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Electronic Supplementary Information (ESI)

Probing the Microhydration of Metal Carbonyl: A Photoelectron Velocity-Map Imaging Spectroscopic and Theoretical Study of $Ni(CO)_3(H_2O)_n^-$

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Table S1. Comparison of experimental and calculated VDEs for the most stable isomer of the $Ni(CO)_3(H_2O)^-$ anion (**1A**) by different density functional theory methods. Parenthetical values are the deviations from the experimental value.

Methods	VDE (eV)
Experiment	*1.429*
B3LYP/def2-TZVP	1.505 (0.076)
BHLYP/def2-TZVP	1.139 (-0.290)
PBE0/def2-TZVP	1.575 (0.146)
BLYP/def2-TZVP	1.625 (0.196)
TPSSH/def2-TZVP	1.644 (0.215)
TPSS/def2-TZVP	1.730 (0.301)
PBE/def2-TZVP	1.803 (0.374)
BP86/def2-TZVP	1.914 (0.485)
B3LYP/aug-cc-pVTZ	1.581 (0.152)

Table S2. Natural population analysis results of the most stable isomers for $Ni(CO)_3(H_2O)_n^-$ (n = 1-4)

$Ni(CO)_3(H_2O)^-$ (**1A**)

Atom	Natural charge	Natural electron configuration
Ni	-0.92372	[core] 4s(0.53) 3d(9.19) 4p(1.21) 4d(0.01)
C	0.54490	[core] 2s(1.26) 2p(2.11) 3S(0.05) 3p(0.03)
C	0.53282	[core] 2s(1.26) 2p(2.12) 3S(0.05) 3p(0.03)
C	0.54490	[core] 2s(1.26) 2p(2.11) 3S(0.05) 3p(0.03)
O	-0.55462	[core] 2s(1.70) 2p(4.82) 3d(0.03)
O	-0.56072	[core] 2s(1.70) 2p(4.83) 3d(0.02)
O	-0.55462	[core] 2s(1.70) 2p(4.82) 3d(0.03)
O	-0.94642	[core] 2s(1.75) 2p(5.18) 3d(0.01)
H	0.44851	1s(0.54)
H	0.46897	1s(0.52) 2s(0.01)

$Ni(CO)_3(H_2O)_2^-$ (**2A**)

Atom	Natural charge	Natural electron configuration
Ni	-0.93171	[core] 4s(0.53) 3d(9.19) 4p(1.21) 4d(0.01)
C	0.55357	[core] 2s(1.26) 2p(2.11) 3S(0.05) 3p(0.03)
C	0.54032	[core] 2s(1.26) 2p(2.12) 3S(0.05) 3p(0.03)
C	0.54722	[core] 2s(1.26) 2p(2.11) 3S(0.05) 3p(0.03)
O	-0.54559	[core] 2s(1.70) 2p(4.81) 3d(0.03)
O	-0.57167	[core] 2s(1.70) 2p(4.84) 3p(0.01) 3d(0.02)
O	-0.55091	[core] 2s(1.70) 2p(4.82) 3d(0.03)
O	-0.95382	[core] 2s(1.75) 2p(5.19) 3p(0.01) 3d(0.01)
H	0.47804	1s(0.51) 2s(0.01)
H	0.45510	1s(0.54) 2s(0.01)
H	0.48491	1s(0.51)
O	-0.96999	[core] 2s(1.75) 2p(5.21) 3d(0.01)
H	0.46454	1s(0.53)

$Ni(CO)_3(H_2O)_3^-$ (**3A**)

Atom	Natural charge	Natural electron configuration
Ni	-0.90279	[core] 4s(0.52) 3d(9.19) 4p(1.20) 4d(0.01)
C	0.53756	[core] 2s(1.26) 2p(2.12) 3s(0.05) 3p(0.03)
C	0.53423	[core] 2s(1.26) 2p(2.12) 3s(0.05) 3p(0.03)
C	0.55761	[core] 2s(1.26) 2p(2.10) 3s(0.05) 3p(0.02)
O	-0.57561	[core] 2s(1.70) 2p(4.84) 3d(0.03)
O	-0.57896	[core] 2s(1.70) 2p(4.84) 3d(0.02)
O	-0.54167	[core] 2s(1.70) 2p(4.81) 3d(0.03)
O	-0.97204	[core] 2s(1.75) 2p(5.21) 3p(0.01) 3d(0.01)
H	0.47446	1s(0.51) 2s(0.01)
H	0.48496	1s(0.51)
H	0.49068	1s(0.50)
O	-0.97341	[core] 2s(1.75) 2p(5.21) 3p(0.01) 3d(0.01)
H	0.47569	1s(0.52)
H	0.47525	1s(0.52)
O	-0.97812	[core] 2s(1.75) 2p(5.22) 3p(0.01) 3d(0.01)
H	0.49215	1s(0.50)

$Ni(CO)_3(H_2O)_4^-$ (**4A**)

Atom	Natural charge	Natural electron configuration
Ni	-0.90005	[core] 4s(0.52) 3d(9.18) 4p(1.20) 4d(0.01)
C	0.53249	[core] 2s(1.26) 2p(2.12) 3s(0.05) 3p(0.03)
C	0.53184	[core] 2s(1.26) 2p(2.12) 3s(0.05) 3p(0.03)
C	0.56641	[core] 2s(1.26) 2p(2.10) 3s(0.05) 3p(0.02)
O	-0.58102	[core] 2s(1.70) 2p(4.85) 3p(0.01) 3d(0.02)
O	-0.58293	[core] 2s(1.70) 2p(4.85) 3p(0.01) 3d(0.02)
O	-0.53749	[core] 2s(1.70) 2p(4.81) 3d(0.03)
O	-0.97838	[core] 2s(1.75) 2p(5.22) 3p(0.01) 3d(0.01)
H	0.47492	1s(0.51) 2s(0.01)
H	0.49409	1s(0.50)
O	-0.97636	[core] 2s(1.75) 2p(5.22) 3p(0.01) 3d(0.01)
H	0.47582	1s(0.52)
H	0.47689	1s(0.52)
O	-0.98071	[core] 2s(1.75) 2p(5.22) 3p(0.01) 3d(0.01)
H	0.50032	1s(0.49)
H	0.49469	1s(0.50)
O	-0.97310	[core] 2s(1.75) 2p(5.21) 3p(0.01) 3d(0.01)
H	0.46314	1s(0.53)
H	0.49943	1s(0.50)

Table S3. Natural population analysis results of the most stable isomers for neutral $Ni(CO)_3(H_2O)_n$ (n = 0-4)

$Ni(CO)_3$ (**0A'**)

Atom	Natural charge	Natural electron configuration
Ni	-0.50036	[core] 4s(0.52) 3d(9.25) 4p(0.73) 4d(0.01)
C	0.60402	[core] 2s(1.30) 2p(2.03) 3s(0.04) 4p(0.02)
C	0.60404	[core] 2s(1.30) 2p(2.03) 3s(0.04) 4p(0.02)
C	0.60407	[core] 2s(1.30) 2p(2.03) 3s(0.04) 4p(0.02)
O	-0.43724	[core] 2s(1.70) 2p(4.71) 3d(0.03)
O	-0.43725	[core] 2s(1.70) 2p(4.71) 3d(0.03)
O	-0.43727	[core] 2s(1.70) 2p(4.71) 3d(0.03)
Sum of $Ni(CO)_3$	0.00000	

$Ni(CO)_3(H_2O)$ (**1A'**)

Atom	Natural charge	Natural electron configuration
Ni	-0.61572	[core] 4s(0.46) 3d(9.20) 4p(0.96) 4d(0.01)
C	0.62388	[core] 2s(1.28) 2p(2.03) 3s(0.05) 4p(0.02)
C	0.63327	[core] 2s(1.28) 2p(2.02) 3s(0.05) 4p(0.02)
C	0.63722	[core] 2s(1.28) 2p(2.01) 3s(0.05) 4p(0.02)
O	-0.46165	[core] 2s(1.70) 2p(4.73) 3d(0.03)
O	-0.45782	[core] 2s(1.70) 2p(4.73) 3d(0.03)
O	-0.45689	[core] 2s(1.70) 2p(4.73) 3d(0.03)
O	-0.86230	[core] 2s(1.72) 2p(5.12) 3p(0.01) 3d(0.01)
H	0.48003	1s(0.52)
H	0.47998	1s(0.52)
Sum of $Ni(CO)_3$	-0.09771	

$Ni(CO)_3(H_2O)_2$ (**2A'**)

Atom	Natural charge	Natural electron configuration
Ni	-0.63832	[core] 4s(0.44) 3d(9.18) 4p(1.02) 4d(0.01)
C	0.65334	[core] 2s(1.28) 2p(2.00) 3s(0.05) 4p(0.02)
C	0.63227	[core] 2s(1.28) 2p(2.02) 3s(0.05) 3p(0.01)
C	0.63643	4p(0.01)
O	-0.46048	[core] 2s(1.28) 2p(2.02) 3s(0.05) 4p(0.02)
O	-0.49292	[core] 2s(1.70) 2p(4.73) 3d(0.03)
O	-0.46364	[core] 2s(1.70) 2p(4.76) 3d(0.03)
O	-0.87552	[core] 2s(1.70) 2p(4.73) 3d(0.03)
H	0.47633	[core] 2s(1.71) 2p(5.15) 3p(0.01) 3d(0.01)
H	0.50688	1s(0.52)
H	0.47725	1s(0.49)
O	-0.93409	1s(0.52)
H	0.48247	[core] 2s(1.74) 2p(5.17) 3p(0.01) 3d(0.01) 1s(0.51)
Sum of $Ni(CO)_3$	-0.13332	

$Ni(CO)_3(H_2O)_3$ (**3A'**)

Atom	Natural charge	Natural electron configuration
Ni	-0.63147	[core] 4s(0.45) 3d(9.19) 4p(1.00) 4d(0.01)
C	0.63599	[core] 2s(1.28) 2p(2.01) 3s(0.05) 4p(0.02)
C	0.63436	[core] 2s(1.28) 2p(2.02) 3s(0.05) 4p(0.02)
C	0.63521	[core] 2s(1.28) 2p(2.02) 3s(0.05) 4p(0.02)
O	-0.46723	[core] 2s(1.70) 2p(4.74) 3d(0.03)
O	-0.46729	[core] 2s(1.70) 2p(4.74) 3d(0.03)
O	-0.45974	[core] 2s(1.70) 2p(4.73) 3d(0.03)
O	-0.91387	[core] 2s(1.71) 2p(5.18) 3p(0.01) 3d(0.01)
H	0.48546	1s(0.51)
H	0.51484	1s(0.48)
H	0.50394	1s(0.49)
O	-0.95613	[core] 2s(1.74) 2p(5.20) 3p(0.01) 3d(0.01)
H	0.47415	1s(0.52)
H	0.47269	1s(0.52)
O	-0.95463	[core] 2s(1.74) 2p(5.20) 3p(0.01) 3d(0.01)
H	0.49369	1s(0.50)
Sum of $Ni(CO)_3$	-0.12017	

$Ni(CO)_3(H_2O)_4$ (**4A'**)

Atom	Natural charge	Natural electron configuration
Ni	-0.63090	[core] 4s(0.45) 3d(9.19) 4p(0.99) 4d(0.01)
C	0.63516	[core] 2s(1.28) 2p(2.01) 3s(0.05) 4p(0.02)
C	0.63715	[core] 2s(1.28) 2p(2.01) 3s(0.05) 4p(0.02)
C	0.63493	[core] 2s(1.28) 2p(2.02) 3s(0.05) 4p(0.02)
O	-0.46961	[core] 2s(1.70) 2p(4.74) 3d(0.03)
O	-0.46760	[core] 2s(1.70) 2p(4.74) 3d(0.03)
O	-0.45942	[core] 2s(1.70) 2p(4.73) 3d(0.03)
O	-0.92247	[core] 2s(1.72) 2p(5.19) 3p(0.01) 3d(0.01)
H	0.48640	1s(0.51)
H	0.51737	1s(0.48)
O	-0.96690	[core] 2s(1.74) 2p(5.22) 3p(0.01) 3d(0.01)
H	0.47577	1s(0.52)
H	0.47426	1s(0.52)
O	-0.96275	[core] 2s(1.74) 2p(5.21) 3p(0.01) 3d(0.01)
H	0.50172	1s(0.49)
H	0.50798	1s(0.49)
O	-0.96587	[core] 2s(1.74) 2p(5.21) 3p(0.01) 3d(0.01)
H	0.46996	1s(0.53)
H	0.50481	1s(0.49)
Sum of $Ni(CO)_3$	-0.12029	

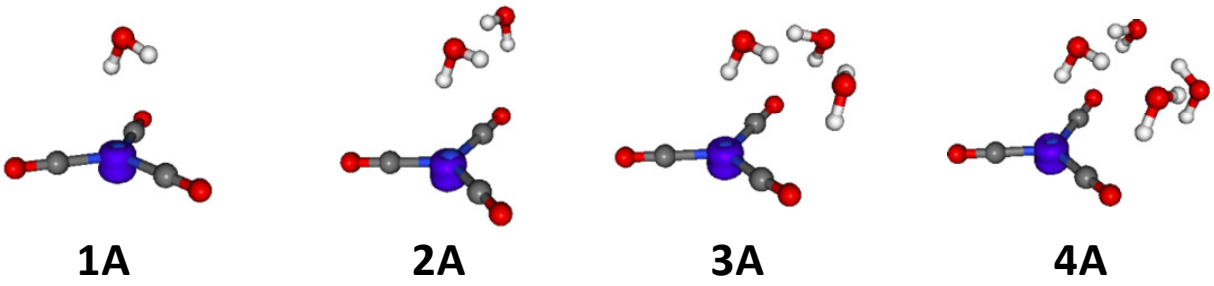

Fig. S1 The spin density isosurfaces of the lowest-lying isomers (**1A-4A**) for $Ni(CO)_3(H_2O)_n^-$.

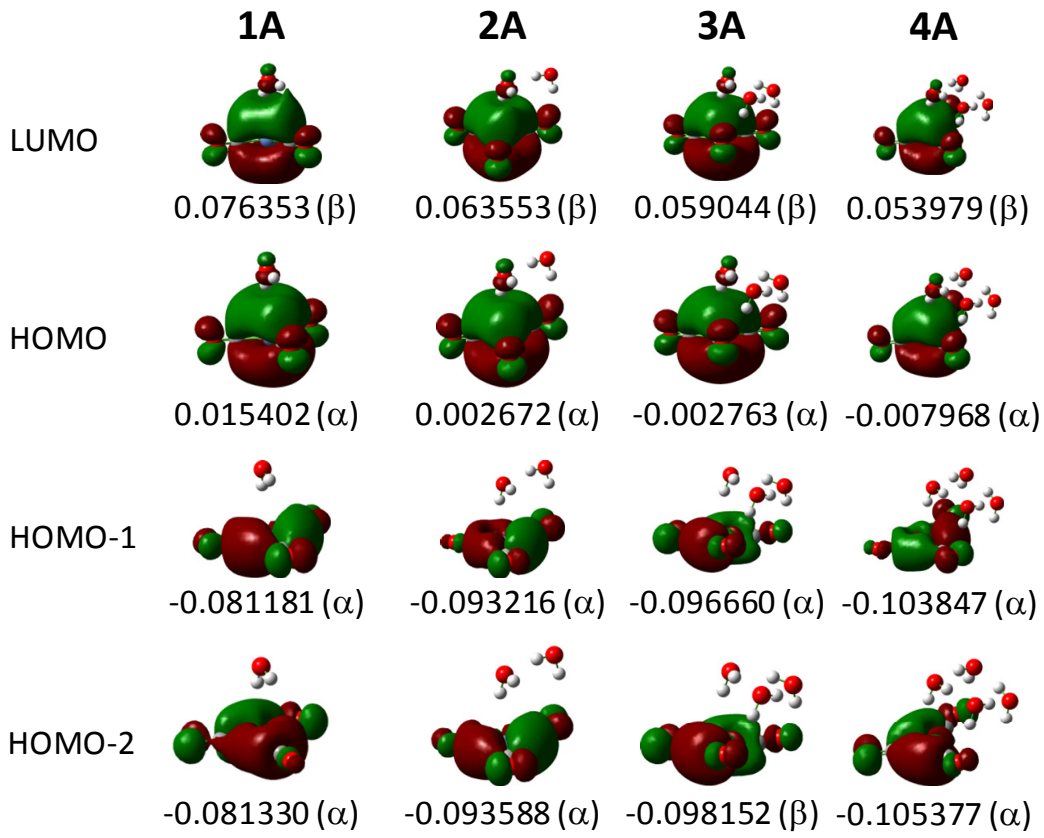

Fig. S2 Molecular orbital pictures of the most stable isomer for $Ni(CO)_3(H_2O)_n^-$ (n = 1-4) (**1A-4A**). The orbital energies are given in hartree. α or β orbital is described in parentheses.

Cartesian coordinates for the isomers of $Ni(CO)_3(H_2O)_n^-$ (n = 0-4) optimized at the B3LYP/def2-TZVP:

$Ni(CO)_3(H_2O)^-$ (**0A**)

Ni	-0.0005291	0.0012838	-0.0008500
C	-0.0000546	0.6066399	-1.6719596
C	-0.0000581	1.1420774	1.3624001
C	-0.0000551	-1.7487357	0.3099046
O	0.0006898	1.0019643	-2.7676102
O	0.0006904	1.8887929	2.2563654
O	0.0006874	-2.8954544	0.5141048

$Ni(CO)_3(H_2O)^-$ (**1A**)

Ni	-0.3684212	-0.0765578	0.0000000
C	-0.2524136	-0.9599305	-1.5425071
C	-0.6334187	1.6843778	0.0000000
C	-0.2524136	-0.9599305	1.5425071
O	-0.1765061	-1.5349619	-2.5478885
O	-0.8090253	2.8334861	0.0000000
O	-0.1765061	-1.5349619	2.5478885
O	3.0582161	0.5992866	0.0000000
H	2.6577721	1.4767845	0.0000000
H	2.2669078	0.0289837	0.0000000

$Ni(CO)_3(H_2O)_2^-$ (**2A**)

Ni	-0.3423137	0.0137194	0.7094233
C	0.2086757	1.5540758	1.4163394
C	-1.3305211	0.0139424	-0.7670783
C	0.1463774	-1.5260233	1.4623123
O	0.5816024	2.5549944	1.8659317
O	-1.9248143	0.0123021	-1.7673188
O	0.4791853	-2.5285574	1.9420719
O	2.1343661	-0.0849643	-1.6264244
H	1.4882417	0.2293706	-0.9572457
H	2.1895661	-1.0277292	-1.4279251

H	1.0897466	0.0310933	-3.2917213
O	0.4434225	0.0110192	-4.0204219
H	-0.4077364	0.0265712	-3.5656932

$Ni(CO)_3(H_2O)_2^-$ (**2B**)

Ni	0.0049889	-0.0154248	-0.0210021
C	0.1234750	0.4410321	-1.7402615
C	-0.1700823	1.2443588	1.2266175
C	0.0485346	-1.7340192	0.4527795
O	0.2020267	0.7375069	-2.8581853
O	-0.2936007	2.0612888	2.0401948
O	0.0752272	-2.8492969	0.7618481
O	-3.5020837	-0.0579203	-0.1392983
H	-2.5914427	-0.1544084	-0.4731583
H	-3.3482617	0.2355379	0.7661190
H	2.5714691	0.2361879	0.6010683
O	3.4973328	0.1860238	0.3010612
H	3.3895691	-0.0711993	-0.6219759

$Ni(CO)_3(H_2O)_3^-$ (**3A**)

Ni	0.3504083	-1.0291454	0.0108522
C	0.8042692	-0.2964809	-1.5396014
C	0.8707635	-0.1557828	1.4632461
C	-0.6782795	-2.4861789	0.0959146
O	1.0664621	0.2795891	-2.5170595
O	1.1795447	0.5100616	2.3683506
O	-1.3641800	-3.4174813	0.1496244
O	-2.1846712	1.5345732	0.0424621
H	-1.7165931	0.6783521	0.0335881
H	-1.7371719	2.0354022	0.7485405
H	0.0302201	3.2680589	0.4516864
O	-0.1863129	3.2126368	1.4017665
H	0.3794989	2.5132535	1.7559164
H	0.2642105	2.3651729	-1.9195109
O	-0.3019052	3.0211005	-1.4919383
H	-1.0781139	2.5038535	-1.1926256

$Ni(CO)_3(H_2O)_3^-$ (**3B**)

Ni	0.3252475	-0.9746763	-0.0070923
C	0.9629828	-0.3730438	-1.5536097
C	0.9693064	-0.3895567	1.5431839
C	-1.0768601	-2.0785694	-0.0094008
O	1.3220267	0.0781685	-2.5622193
O	1.3326911	0.0494172	2.5556421
O	-2.0085902	-2.7657000	-0.0110217
O	-1.2428718	1.9709363	0.0137086
H	-0.6877844	1.1524207	0.0082793
H	-2.1447823	1.6268995	0.0101648
H	-0.7614094	2.6461422	1.8552908
O	-0.4891518	2.7815703	2.7783378
H	0.1091513	2.0442629	2.9501019
H	0.1055938	2.0879032	-2.9254255
O	-0.4891087	2.8245266	-2.7386592
H	-0.7586291	2.6741110	-1.8171218

$Ni(CO)_3(H_2O)_3^-$ (**3C**)

Ni	-0.0063724	-0.4687088	-0.1150099
C	0.3386927	0.6386113	1.2338246
C	-1.6586907	-1.0891338	-0.3742537
C	1.2892217	-0.9309684	-1.2523673
O	0.5553234	1.3992267	2.0833737
O	-2.7321086	-1.4847143	-0.5521134
O	2.1248056	-1.2243513	-1.9973394
O	-0.5209013	2.6026695	-1.5797940
H	-0.6579111	1.7452229	-1.1253587
H	0.3298683	2.4742604	-2.0164118
H	0.2756706	3.6420535	1.3455788
O	0.0679958	4.3386906	0.7114662
H	-0.1944943	3.8484967	-0.0879710
H	0.7366055	-2.3754020	1.5800474
O	0.5397175	-3.2444812	1.9721523
H	-0.3047326	-3.4614607	1.5607221

$Ni(CO)_3(H_2O)_4^-$ (**4A**)

Ni	0.3825360	-1.2686693	0.0106339
C	0.7464745	-0.5421953	-1.5655177
C	0.8023099	-0.4333752	1.5172166
C	-0.5569965	-2.7865699	0.0748488
O	0.9164337	-0.0115481	-2.5892252
O	1.0111266	0.1667950	2.4946571
O	-1.1921861	-3.7524892	0.1127187
O	-2.1706590	1.2824406	-0.0160421
H	-1.6810430	0.4391260	-0.0018626
H	-1.8238601	1.7685195	0.7608271
O	-0.7534518	2.7027843	2.0411779
H	-0.2693658	1.9733385	2.4522552
H	-0.3009048	1.8553905	-2.4749102
O	-0.7548588	2.5836890	-2.0292971
H	-1.3650846	2.1370869	-1.3952838
H	-0.1210010	3.0746780	1.3905497
O	1.0171462	3.4274770	-0.0647656
H	1.6248521	2.6792273	-0.0409949
H	0.4152970	3.2246039	-0.8203367

$Ni(CO)_3(H_2O)_4^-$ (**4B**)

Ni	-0.1171289	-0.4034757	1.1608706
C	-0.0576821	-2.1134197	0.6629469
C	1.3562813	0.5291080	1.5041822
C	-1.6193936	0.5354759	1.0345605
O	-0.0118014	-3.1951347	0.2457292
O	2.2921665	1.2108749	1.6071716
O	-2.5412146	1.2162189	0.8337033
O	0.3447547	0.1572389	-2.1726070
H	0.2590773	-0.1332192	-1.2377793
H	-0.4109026	0.7641378	-2.2893948
H	1.4179203	1.7522275	-1.7132547
O	1.5441862	2.6470627	-1.3425524
H	1.8415188	2.4861079	-0.4376658

H	0.1650097	-3.0125470	-2.2424646
O	0.2701793	-2.6370100	-3.1245546
H	0.3034650	-1.6776787	-2.9674894
O	-1.3128385	2.5341478	-1.8596095
H	-1.7937467	2.3072324	-1.0523763
H	-0.4299344	2.8239862	-1.5626185

$Ni(CO)_3(H_2O)_4^-$ (**4C**)

Ni	-0.0165941	0.0058862	0.3718653
C	1.2560527	1.0348818	-0.3294458
C	-0.2333011	-0.0510374	2.1441183
C	-1.0795333	-0.9652200	-0.6729963
O	2.0620162	1.7289680	-0.7890458
O	-0.3751888	-0.0896789	3.2904688
O	-1.7566797	-1.6224902	-1.3477540
O	-1.7584215	2.9111082	-0.2870525
H	-1.2563562	2.1973345	0.1563371
H	-2.1317953	2.4625629	-1.0552217
H	1.1213635	3.8850327	-1.3120302
O	0.4255940	4.5508048	-1.3634100
H	-0.3472388	4.1074445	-0.9708851
H	1.3884542	-2.0800688	0.0123045
O	1.6745071	-3.0028903	0.1687670
H	1.3410422	-3.1804144	1.0564633
H	-0.8197274	-3.7884118	-1.6885099
O	-0.1578405	-4.4826409	-1.5877262
H	0.5381139	-4.0600132	-1.0539229

$Ni(CO)_3(H_2O)_4^-$ (**4D**)

Ni	-0.0827717	-0.6857731	-0.0102780
C	0.6883541	-0.2489986	-1.5537880
C	0.6785021	-0.2760602	1.5456544
C	-1.7097469	-1.4250463	-0.0253925
O	1.1537753	0.0986073	-2.5570738
O	1.1406162	0.0512918	2.5571093

O	-2.7745294	-1.8761144	-0.0358760
O	-0.7541176	2.6112875	0.0189701
H	-0.4659699	1.6676473	0.0114956
H	-1.7175875	2.5533800	0.0129746
H	-0.1268962	3.1304517	1.8748260
O	0.1410748	3.1827180	2.8070595
H	0.5159262	2.3123301	2.9875763
H	0.5423726	2.3728779	-2.9446089
O	0.1702508	3.2407494	-2.7474338
H	-0.1079631	3.1676967	-1.8195978
H	1.4290644	-2.8795577	-0.0705620
O	1.4469734	-3.8491242	0.0059322
H	0.5200168	-4.0545653	0.1732348