Supporting Information

Analysis of Molecular Structures, Spectroscopic Properties (FT-IR, Micro-Raman and UV-vis.) and Quantum Chemical Calculations of Free and Ligand Dimethyl Phenylphosphonite in Cd(II) Halide Complex

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Table 1: The optimized molecular geometric parameters of free DMPP and its Cd(DMPP)Cl_2.H_2O metal halide complex.

Bond lenghts (Å)	Free DMPP	Cd(DMPP)Cl_2.H_2O		Bond angles (°)	Free DMPP	Cd(DMPP)Cl_2.H_2O	
	B3LYP/6-311++G(d,p)	B3LYP/LanL2DZ	M06-L/LanL2DZ		B3LYP/6-311++G(d,p)	B3LYP/LanL2DZ	M06-L/LanL2DZ
P1-C2	1.851	1.865	1.866	C2-P1-O10	101.948	105.259	98.308
P1-O10	1.659	1.735	1.831	C2-P1-O11	95.790	97.575	94.464
P1-O11	1.673	1.735	1.764	O10-P1-O11	103.652	104.536	97.608
C2-C3	1.399	1.410	1.406	P1-C2-C3	123.702	122.071	122.494
C2-C4	1.402	1.413	1.409	P1-C2-C4	117.102	117.383	117.083
C3-C6	1.395	1.407	1.402	C3-C2-C4	119.083	120.545	120.409
C3-H12	1.083	1.086	1.084	C2-C3-C6	120.249	119.552	119.575
C4-C5	1.393	1.408	1.402	C2-C3-H12	119.303	119.510	119.327
C4-H13	1.086	1.089	1.088	C6-C3-H12	120.447	120.937	121.097
C5-C7	1.395	1.409	1.403	C2-C4-C5	120.601	119.483	119.583
C5-H15	1.084	1.087	1.083	C2-C4-H13	119.903	120.819	120.240
C6-C7	1.394	1.409	1.404	C5-C4-H13	119.496	119.698	120.176
C6-H14	1.085	1.087	1.084	C4-C5-C7	119.948	120.151	120.100
C7-H16	1.084	1.088	1.084	C4-C5-H15	119.907	119.576	119.663
C8-O10	1.436	1.470	1.475	C7-C5-H15	120.144	120.272	120.237
C8-H17	1.093	1.097	1.092	C3-C6-C7	120.296	120.172	120.194
C8-H18	1.090	1.092	1.091	C3-C6-H14	119.727	119.738	119.749
C8-H19	1.093	1.097	1.094	C7-C6-H14	119.977	120.091	120.057
C9-O11	1.432	1.475	1.461	C5-C7-C6	119.814	120.093	120.136
C9-H20	1.095	1.097	1.095	C5-C7-H16	120.063	119.944	119.924
C9-H21	1.094	1.096	1.095	C6-C7-H16	120.122	119.962	119.940
C9-H22	1.090	1.092	1.088	O10-C8-H17	110.815	110.628	109.410
P1-Cd23	-	2.850	3.515	O10-C8-H18	106.532	105.235	105.866
Cd23-Cl24	-	2.446	2.509	O10-C8-H19	110.857	110.913	109.925
Cd23-Cl25	-	2.495	2.427	H17-C8-H18	109.633	110.116	110.865
Cd23-O26	-	2.304	2.281	H17-C8-H19	109.335	109.833	110.019
O26-H27	-	0.983	0.970	H18-C8-H19	109.626	110.034	110.672
O26-H28	-	0.974	0.982	O11-C9-H20	111.325	111.567	111.464
O10-Cd23		3.592	2.252	O11-C9-H21	110.971	109.991	110.591
O11-Cd23		4.077	4.789				
Selected dihedral angles (°)				O11-C9-H22	106.918	105.426	105.725
O10-P1-C2-C3	-116.142	-101.346	-99.136	H20-C9-H21	109.120	109.349	109.471

O10-P1-C2-C4	67.781	79.021	79.522	H20-C9-H22	109.311	110.374	109.688
O11-P1-C2-C3	-10.838	6.036	-0.764	H21-C9-H22	109.144	110.080	109.840
O11-P1-C2-C4	173.085	-173.598	177.894	P1-O10-C8	123.709	123.271	119.200
C8-O10-P1-C2	47.518	43.488	47.859	P1-O11-C9	118.236	119.885	117.140
C8-O10-P1-O11	-51.545	-58.745	-47.814	P1-Cd23-Cl24	-	99.883	72.676
C9-O11-P1-C2	165.993	175.478	-179.319	P1-Cd23-Cl25	-	103.227	130.949
C9-O11-P1-O10	-90.194	-76.538	-80.307	P1-Cd23-O26	-	106.127	81.440
P1-C2-C3-C6	-176.828	179.749	178.071	C2-P1-Cd23	-	123.141	109.321
P1-C2-C4-C5	177.388	-179.557	-177.976	O10-P1-Cd23	-	100.278	34.270
C8-O10-P1-Cd23	-	172.198	160.162	O11-P1-Cd23	-	123.735	127.036
C9-O11-P1-Cd23	-	36.716	-60.983	Cl24-Cd23-Cl25	-	151.733	149.216
O10-P1-Cd23-Cl24	-	-77.181	-151.030	Cl24-Cd23-O26	-	109.811	78.458
O10-P1-Cd23-Cl25	-	86.423	6.017	Cl25-Cd23-O26	-	79.102	119.888
O10-P1-Cd23-O26	-	168.709	128.468	Cd23-O26-H27	-	103.006	140.861
O11-P1-Cd23-Cl24	-	167.490	173.344	Cd23-O26-H28	-	137.771	102.843
O11-P1-Cd23-Cl25	-	-28.907	-29.609	H27-O26-H28	-	114.521	113.500
O11-P1-Cd23-O26	-	53.380	92.842				

Table 2: Experimental and calculated vibrational wavenumbers (cm^{-1}) and assignments of free DMPP molecule

Assingments	Experimental frequencies(cm^{-1})		Calculated at B3LYP/6-311++G(d,p)			
	IR	Raman	Freq. (unscaled)	Freq. (scaled)	I_{IR}	S_{Raman}
τOPCC(87)	-	-	26,23	25,79	0,170	4,993
τCOPC(63)+γPCCC(12)	-	74 vs	69,59	68,41	1,448	1,652
τCOPC(61)+τCH_3(17)	-	-	80,85	79,47	1,432	1,778
τCH_3(76)	-	-	91,78	90,22	0,031	0,165
τCH_3(35)+δOPC(20)+γPCCC(16)	-	-	95,31	93,69	0,053	1,664
γOCOP(31)+δPCC(27)+δCOP(12)	-	-	129,27	127,07	1,850	0,935
τCOPC(42)	-	-	156,70	154,03	6,505	0,692
δCOP(43)+τCCCC(19)+δOPC(17)	-	-	218,57	214,86	3,585	1,484
δCOP(24)+δOPO(21)+δPCC(19)	-	237 w	260,15	255,73	7,542	0,572
δCOP(34)+νPC(34)	-	298 m	295,21	290,19	1,334	5,961
δPCC(23)+δOPC(17)+γOCOP(17)	-	335 sh	329,87	324,26	7,317	1,171
τCCCC(78)	-	396 vw	404,68	397,80	0,627	0,230
δOPO(36)+δCOP(23)	-	-	422,28	415,10	10,460	1,195
τCCCC(32)+γPCCC(14)+δCOP(13)+νPC(10)	-	438 w	440,85	433,35	9,942	0,708
δOCP(22)+γPCCC(12)+δCOP(11)+γOCOP(11)	578 m	546 w	547,82	538,50	37,281	1,076
δCCC(90)	617 m	619 m	631,14	620,41	1,142	4,657
νPO(47)	-	-	690,79	679,04	68,572	11,301
δCCC(29)+νPO(23)+νPC(14)	-	-	704,22	692,24	55,874	4,613
νPO(68)	692 vw	695 w	710,74	698,65	95,238	2,605
τHCCC(52)+γPCCC(11)	716 vw	722 w	713,83	701,70	45,625	0,637
τHCCC(55)+τCCCC(26)	740 vw	752 w	761,19	748,25	27,365	1,885
τHCCC(100)	853 m	853 vw	864,45	849,75	0,026	0,132
τHCCC(76)	921 m	922 vw	935,33	919,43	1,352	0,763
τHCCC(84)	-	-	990,83	973,98	0,160	0,237
τHCCC(69)+τCCCC(13)	-	-	1006,20	989,09	0,026	0,316
δCCC(48)+νCC(48)	-	-	1013,91	996,67	5,045	48,755
νO-CH_3(83)	999 vw	1000 s	1026,58	1009,13	214,804	9,666
νCC(39)+δCCC(22)+δHCC(15)	-	-	1045,85	1028,07	4,773	17,042
νO-CH_3(85)	1035 vw	1029 m	1062,02	1043,96	260,546	9,693
νCC(40)+δHCC(39)	-	-	1097,38	1078,72	4,696	0,921
δCCC(30)+νPC(19)+δHCC(18)+νCC(14)	1102 s	1104 m	1108,78	1089,93	19,921	15,481
ρCH_3(81)	1132 m	-	1163,77	1143,99	1,060	1,979
ρCH_3(55)	-	1159 w	1172,17	1152,25	0,859	2,203
δHCC(61)+νCC(15)	-	-	1182,56	1162,46	0,521	4,015
ρCH_3(79)	-	-	1182,88	1162,77	2,745	1,955
ρCH_3(71)	1178 s	1183 w	1192,21	1171,94	13,232	0,648
δHCC(72)+νCC(22)	1259 m	-	1204,66	1184,18	1,162	3,379
νCC(67)+δHCC(20)	1307 m	-	1314,40	1292,06	1,982	0,299
δHCC(62)+νCC(25)	1330 m	-	1350,51	1327,55	2,125	0,731
δCH_3(43)+δHCC(21)	1435 vs	1441 w	1462,41	1437,55	4,677	1,178
δHCC(34)+δCH_3(28)	-	-	1464,70	1439,80	5,631	1,898
δCH_3(92)	-	-	1472,52	1447,49	1,123	1,480
$\delta_s$$CH_3$(89)	1456 w	1456 w	1489,45	1464,13	5,946	11,117
$\delta_s$$CH_3$(62)	-	-	1492,13	1466,76	11,285	9,338
$\delta_s$$CH_3$(86)	-	-	1500,71	1475,20	4,343	3,907
$\delta_s$$CH_3$(79)	-	-	1504,44	1478,87	9,707	10,911
δHCC(65)+νCC(12)	1483 m	-	1511,62	1485,92	3,412	0,776
νCC(61)+δHCC(10)	1574 w	-	1611,34	1583,94	0,090	8,793
νCC(56)+δHCC(21)	1589 w	1590 m	1627,54	1599,87	0,070	43,487
$\nu_s$$CH_3$(93)	2831 vs	2831 w	3010,96	2884,50	78,183	158,478
$\nu_s$$CH_3$(92)	2895 w	-	3026,15	2899,05	40,169	132,396
$\nu_{as}$$CH_3$(98)	2936 s	2935 w	3072,86	2943,80	31,495	65,706
$\nu_{as}$$CH_3$(100)	-	-	3094,10	2964,14	26,738	28,557
$\nu_{as}$$CH_3$(92)	2973 m	-	3114,82	2984,00	22,182	91,852
$\nu_{as}$$CH_3$(98)	2982 vw	-	3122,44	2991,30	23,268	112,837
νCH(84)	-	-	3151,32	3018,97	2,101	29,233

νCH(100)	-	-	3162,04	3029,24	0,474	95,863
νCH(88)	-	-	3172,87	3039,61	18,508	94,910
νCH(100)	3056 m	3055 w	3185,66	3051,86	20,422	233,899
νCH(89)	3073 m	-	3198,62	3064,28	8,586	118,258

ν, stretching; δ, bending; γ, out-of-plane bending; τ, torsion; ρ, rocking; s, strong, m, medium; w, weak; sh, shoulder; v, very. I_{IR}, IR intensities (km/mole); S_R, Raman scattering activities ($Å^4$/amu).

Table 3: Experimental and calculated vibrational wavenumbers (cm^{-1}) and assignments of $[Cd(C_8H_{11}PO_2)].Cl_2.H_2O$ complex

Assignments	Exp. (cm^{-1})		Calculated at B3LYP/LanL2DZ level				Calculated at M06-L/LanL2DZ level			
	IR	Raman	Freq. (unscaled)	Freq. (scaled)	I_{IR}	S_{Raman}	Freq. (unscaled)	Freq. (scaled)	I_{IR}	S_{Raman}
τOCdPC(61)+δOCdP(16)	-	-	17.61	16.92	1.712	1.391	27.43	26.33	1.851	3.084
γCdCOP(36)+τOCdPC(19)+δOCdP(18)	-	-	30.05	28.89	4.848	0.319	43.45	41.71	0.401	2.622
γClPOCd(36)+τOCPCd(31)	-	-	45.19	43.44	0.155	5.004	49.84	47.84	0.137	3.150
δOCdP(42)+γCdCOP(20)	-	-	46.84	45.02	4.655	1.595	52.11	50.03	2.929	4.966
τOPCC(44)+γClPOCd(24)	-	-	47.50	45.66	0.537	3.841	59.11	56.75	3.304	2.278
δCdPO(37)+νCdP(11)	-	-	59.39	57.09	0.157	2.069	63.06	60.54	5.374	0.978
γClPClCd(62)	-	-	64.29	61.80	5.305	0.527	71.37	68.51	4.278	1.118
δClCdCl(36)	-	-	70.59	67.85	8.262	1.046	81.05	77.80	12.936	0.734
δClCdCl(39)+τCH_3(16)	-	-	71.97	69.18	11.389	0.733	91.14	87.50	2.390	0.460
τCOPCd(26)+τCH_3(19)+δOPC(13)	-	-	79.13	76.06	0.714	1.849	99.97	95.98	1.214	0.082
τCOPCd(37)+τCH_3(13)	-	-	85.67	82.35	0.941	1.610	115.35	110.73	1.714	0.413
νCdP(51)	-	-	93.74	90.11	4.911	1.383	125.19	120.18	17.797	1.013
τCH_3(41)+τCOPCd(13)+δOPC(11)	-	-	106.91	102.76	1.240	0.678	129.53	124.35	9.861	0.828
δClCdO(72)+γClPClCd(13)	-	146 w	114.83	110.38	33.053	0.861	152.23	146.14	5.406	1.641
τCOPCd(25)+δPCC(16)+τCH_3(11)	-	162 w	135.39	130.14	9.968	0.521	197.51	189.61	3.245	1.178
δCOP(18)+δCdPO(12)+νCdP(10)+τCOPCd(10)	-	196 m	145.68	140.02	8.647	2.119	203.07	194.94	7.375	0.875
δCOP(38)+δOPC(12)+γCCCC(10)+γPCCC(10)	-	230 vw	214.62	206.29	5.339	2.034	234.21	224.84	3.115	1.532
δOPO(23)+δPCC(18)+δCOP(14)	-	242 vw	250.79	241.06	15.607	0.640	257.55	247.25	12.192	1.419
νCdCl(57)+νCdO(30)	-	256 vw	255.69	245.77	31.385	5.502	262.37	251.87	10.050	5.456
τHOCdP(77)+νCdCl(10)	-	283 vw	271.46	260.93	123.337	7.500	295.81	283.98	98.596	6.167
νPC(27)+δCOP(23)	-	-	294.12	282.71	24.815	9.704	297.82	285.91	0.814	6.616
νCdO(36)+νCdCl(36)+τHOCdP(10)	-	-	295.37	283.91	31.711	3.018	312.61	300.11	90.235	5.178
δPCC(28)+γOCOP(18)+δOPC(14)	-	314 m	316.29	304.02	4.395	2.186	317.26	304.57	11.759	3.010
νCdCl(77)+νCdO(18)	-	342 w	330.94	318.10	41.634	1.648	347.64	333.73	31.081	0.936
δCOP(31)+δOPO(25)+τCCCC(13)	-	375 m	400.12	384.59	7.060	1.829	410.54	394.12	0.581	0.092
τCCCC(65)+τHCCC(12)	407 m	-	415.99	399.85	0.616	0.496	437.34	419.84	9.205	3.084
τCCCC(22)+γPCCC(12)+νPO(10)	421 m	424 m	466.03	447.95	38.544	0.438	454.78	436.58	31.729	1.630
wH_2O(83)	-	476 m	473.86	455.47	195.834	2.153	476.36	457.31	236.245	1.966
δOPC(19)+γPCCC(15)+δCOP(10)	-	-	536.00	515.20	42.134	1.422	535.21	513.80	40.067	2.010
ρH_2O(88)	-	-	553.01	531.56	140.740	6.457	546.88	525.00	147.364	4.702
δCCC(83)	564 s	564 w	630.44	605.98	1.224	9.799	577.91	554.79	198.504	29.913
νPO(73)	-	615 m	641.75	616.85	63.730	29.626	631.47	606.22	4.225	11.177
νPO(71)	669 w	-	674.93	648.74	64.076	17.952	659.43	633.06	66.226	33.888
δCCC(42)+νPC(23)	688 s	695 w	707.43	679.98	8.893	5.456	707.68	679.38	11.127	7.001

τCCCC(51)+τHCCC(18)	709 s	713 s	726.30	698.12	50.648	2.201	731.77	702.50	43.487	0.651
τHCCC(76)+τCCCC(10)	754 s	752 w	788.75	758.15	56.115	1.845	790.76	759.13	59.235	1.671
τHCCC(100)	870 w	-	902.85	867.82	0.157	0.133	906.77	870.50	0.311	0.117
τHCCC(87)	930 m	930 w	986.19	947.93	1.934	0.409	969.00	930.24	112.497	3.586
νO-CH_3(79)+νPO(12)	-	-	1000.34	961.53	219.581	6.473	986.99	947.51	3.049	0.587
νO-CH_3(43)+δCCC(22)+νCC(15)	-	-	1008.70	969.56	102.333	21.116	1017.64	976.93	40.209	48.003
νO-CH_3(37)+δCCC(21)+νCC(16)	988 vs	988 w	1015.86	976.45	85.255	37.777	1027.64	986.53	184.388	14.842
τHCCC(73)+τCCCC(11)	1006 s	1001 vs	1036.79	996.57	0.077	0.196	1032.07	990.79	0.607	0.125
δCCC(38)+νCC(36)	-	-	1045.24	1004.68	2.522	13.105	1044.92	1003.13	0.384	0.112
τHCCC(51)+τCCCC(27)	1022 vs	-	1051.99	1011.17	0.142	0.062	1053.22	1011.09	3.573	12.920
δHCC(30)+δCCC(19)+νCC(12)	1036 s	1034 m	1104.34	1061.49	8.829	3.683	1104.02	1059.86	9.901	7.691
νCC(35) +δHCC(16)+νPC(12)	1070 m	1071 w	1117.09	1073.75	22.412	4.513	1123.42	1078.49	27.577	7.128
ρCH_3(96)	-	1090 m	1147.16	1102.65	0.202	5.952	1169.33	1122.56	0.159	6.990
ρCH_3(68)	1114 vs	-	1151.48	1106.81	0.501	7.763	1173.54	1126.60	0.744	7.990
ρCH_3(86)	-	-	1166.14	1120.89	0.286	5.679	1184.49	1137.11	4.279	4.597
ρCH_3(85)	1139 s	1141 s	1180.01	1134.23	5.088	1.714	1197.35	1149.45	2.703	9.370
δHCC(83)	-	1163 w	1208.47	1161.59	0.455	3.640	1212.92	1164.40	0.985	3.980
δHCC(73)+νCC(19)	-	1187 m	1230.02	1182.30	6.050	2.791	1232.86	1183.55	6.682	1.903
νCC(43)+δHCC(35)	1314 m	1317 w	1353.34	1300.83	2.753	0.426	1359.37	1304.99	1.180	1.044
δHCC(46)+νCC(28)	-	1341 vw	1381.87	1328.25	3.275	2.090	1403.32	1347.19	1.477	2.390
δHCC(53)+νCC(22)	1405 w	-	1466.90	1409.99	22.921	1.701	1478.03	1418.90	13.358	1.283
δCH_3(85)	-	-	1472.37	1415.25	0.724	4.533	1485.49	1426.07	6.010	11.279
δCH_3(75)	-	-	1485.49	1427.85	0.775	7.316	1489.47	1429.90	1.304	10.162
$\delta_s$$CH_3$(90)	1439 s	1442 w	1507.64	1449.15	13.994	12.518	1519.22	1458.45	8.337	1.332
$\delta_s$$CH_3$(79)	-	-	1510.65	1452.04	9.939	23.187	1522.12	1461.24	9.238	19.812
δHCC(55)	-	-	1514.39	1455.64	4.662	2.234	1524.77	1463.78	16.600	11.275
$\delta_s$$CH_3$(61)+δHCC(14)	-	-	1514.71	1455.94	13.992	7.082	1531.00	1469.76	8.310	8.718
$\delta_s$$CH_3$(81)	1483 m	-	1523.03	1463.94	14.761	10.095	1537.01	1475.53	12.494	16.438
δH_2O(96)	1649 s	-	1566.24	1505.47	224.195	8.651	1610.90	1546.46	230.799	8.642
νCC(58)+δHCC(31)	-	1576 w	1622.66	1559.70	1.027	9.829	1628.20	1563.07	0.626	10.913
νCC(54)+δHCC(19)	1590 m	1592 s	1636.19	1572.71	0.512	38.588	1645.26	1579.45	0.960	52.801
$\nu_s$$CH_3$(84)	-	2941 vw	3047.86	2929.61	44.323	63.123	3047.22	2925.33	106.422	154.737
$\nu_s$$CH_3$(75)	-	2958 vw	3049.36	2931.05	53.016	188.771	3059.40	2937.02	39.664	119.659
$\nu_{as}$$CH_3$(99)	-	3024 vw	3142.68	3020.74	32.394	27.222	3152.41	3026.31	59.933	50.079
$\nu_{as}$$CH_3$(92)	-	-	3147.71	3025.58	27.749	49.150	3186.78	3059.31	25.793	40.183
$\nu_{as}$$CH_3$(91)	-	-	3184.27	3060.72	20.685	83.650	3198.88	3070.92	10.065	40.150
$\nu_{as}$$CH_3$(97)	-	-	3185.64	3062.03	15.557	102.614	3201.85	3073.78	8.400	67.407
νCH(90)	3039 sh	3042 vw	3189.44	3065.69	3.148	44.958	3210.18	3081.77	4.362	69.874
νCH(91)	3060 w	3059 w	3197.89	3073.81	3.462	72.520	3211.82	3083.35	33.376	109.862
νCH(87)	3077 w	3069 vw	3213.37	3088.69	12.506	70.797	3228.58	3099.44	33.288	110.917
νCH(100)	-	-	3229.47	3104.16	20.942	144.846	3249.34	3119.36	37.706	96.038

νCH(81)	-	-	3240.89	3115.14	18.928	167.529	3255.52	3125.30	35.375	230.119
$\nu_s H_2O$(100)	3423 sh	-	3614.62	3474.37	64.137	169.902	3610.91	3466.47	84.842	179.446
$\nu_{as} H_2O$(100)	3470 s	-	3838.62	3689.68	89.718	92.730	3873.58	3718.63	100.723	135.384
Linear correlation coefficients (R^2)			0.99738 for IR wavenumbers 0.99959 for Raman wavenumbers				0.99773 for IR wavenumbers 0.99974 for Raman wavenumbers			

ν, stretching; δ, bending; δ_s, scissoring, γ, out-of-plane bending; τ, torsion; ρ, rocking; s, strong, w, wagging; m, medium; w, weak; sh, shoulder; v, very.
I_{IR}, IR intensities (km/mole); S_R, Raman scattering activities ($Å^4$/amu).