-0.01	-0.74	0.78	2.50	-0.01	-0.82	0.80	4.98	-0.01	-0.76	0.78
$^{1(h)}J_{O8-H7}$	5.86	-0.58	0.88	-0.48	-2.20	-0.69	0.96	-0.21	-69.20	-0.45	-4.25	0.17
$^{1(h)}J_{N1-H7}$	-100.42	-0.36	-1.12	-0.14	-64.58	-0.51	0.09	-0.32	0.19	-0.57	0.60	-0.41
$^{1(h)}J_{N10-H11}$	-97.43	-0.35	-0.89	-0.14	-1.53	-0.51	0.64	-0.34	4.00	-0.44	0.48	-0.31
$^{1(h)}J_{N3-H11}$	3.92	-0.44	0.51	-0.30	-88.31	-0.40	-0.36	-0.21	-99.77	-0.35	-1.00	-0.14
$^{2h}J_{O8-N1}$	5.66	0.01	-0.16	0.09	20.20	0.02	-0.26	0.18	13.20	0.01	-0.19	0.14
$^{2h}J_{N10-N3}$	8.82	0.01	-0.06	0.04	17.42	0.01	-0.10	0.04	8.24	0.01	-0.06	0.03
$^{2h}J_{C9-H7}$	-0.11	0.12	-0.37	-0.10	-1.33	-0.06	-0.56	-0.13	-3.64	-0.49	-0.87	-0.10
$^{2h}J_{C2-H11}$	0.05	0.17	-0.43	-0.12	0.24	-0.42	-0.69	-0.15	0.89	-0.52	-0.66	-0.13
$^{3h}J_{N1-C9}$	0.23	0.01	0.00	0.00	0.54	0.01	0.03	0.01	0.41	0.00	0.02	0.01
$^{3h}J_{N3-C9}$	0.22	0.00	0.02	0.01	0.46	0.00	0.03	0.02	0.19	0.01	0.01	0.01
$^{3h}J_{O8-C2}$	-0.03	0.01	0.03	0.01	-0.46	0.01	-0.05	0.01	-0.42	0.02	-0.05	-0.01
$^{3h}J_{N10-C2}$	0.17	0.00	0.01	0.00	0.35	0.00	0.02	0.01	0.22	0.00	0.03	0.01
$^{6h}J_{H12-H5}$	0.64	-1.18	1.15	0.00	1.36	-1.32	1.28	0.00	0.78	-1.22	1.19	0.00

TABLE II: SUPPLEMENTARY INFORMATION: The three-bond proton-proton spin-spin coupling constants [Hz] for the formamide-formic acid and formamide-formamidine complexes calculated at the B3LYP/HuzIIIsu3 level

	FM$\cdots$FA	FM$\cdots$FA (TS)	FMA$\cdots$FA		FM$\cdots$FI	FM$\cdots$FI (TS)	FMA$\cdots$FI
$^{3}J_{\mathrm{H5-H4}}$	2.30	7.64	9.59	$^{3}J_{\mathrm{H13-H12}}$	2.37	7.99	10.33
$^{3(\mathrm{h})}J_{\mathrm{H6-H4}}$	14.27	7.89	0.87	$^{3(\mathrm{h})}J_{\mathrm{H12-H11}}$	14.35	1.17	-0.19
				$^{3}J_{\mathrm{H6-H5}}$	4.60	9.71	12.91
				$^{3(\mathrm{h})}J_{\mathrm{H7-H5}}$	14.76	10.33	0.88
				$^{3}J_{\mathrm{H5-H4}}$	13.53	7.63	4.80
				$^{3(\mathrm{h})}J_{\mathrm{H11-H5}}$	-0.10	12.96	14.13

TABLE III: SUPPLEMENTARY INFORMATION: The anisotropic ($\Delta\sigma_X$) nuclear shielding constants [ppm] for the formamide-formic acid and formamide-formamidine complexes calculated at the B3LYP/HuzIV-su4 level

	FM$\cdots$FA	FM$\cdots$FA (TS)	FMA$\cdots$FA		FM$\cdots$FI	FM$\cdots$FI (TS)	FMA$\cdots$FI
$\Delta\sigma_{H10}$	22.14	29.07	21.95	$\Delta\sigma_{H7}$	18.38	34.35	27.32
$\Delta\sigma_{H6}$	16.28	34.63	25.89	$\Delta\sigma_{H11}$	20.90	29.09	20.01
$\Delta\sigma_{O1}$	516.84	270.99	167.81	$\Delta\sigma_{O8}$	536.20	293.76	162.40
$\Delta\sigma_{O7}$	162.48	386.21	490.26	$\Delta\sigma_{N1}$	94.45	154.60	234.75
$\Delta\sigma_{N3}$	119.32	180.35	238.43	$\Delta\sigma_{N10}$	125.47	181.89	248.67
$\Delta\sigma_{O9}$	508.16	292.33	189.85	$\Delta\sigma_{N3}$	248.34	113.26	88.64
$\Delta\sigma_{C2}$	128.70	142.59	134.55	$\Delta\sigma_{C9}$	123.39	132.04	130.72
$\Delta\sigma_{C8}$	105.11	114.03	108.63	$\Delta\sigma_{C2}$	151.61	159.53	152.41
$\Delta\sigma_{H4}$	3.21	4.24	5.21	$\Delta\sigma_{H12}$	3.45	4.91	5.68
$\Delta\sigma_{H5}$	5.94	2.36	2.98	$\Delta\sigma_{H13}$	4.90	2.35	3.20
				$\Delta\sigma_{H6}$	7.79	3.77	3.08
$\Delta\sigma_{H11}$	4.23	4.02	4.16	$\Delta\sigma_{H5}$	4.57	3.28	4.28
				$\Delta\sigma_{H4}$	3.29	5.03	7.32