

Supporting Information for

**Influence of the d Orbital Occupation on the Structures and Sequential Binding Energies of Pyridine to the
Late First-Row Divalent Transition Metal Cations: A DFT Study**

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Table S1. Vibrational Frequencies and Average Vibrational Energies at 298 K.^a

Species	E_{vib} (eV) ^b	Vibrational frequencies (cm ⁻¹) ^c
Pyr	0.08 (0.01)	379, 413, 602, 657, 705, 748, 881, 938, 975, 990, 992, 1030, 1065, 1079, 1158, 1229, 1283, 1371, 1458, 1501, 1606, 1611, 3106, 3108, 3129, 3144, 3152
Fe ²⁺ (Pyr)	0.13 (0.01)	100, 135, 293, 368, 397, 631, 655, 662, 727, 769, 924, 970, 1006, 1031, 1032, 1060, 1083, 1183, 1215, 1283, 1367, 1456, 1486, 1568, 1589, 3137, 3138, 3164, 3172, 3176
Fe ²⁺ (Pyr) ₂	0.30 (0.02)	21, 22, 29, 99, 100, 152(2), 193, 350, 382, 385, 406(2), 641(2), 658, 675, 682(2), 755(2), 856, 857, 945(2), 978, 979, 1009, 1013, 1034, 1035, 1044, 1048, 1069, 1071, 1084, 1085, 1182(2), 1219, 1223, 1295(2), 1371(2), 1465(2), 1495, 1496, 1579(2), 1621(2), 3143(2), 3144(2), 3167(2), 3180(2), 3182, 3183
Fe ²⁺ (Pyr) ₃	0.46 (0.04)	10, 25, 26, 30, 34, 36, 100, 103, 108, 132, 149, 178, 193, 290, 291, 386, 389, 390, 414(2), 418, 646(2), 647, 649, 654, 655, 691, 692, 695, 755(3), 869, 870, 872, 943, 944, 946, 976, 977, 978, 1015(2), 1018, 1030(3), 1041, 1042, 1043, 1071, 1072, 1074, 1084, 1085(2), 1178, 1179(2), 1222, 1223, 1227, 1295(2), 1296, 1371(2), 1372, 1464, 1465(2), 1500(2), 1501, 1588(2), 1589, 1627(3), 3140(2), 3140, 3143, 3145, 3149, 3150, 3165, 3166(2), 3177, 3178(2), 3181(2), 3182
Fe ²⁺ (Pyr) ₄	0.62 (0.05)	23, 26, 27, 30, 35, 36, 42, 50, 56, 106, 112, 114, 137, 141(2), 145, 167, 193, 255(2), 256, 390, 391, 394, 398, 416, 420(2), 426, 641, 642(2), 643, 649, 649(2), 651, 699(2), 701, 703, 755(2), 756(2), 877, 878, 880, 883, 947, 948, 950, 952, 978(2), 979, 981, 1014, 1015(2), 1018, 1025(4), 1038(3), 1039, 1074(3), 1077, 1083(2), 1084, 1088, 1176(4), 1225(2), 1226, 1231, 1292(3), 1294, 1372(2), 1373(2), 1463(3), 1465, 1503(4), 1592(3), 1593, 1628(3), 1629, 3143(2), 3145(2), 3151(3), 3152, 3163, 3164(3), 3175(4), 3179(4)
Fe ²⁺ (Pyr) ₅	0.79 (0.06)	14, 23, 31, 36, 38, 40(2), 42, 51, 57, 63, 81, 98, 103, 117, 124, 126, 130, 143, 150, 153, 158, 167, 168, 209, 235, 243, 389, 390, 394, 396, 407, 421, 422, 424, 427, 428, 624, 625, 632, 633, 634, 650, 651, 652(2), 653, 700(2), 706(2), 710, 756(2), 757(3), 879, 880, 884, 885, 888, 946, 947, 950, 951, 958, 976, 977, 979(2), 985, 1005, 1008, 1011, 1013, 1016, 1019, 1020, 1021(3), 1035(2), 1036, 1037, 1038, 1074, 1075, 1076(2), 1078, 1080, 1082(2), 1083, 1084, 1172(2), 1173, 1174(2), 1224, 1225, 1226, 1227, 1233, 1286(2), 1289, 1290(2), 1369, 1371(2), 1372, 1373, 1460(2), 1461, 1462(2), 1502, 1503, 1504, 1505(2), 1594, 1595(2), 1596(2), 1626, 1627, 1628, 1629(2), 3149, 3150, 3152, 3153, 3154(2), 3156(3), 3159, 3162(2), 3163(2), 3165, 3171, 3172, 3173(2), 3174, 3176(2), 3178(3)
Fe ²⁺ (Pyr) ₆	0.96 (0.07)	17, 23, 26, 27, 31, 38, 40, 42, 44, 46, 51, 57, 64, 72, 76, 92, 100, 114, 115, 122, 130, 136, 139, 145, 146, 149, 153, 160, 162, 165, 200, 201, 209, 387, 389, 390, 393, 394, 401, 422, 424(2), 425, 427(2), 616, 619, 620(2), 624(2), 653(4), 654, 655, 701, 703(2), 705, 707, 708, 755, 756, 757(2), 759(2), 883, 884, 885, 886, 887, 889, 949, 951(2), 954, 955, 957, 978, 980(2), 982, 983, 984, 1001, 1002, 1003, 1004, 1006, 1009, 1017(2), 1018(3), 1019, 1033, 1035, 1036, 1037(2), 1038, 1076(2), 1077(3), 1079(2), 1080(2), 1081, 1082, 1083, 1171(4), 1172(2), 1225, 1226, 1227, 1229(2), 1236, 1280(2), 1282, 1283(2), 1284, 1369(2), 1371(3), 1372, 1458, 1459(3), 1460(2), 1501, 1502, 1503, 1504(2), 1505, 1594, 1595(2), 1596(3), 1624, 1625(2), 1626, 1627(2), 3155(4), 3156(2), 3164(4), 3165, 3166, 3170(2), 3171(4), 3179, 3180, 3183(2), 3187, 3188, 3189, 3190(2), 3191(2), 3193

Table S1. (continued) Vibrational Frequencies and Average Vibrational Energies at 298 K.^a

Species	E_{vib} (eV) ^b	Vibrational frequencies (cm ⁻¹) ^c
Co ²⁺ (Pyr)	0.13 (0.01)	114, 135, 308, 368, 391, 622, 645, 677, 747, 811, 941, 978, 999, 1031(2), 1053, 1084, 1180, 1215, 1284, 1362, 1465, 1475, 1539, 1590, 3142, 3143, 3164, 3175, 3177
Co ²⁺ (Pyr) ₂	0.30 (0.02)	15, 16, 23, 96(2), 139(2), 197, 347, 380, 382, 401, 402, 639(2), 662, 673(2), 680, 753(2), 848, 849, 944(2), 978(2), 1009, 1013, 1034(2), 1044, 1048, 1068, 1072, 1084, 1085, 1182(2), 1217, 1220, 1297(2), 1368(2), 1464(2), 1492(2), 1575(2), 1617, 1618, 3145(2), 3146(2), 3167(2), 3180(2), 3183(2)
Co ²⁺ (Pyr) ₃	0.46 (0.04)	19, 22, 24, 27, 29, 34, 105, 106, 108, 139, 141, 175, 190, 295, 296, 389(2), 390, 412, 417(2), 645, 646(2), 653, 659(2), 689, 691(2), 756(3), 868(2), 869, 944(2), 945, 977(2), 978, 1016(2), 1019, 1030(3), 1043, 1044(2), 1072(2), 1075, 1084, 1085(2), 1178(3), 1220, 1221, 1226, 1297, 1298(2), 1369(2), 1370, 1464(2), 1465, 1499, 1500(2), 1588(3), 1626(2), 1627, 3145, 3146, 3147, 3148(2), 3149, 3166(3), 3178(3), 3181(3)
Co ²⁺ (Pyr) ₄	0.62 (0.05)	22, 27(2), 28, 37, 41(3), 46, 110, 120(2), 138, 153, 161(2), 171, 175, 270(2), 286, 391(2), 392, 395, 420, 423, 424, 426, 644, 645(2), 646, 648, 649(2), 650, 697(3), 698, 755, 756(3), 875, 876(2), 879, 945, 947(3), 977, 978(2), 979, 1017(3), 1020, 1025(4), 1040(4), 1075(3), 1077, 1083, 1084(2), 1085, 1176(4), 1224(2), 1225, 1230, 1292(2), 1293, 1294, 1371, 1372(3), 1463, 1464(2), 1465, 1503(4), 1592, 1593(3), 1629(4), 3146, 3147(2), 3148, 3157(4), 3164(4), 3176(4), 3180(4)
Co ²⁺ (Pyr) ₅	0.78 (0.06)	14, 18, 34, 36, 41, 42, 43, 44, 56, 61, 67, 79, 104, 115, 125, 133, 136, 143, 158(2), 166, 167, 177, 185, 253, 255, 266, 389, 390, 396, 398, 405, 425, 426, 428, 431, 440, 623, 624, 635, 636, 637, 649, 651, 652, 653(2), 698, 699, 705, 706, 707, 755(2), 756(2), 760, 876, 877, 883(3), 943(2), 949, 950, 956, 974, 975, 979(2), 982, 1006, 1008, 1014, 1016, 1018, 1019, 1020, 1021(2), 1022, 1035, 1036, 1037, 1038, 1039, 1075(3), 1077, 1078, 1081, 1083(2), 1084, 1087, 1172(2), 1174(3), 1223, 1225(2), 1229, 1233, 1286(2), 1289, 1290, 1293, 1366, 1371(2), 1372(2), 1460, 1461(2), 1462, 1463, 1501, 1504, 1505(2), 1506, 1593, 1595, 1596, 1597(2), 1627(2), 1628, 1629(2), 3147, 3148, 3154(2), 3155(2), 3157(2), 3159, 3163(2), 3165(2), 3166, 3170, 3171, 3172, 3173, 3174, 3177(3), 3178(2), 3181
Co ²⁺ (Pyr) ₆	0.92 (0.08)	16, 23, 28, 30, 33, 41, 43, 48, 51, 53, 59, 60, 63, 70, 76, 77, 78, 102, 119, 138, 148, 157, 160, 165, 176, 189, 194, 206, 217, 225, 292, 308, 326, 388, 395, 398, 401, 403, 414, 415, 427, 442, 456, 461, 470, 608, 618, 637, 641(2), 644, 651, 652(2), 654(2), 655, 700, 701, 704, 705, 711, 717, 752, 755, 758, 759, 763, 764, 874(2), 884, 886, 890, 893, 944, 948, 949, 954, 958, 965, 976, 977(2), 987, 990, 993, 996, 1003, 1012, 1016, 1017(2), 1018(2), 1019(2), 1020, 1023, 1032, 1035, 1039(2), 1041, 1043, 1072, 1076(2), 1077, 1078(2), 1080(2), 1087, 1089(2), 1092, 1167, 1171, 1172(2), 1173(2), 1226, 1227, 1229, 1231, 1232, 1238, 1282, 1283, 1285, 1285, 1286, 1287, 1370, 1371, 1372(2), 1379, 1380, 1458(2), 1463(2), 1464, 1466, 1503, 1504, 1506, 1507, 1510, 1512, 1595, 1596(3), 1597, 1600, 1618, 1624, 1632, 1633(2), 1634, 3113, 3115, 3121, 3124, 3151(2), 3152, 3158(2), 3159(2), 3161, 3162, 3167(2), 3169(4), 3174(2), 3175(3), 3189, 3190, 3193, 3194, 3196(2)

Table S1. (continued) Vibrational Frequencies and Average Vibrational Energies at 298 K.^a

Species	E_{vib} (eV) ^b	Vibrational frequencies (cm ⁻¹) ^c
Ni ²⁺ (Pyr)	0.13 (0.01)	128, 140, 309, 400, 427, 623, 681, 722, 786, 924, 971, 1005, 1034, 1065, 1085, 1096, 1181, 1209, 1291, 1313, 1354, 1447, 1478, 1556, 1572, 3127, 3131, 3154, 3170, 3172
Ni ²⁺ (Pyr) ₂	0.25 (0.02)	33, 68(2), 126(2), 196, 365, 377, 380, 392(2), 634(2), 657, 674(2), 679, 755(2), 858, 859, 950(2), 981(2), 1001, 1008, 1033(2), 1041, 1045, 1062, 1066, 1083(2), 1180(2), 1221, 1225, 1287(2), 1372(2), 1468(2), 1487, 1488, 1558(2), 1616, 1623, 3161(2), 3163(2), 3169(2), 3180(2), 3183(2)
Ni ²⁺ (Pyr) ₃	0.45 (0.04)	19, 24, 35, 36, 41, 42, 114, 115, 124, 151, 152, 168, 235, 303(2), 389, 390, 393, 416(2), 421, 645(3), 655, 660(2), 688, 689, 690, 755(2), 756, 867(2), 870, 947(2), 948, 979, 980, 981, 1018(2), 1020, 1030(3), 1044(3), 1074(2), 1076, 1086(3), 1178, 1179(2), 1221(2), 1226, 1297, 1298(2), 1370(2), 1371, 1465(3), 1499, 1500, 1501, 1587(3), 1625, 1626(2), 3145(2), 3146, 3163(3), 3168(3), 3179(3), 3182(3)
Ni ²⁺ (Pyr) ₄	0.61 (0.05)	21, 22, 29, 31, 41, 42, 46, 48, 59, 117, 126, 127, 142, 148, 154, 167, 171, 180, 254, 275, 292, 390, 392, 393, 399, 421, 425, 426, 429, 641, 642, 645, 646, 649(3), 650, 697(2), 698, 699, 756, 757(2), 758, 874, 876, 878, 881, 946, 948, 951(2), 978, 979, 980, 982, 1015, 1017, 1019, 1021, 1024, 1025(2), 1026, 1038, 1039, 1040, 1041, 1074, 1075, 1076, 1079, 1084, 1084, 1085, 1086, 1175, 1176(3), 1224(2), 1225, 1230, 1292(2), 1293, 1294, 1369, 1370, 1371, 1373, 1463, 1464(3), 1502, 1503(2), 1504, 1592(2), 1593, 1594, 1628(2), 1629(2), 3136, 3147, 3150, 3157, 3159, 3160, 3161, 3163, 3165, 3166, 3167, 3171, 3176(3), 3177, 3180(3), 3183
Ni ²⁺ (Pyr) ₅	0.77 (0.06)	17, 26, 39, 40(2), 48, 49, 52, 53, 63, 66, 89, 114, 127, 129, 136, 150(2), 155, 163, 168, 173, 191, 198, 244, 248, 256, 390, 391, 396, 397, 411, 427, 429, 431, 435, 436, 626, 630(2), 634, 636, 650, 652(3), 653, 701, 702, 703, 704, 710, 756(2), 757(2), 758, 880(2), 882(2), 888, 946(2), 952, 953, 960, 977(2), 980, 981, 987, 1008, 1012, 1013, 1015, 1019, 1020(4), 1021, 1036(2), 1037(2), 1038, 1075, 1076(2), 1077, 1079, 1081, 1084(2), 1085, 1086, 1173(4), 1174, 1225(2), 1227, 1228, 1234, 1287(2), 1288, 1290, 1291, 1368, 1370(2), 1371(2), 1461(2), 1462(3), 1503, 1504(2), 1505, 1506, 1594, 1596(3), 1597, 1628(2), 1629(2), 1630, 3144(2), 3156(2), 3158(3), 3162(2), 3164, 3166(2), 3169(2), 3170, 3173(2), 3175(2), 3177, 3178(2), 3180, 3182(2)
Ni ²⁺ (Pyr) ₆	0.94 (0.08)	16, 18, 29, 32, 38, 43, 44, 47, 49, 53, 60, 69, 75, 77, 88, 105, 111, 112, 128, 138, 150, 151, 156(2), 163, 171, 176, 183, 184, 186, 219, 223, 229, 390, 392, 394, 394, 401, 407, 428, 429, 431, 432, 433, 434, 619(2), 622(2), 624, 626, 653(3), 654, 655(2), 702, 703(2), 705, 707(2), 756, 757(2), 758, 759(2), 759, 881, 883, 884, 885, 886, 888, 950, 951, 954, 957, 958(2), 979, 982(2), 983, 985, 986, 1002, 1003, 1004, 1005, 1007, 1011, 1018, 1018(5), 1036, 1037, 1038, 1039, 1040(2), 1077(3), 1078, 1079, 1080, 1082, 1083(2), 1084, 1085(2), 1171(4), 1172(2), 1227, 1230(2), 1231, 1233, 1239, 1279, 1280, 1281(3), 1282, 1369, 1371, 1372, 1373(2), 1374, 1458, 1459(4), 1460, 1502, 1504(2), 1506, 1507, 1508, 1595(3), 1596(2), 1597, 1625, 1626, 1627(2), 1628(2), 3156(6), 3165(2), 3166(4), 3172(6), 3194, 3195, 3197, 3198(2), 3200, 3201, 3203, 3205(2), 3208(2)

Table S1. (continued) Vibrational Frequencies and Average Vibrational Energies at 298 K.^a

Species	E_{vib} (eV) ^b	Vibrational frequencies (cm ⁻¹) ^c
Cu ²⁺ (Pyr)	0.13 (0.01)	117, 151, 276, 342, 365, 620, 627, 630, 724, 911, 936, 981, 993, 1009, 1028, 1040, 1086, 1123, 1186, 1311, 1368, 1433, 1444, 1496, 1575, 3162, 3166, 3170, 3175, 3177
Cu ²⁺ (Pyr) ₂	0.29 (0.02)	23, 30, 32, 106, 131, 137, 168, 243, 329, 381(2), 403, 410, 628, 629, 656, 664, 672, 676, 751, 752, 820, 822, 943, 945, 978, 979, 1006, 1013, 1029, 1030, 1039, 1040, 1065, 1066, 1085, 1086, 1179(2), 1214, 1220, 1289, 1291, 1364, 1365, 1462, 1463, 1485, 1486, 1555(2), 1590, 1603, 3161(2), 3162(2), 3167(2), 3179(2), 3181, 3182
Cu ²⁺ (Pyr) ₃	0.45 (0.04)	29(2), 35, 40, 42, 46, 117(2), 128, 168, 174, 200, 217, 274, 334, 390, 391, 393, 420, 423, 425, 644, 645(2), 655, 658, 665, 686, 688, 689, 755(2), 756, 861, 866, 867, 946, 947, 949, 980(2), 981, 1018, 1019, 1021, 1029, 1030(2), 1038, 1046, 1047, 1074, 1077, 1079, 1087(2), 1087, 1088, 1178, 1179(2), 1220, 1221, 1225, 1297, 1298, 1300, 1367, 1369, 1370, 1464, 1465, 1466, 1499(2), 1500, 1587(2), 1588, 1620, 1625(2), 3145(2), 3161(2), 3163, 3166, 3167(2), 3171, 3179(3), 3182(3)
Cu ²⁺ (Pyr) ₄	0.60 (0.05)	16, 23, 32, 38, 41, 42, 47, 51, 55, 116, 136, 142, 151, 165, 176, 180, 191, 193, 214, 282, 285, 389(2), 393, 397, 426, 430, 434, 440, 639, 644(2), 647, 649, 649, 650(2), 696, 697(2), 698, 758, 760(3), 876(2), 877, 878, 948(2), 953, 954, 981(2), 982(2), 1016, 1018(2), 1023, 1025(4), 1038(2), 1039, 1042, 1075, 1076, 1077, 1080, 1084(2), 1087, 1088, 1175(2), 1176(2), 1224, 1226(2), 1231, 1291, 1293(2), 1295, 1370, 1371, 1373, 1374, 1463, 1464, 1465(2), 1503(2), 1505(2), 1593(2), 1594(2), 1627, 1628(2), 1629, 3141, 3142, 3158(2), 3159(2), 3164(4), 3174(2), 3175(2), 3179(4), 3191(2)
Cu ²⁺ (Pyr) ₅	0.77 (0.06)	12(2), 35, 40, 42, 45(2), 49, 53, 59, 66, 84, 113, 122, 123, 129, 130, 139, 149, 157, 173, 174, 198, 207, 221, 247, 250, 389, 390, 395, 398, 404, 421, 429, 432, 440, 441, 621, 628, 634, 637, 640, 650, 651(2), 652, 654, 699, 700, 701, 702, 713, 756, 757(2), 759(2), 879(2), 880(2), 890, 948, 949, 952, 953, 957, 979(2), 980, 981, 985, 1006, 1010, 1016, 1017, 1019, 1021(2), 1022(3), 1034, 1035, 1036(2), 1039, 1076, 1077(2), 1078, 1079, 1081, 1084(2), 1087(2), 1172, 1173(2), 1174(2), 1225, 1226, 1227, 1228, 1235, 1287, 1289, 1290, 1291, 1292, 1369(2), 1370, 1372, 1375, 1460, 1463(3), 1464, 1503, 1504(2), 1505, 1507, 1596(3), 1597(2), 1625, 1627(2), 1629(2), 3146, 3147, 3151(2), 3159(2), 3160(3), 3167(4), 3169, 3172(2), 3174(2), 3175, 3179(4), 3185(2)
Cu ²⁺ (Pyr) ₆	0.94 (0.07)	16, 18, 19, 28, 31, 37, 38, 43, 45, 46, 48, 51, 56, 57, 62, 69, 80, 90, 92, 96, 121, 129(2), 142, 155, 180, 187, 198, 212, 220, 267, 275, 388, 390, 391(2), 400, 404, 414, 415, 428, 435, 441, 445, 607(2), 631, 641, 642, 646, 650, 651(3), 655, 656, 696(2), 701, 702, 713, 715, 751(2), 758(2), 759, 760, 878(2), 882(2), 891, 892, 945, 947, 949, 951, 955, 957, 977, 978, 979(2), 983, 984, 994, 995, 1014(3), 1019(3), 1020(2), 1021, 1025, 1032(2), 1035, 1036, 1037, 1040, 1072, 1073, 1076, 1078(3), 1079, 1082, 1083(2), 1086(2), 1168(2), 1172(2), 1173(2), 1223, 1224, 1226, 1228(2), 1233, 1283, 1284, 1290, 1291, 1293, 1294, 1368(2), 1370(2), 1372, 1373, 1457(2), 1464(3), 1465, 1503(4), 1504, 1505, 1596, 1597(3), 1598, 1599, 1617, 1618, 1630(4), 3117, 3119(2), 3121, 3153(2), 3158(4), 3162, 3163, 3167(2), 3168(2), 3170(2), 3172(2), 3173(2), 3181, 3182, 3184(2), 3187(2), 3189(2)

Table S1. (continued) Vibrational Frequencies and Average Vibrational Energies at 298 K.^a

Species	E_{vib} (eV) ^b	Vibrational frequencies (cm ⁻¹) ^c
Zn ²⁺ (Pyr)	0.13 (0.01)	115, 171, 299, 381, 395, 624, 635, 668, 726, 776, 935, 969, 1003, 1021, 1030, 1054, 1084, 1181, 1216, 1287, 1362, 1464, 1477, 1563, 1578, 3158, 3160, 3167, 3174, 3175
Zn ²⁺ (Pyr) ₂	0.29 (0.02)	30(3), 115(2), 195(2), 205, 364, 386, 388, 407(2), 641(2), 662, 678(2), 682, 750(2), 859(2), 944(2), 980(2), 1015, 1017, 1037(2), 1045, 1048, 1077, 1085, 1089(2), 1183(2), 1222, 1225, 1302(2), 1372(2), 1472(2), 1498(2), 1582(2), 1626(2), 3158, 3159, 3160(2), 3169(2), 3180(2), 3183(2)
Zn ²⁺ (Pyr) ₃	0.45 (0.04)	21, 24, 29, 30, 31, 42, 104, 105, 113, 172, 174, 188, 197, 284, 285, 390, 391, 394, 416, 417(2), 647(3), 653, 657, 658, 693, 695(2), 757, 759(2), 876(2), 879, 951, 953(2), 982(2), 983, 1019(2), 1021, 1032(3), 1045, 1046, 1047, 1077(2), 1081, 1086, 1087(2), 1179(3), 1224, 1225, 1230, 1299(2), 1300, 1374(2), 1375, 1468, 1469(2), 1503, 1504(2), 1590(3), 1631(3), 3154(2), 3155(3), 3156, 3167(3), 3178(3), 3182(3)
Zn ²⁺ (Pyr) ₄	0.62 (0.05)	23, 26, 27(2), 35, 39(3), 48, 110, 119(2), 137, 156, 167(2), 175, 176, 241, 243, 254, 391(3), 395, 421, 424(2), 426, 644(2), 645(2), 649, 650(2), 651, 700(3), 701, 759(2), 760(2), 882, 883(2), 886, 951, 954(2), 955, 981, 982(2), 984, 1019(3), 1022, 1027(4), 1041(4), 1077(3), 1081, 1084, 1085(2), 1086, 1176(4), 1226(2), 1227, 1233, 1295(3), 1296, 1373, 1374(3), 1466(3), 1467, 1505(4), 1594(3), 1595, 1631, 1632(3), 3149(3), 3150, 3158(4), 3164(4), 3176(4), 3180(4)
Zn ²⁺ (Pyr) ₅	0.79 (0.06)	7, 18, 30, 33, 37, 39, 40, 42, 51, 53, 60, 72, 90, 114(2), 125, 134, 139, 146, 156, 165, 166, 172, 180, 192, 227, 230, 388, 390, 394, 395, 402, 422, 423, 427, 431, 435, 623, 624, 636(2), 637, 651, 652, 653(3), 701(2), 705, 706, 707, 757(2), 759(2), 762, 880, 882, 884, 885, 887, 948, 949, 950, 951, 960, 977, 979, 980(2), 985, 1007, 1009, 1017(2), 1020(2), 1021, 1022(2), 1023, 1035, 1036, 1038, 1039, 1040, 1076, 1077(2), 1078, 1081(2), 1083(2), 1084, 1085, 1172(2), 1174(3), 1225, 1226, 1228, 1229, 1235, 1289(2), 1292, 1293(2), 1370(2), 1372, 1376(2), 1461(2), 1463, 1465(2), 1504, 1505, 1506, 1507(2), 1595, 1597(3), 1598, 1627, 1628, 1631(3), 3146(2), 3150, 3151, 3152, 3153, 3157(2), 3158, 3162(2), 3163, 3164(2), 3168, 3172(2), 3173, 3174, 3176, 3177(2), 3178(2), 3180
Zn ²⁺ (Pyr) ₆	0.96 (0.07)	10, 24, 28, 30, 31, 38, 40, 42(2), 49(2), 63, 64, 67, 71, 82, 89, 106, 111, 122, 144, 146, 149, 151, 153, 158, 159, 160, 162, 164, 182, 183, 184, 388, 390, 392, 394, 395, 402, 425(2), 426(3), 427, 619, 620(2), 621, 622, 624, 653, 654(3), 655(2), 703, 704, 705(2), 706, 707, 759(3), 760(2), 761, 885, 887(2), 888, 889, 891, 953, 954, 956, 958, 959, 960, 982, 984(2), 985, 987, 988, 1003(2), 1004, 1005, 1006, 1011, 1019(6), 1034, 1036, 1037(2), 1039(2), 1077(2), 1078(3), 1080, 1081(2), 1082, 1083(2), 1084, 1171(5), 1172, 1225, 1228, 1229, 1230, 1231, 1238, 1282, 1283(3), 1284(2), 1368, 1372, 1373(3), 1374, 1459(3), 1460(2), 1461, 1502, 1504, 1505(2), 1507(2), 1596(3), 1597(3), 1625, 1626(2), 1627(2), 1628, 3155(3), 3156(3), 3165(3), 3166(3), 3171(2), 3172(4), 3190, 3191, 3192(3), 3193, 3194(2), 3195(2), 3196, 3197

^a The spin states of the Fe²⁺(Pyr)_x, Co²⁺(Pyr)_x, Ni²⁺(Pyr)_x, Cu²⁺(Pyr)_x, and Zn²⁺(Pyr)_x complexes are quintet, quartet, triplet, doublet, and singlet, respectively, for all values of x. ^b Uncertainties listed in parentheses are determined as described in the text. ^c Vibrational frequencies scaled by 0.9804 obtained from vibrational analyses of the B3LYP/6-31G* geometry optimized structures. Degeneracies are indicated in parentheses.

Table S2. Rotational Constants (in cm^{-1}) of $\text{M}^{2+}(\text{Pyr})_x$ Complexes where $x = 1-6$ and the Corresponding PSL Transition States for Dissociation.

Complex	Energized Molecule		Transition State	
	1-D ^a	2-D ^b	1-D ^c	2-D ^c
Fe ²⁺ (Pyr)	0.1935	0.0347	0.2013	0.1382
Fe ²⁺ (Pyr) ₂	0.0974	0.0084	0.1935, 0.2013	0.0347, 0.1382
Fe ²⁺ (Pyr) ₃	0.0100	0.0073	0.0974, 0.2013	0.0084, 0.1382
Fe ²⁺ (Pyr) ₄	0.0057	0.0056	0.0100, 0.2013	0.0073, 0.1382
Fe ²⁺ (Pyr) ₅	0.0048	0.0041	0.0057, 0.2013	0.0056, 0.1382
Fe ²⁺ (Pyr) ₆	0.0034	0.0034	0.0048, 0.2013	0.0041, 0.1382
Co ²⁺ (Pyr)	0.1915	0.0353	0.2013	0.1382
Co ²⁺ (Pyr) ₂	0.0971	0.0086	0.1915, 0.2013	0.0353, 0.1382
Co ²⁺ (Pyr) ₃	0.0101	0.0075	0.0971, 0.2013	0.0086, 0.1382
Co ²⁺ (Pyr) ₄	0.0061	0.0057	0.0101, 0.2013	0.0075, 0.1382
Co ²⁺ (Pyr) ₅	0.0049	0.0041	0.0061, 0.2013	0.0057, 0.1382
Co ²⁺ (Pyr) ₆	0.0041	0.0029	0.0049, 0.2013	0.0041, 0.1382
Ni ²⁺ (Pyr)	0.1923	0.0359	0.2013	0.1382
Ni ²⁺ (Pyr) ₂	0.0969	0.0086	0.1923, 0.2013	0.0359, 0.1382
Ni ²⁺ (Pyr) ₃	0.0106	0.0078	0.0816, 0.2013	0.0091, 0.1382
Ni ²⁺ (Pyr) ₄	0.0066	0.0056	0.0106, 0.2013	0.0078, 0.1382
Ni ²⁺ (Pyr) ₅	0.0048	0.0043	0.0066, 0.2013	0.0056, 0.1382
Ni ²⁺ (Pyr) ₆	0.0035	0.0035	0.0048, 0.2013	0.0043, 0.1382
Cu ²⁺ (Pyr)	0.1947	0.0339	0.2013	0.1382
Cu ²⁺ (Pyr) ₂	0.0721	0.0097	0.1946, 0.2013	0.0339, 0.1382
Cu ²⁺ (Pyr) ₃	0.0132	0.0072	0.0713, 0.2013	0.0097, 0.1382
Cu ²⁺ (Pyr) ₄	0.0069	0.0056	0.0132, 0.2013	0.0072, 0.1382
Cu ²⁺ (Pyr) ₅	0.0048	0.0043	0.0069, 0.2013	0.0055, 0.1382
Cu ²⁺ (Pyr) ₆	0.0039	0.0029	0.0048, 0.2013	0.0043, 0.1382
Zn ²⁺ (Pyr)	0.1920	0.0340	0.2013	0.1382
Zn ²⁺ (Pyr) ₂	0.0973	0.0088	0.1920, 0.2013	0.0340, 0.1382
Zn ²⁺ (Pyr) ₃	0.0103	0.0075	0.0973, 0.2013	0.0088, 0.1382
Zn ²⁺ (Pyr) ₄	0.0060	0.0057	0.0103, 0.2013	0.0075, 0.1382
Zn ²⁺ (Pyr) ₅	0.0049	0.0041	0.0060, 0.2013	0.0057, 0.1382
Zn ²⁺ (Pyr) ₆	0.0034	0.0034	0.0049, 0.2013	0.0041, 0.1382

^aActive external. ^bInactive external. ^cRotational constants of the PSL TS treated as free internal rotors.

Table S3. Relative Energies of the Various Spin States of a $M^{2+}(\text{Pyr})_x$ Complexes in Their Ground-State Conformations, where $M^{2+} = \text{Fe}^{2+}$, Co^{2+} , and Ni^{2+} at 0 K in kJ/mol.

Complex	Multiplicity	B3LYP ^a	BHandHLYP ^b	M06 ^c	Complex	Multiplicity	B3LYP ^a	BHandHLYP ^b	M06 ^c
Fe ²⁺	5	0.0	0.0	0.0	Co ²⁺ (Pyr) ₅	4	0.0	0.0	0.0
	3	241.3	263.6	260.2		2	6.8	152.4	14.3
	1	378.4	404.4	408.5	Co ²⁺ (Pyr) ₆	4	0.0	0.0	0.0
Fe ²⁺ (Pyr)	5	0.0	0.0	0.0		2	78.3	170.2	103.3
	3	101.5	158.1	112.5	Ni ²⁺	3	0.0	0.0	0.0
	1	242.4	297.3	257.0		1	297.0	317.3	234.6
Fe ²⁺ (Pyr) ₂	5	0.0	0.0	0.0	Ni ²⁺ (Pyr)	3	0.0	0.0	0.0
	3	131.4	168.7	145.4		1	98.9	163.4	105.7
	1	263.3	304.2	283.7	Ni ²⁺ (Pyr) ₂	3	0.0	0.0	0.0
Fe ²⁺ (Pyr) ₃	5	0.0	0.0	0.0		1	77.7	145.2	62.4
	3	122.6	143.2	134.4	Ni ²⁺ (Pyr) ₃	3	0.0	0.0	0.0
	1	188.5	269.4	212.5		1	19.9	105.6	19.1
Fe ²⁺ (Pyr) ₄	5	0.0	0.0	0.0	Ni ²⁺ (Pyr) ₄	3	0.0	0.0	0.0
	3	81.4	142.2	137.3		1	13.5	44.8	76.7
	1	244.6	342.5	307.4	Ni ²⁺ (Pyr) ₅	3	0.0	0.0	0.0
Fe ²⁺ (Pyr) ₅	5	0.0	0.0	0.0		1	26.3	122.6	20.8
	3	44.0	101.0	61.6	Ni ²⁺ (Pyr) ₆	3	0.0	0.0	0.0
	1	89.2	170.0	131.5		1	19.6	129.6	46.2
Fe ²⁺ (Pyr) ₆	5	0.0	0.0	0.0					
	3	70.1	127.3	119.7					
	1	85.9	170.1	117.4					
Co ²⁺	4	0.0	0.0	0.0					
	2	252.6	273.5	304.6					
Co ²⁺ (Pyr)	4	0.0	0.0	0.0					
	2	66.9	87.7	62.5					
Co ²⁺ (Pyr) ₂	4	0.0	0.0	0.0					
	2	37.3	100.6	117.2					
Co ²⁺ (Pyr) ₃	4	0.0	0.0	0.0					
	2	71.6	135.6	74.2					
Co ²⁺ (Pyr) ₄	4	0.0	0.0	0.0					
	2	48.1	132.4	187.7					

^aCalculated at the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G* level of theory including ZPE corrections with frequencies scaled by 0.9804. ^bCalculated at the BHandHLYP/6-311+G(2d,2p)//BHandHLYP/6-31G* level of theory including ZPE corrections with frequencies scaled by 0.9472. ^cCalculated at the M06/6-311+G(2d,2p)//M06/6-31G* level of theory including ZPE corrections with frequencies scaled by 0.9940.

Table S4. Geometrical Parameters of the BHandHLYP/6-31G* and M06/6-31G* Ground-State Structures of the $M^{2+}(\text{Pyr})_x$ Complexes^a

Complex	BHandHLYP		M06	
	$M^{2+}-N$	$\angle NM^{2+}N$	$M^{2+}-N$	$\angle NM^{2+}N$
$\text{Fe}^{2+}(\text{Pyr})$	1.958	–	1.932	–
$\text{Fe}^{2+}(\text{Pyr})_2$	1.971	179.7	1.947	180.0
$\text{Fe}^{2+}(\text{Pyr})_3$	2.031	120.0	1.995	119.8
$\text{Fe}^{2+}(\text{Pyr})_4$	2.093	109.0 (2), 110.5 (4)	2.045	107.7 (2), 110.4 (4)
$\text{Fe}^{2+}(\text{Pyr})_5$	2.171 (3), 2.235 (2)	86.5 (3), 90.2 (2), 95.5 (2), 108.9 (2), 169.0	2.107 (3), 2.197 (2)	86.2 (2), 89.9 (2), 94.0 (2), 114.6, 122.7 (2), 179.7
$\text{Fe}^{2+}(\text{Pyr})_6$	2.302	89.3 (6), 90.7 (6), 179.3 (3)	2.251	88.1 (6), 92.0 (6), 177.0 (3)
$\text{Co}^{2+}(\text{Pyr})$	1.873	–	1.892	–
$\text{Co}^{2+}(\text{Pyr})_2$	1.920	180.0	1.901	180.0
$\text{Co}^{2+}(\text{Pyr})_3$	1.991	118.5	1.949	119.9
$\text{Co}^{2+}(\text{Pyr})_4$	2.045	105.7 (2), 111.4 (4)	1.994	106.5 (2), 110.0 (4)
$\text{Co}^{2+}(\text{Pyr})_5$	2.110 (3), 2.215 (2)	86.2 (2), 91.3 (2), 93.1 (2), 114.5 (2), 131.0, 173.8	2.057 (3), 2.163 (2)	86.4 (2), 91.9 (4), 118.7 (2), 122.8, 176.8
$\text{Co}^{2+}(\text{Pyr})_6$	2.270	89.3 (6), 90.7 (6), 179.3 (3)	2.212	88.0 (6), 92.1 (6), 176.7 (3)
$\text{Ni}^{2+}(\text{Pyr})$	1.868	–	1.851	–
$\text{Ni}^{2+}(\text{Pyr})_2$	1.922	180.0	1.887	179.7
$\text{Ni}^{2+}(\text{Pyr})_3$	1.967 (2), 1.975	106.5 (2), 147.1	1.914, 1.922 (2)	106.5 (2), 147.1
$\text{Ni}^{2+}(\text{Pyr})_4$	2.028	101.1 (2), 108.3 (2), 119.6 (2)	1.981	99.8 (2), 107.3 (2), 122.2 (2)
$\text{Ni}^{2+}(\text{Pyr})_5$	2.081, 2.127 (4)	86.6 (2), 89.4 (2), 100.8 (4), 158.5 (2)	2.061 (4), 2.100	88.3 (4), 97.2 (2), 104.0 (2), 158.9 (2)
$\text{Ni}^{2+}(\text{Pyr})_6$	2.226	89.9 (2), 90.0 (10), 180.0 (3)	2.176	88.3 (6), 91.8 (6), 177.2 (3)

Table S4. (continued) Geometrical Parameters of the BHandHLYP/6-31G* and M06/6-31G* Ground-State Structures of the $M^{2+}(\text{Pyr})_x$ Complexes^a

Complex	BHandHLYP		M06	
	$M^{2+}-N$	$\angle NM^{2+}N$	$M^{2+}-N$	$\angle NM^{2+}N$
$\text{Cu}^{2+}(\text{Pyr})$	1.836	–	1.819	–
$\text{Cu}^{2+}(\text{Pyr})_2$	1.896	180.0	1.848	180.0
$\text{Cu}^{2+}(\text{Pyr})_3$	1.925 (2), 1.937	105.8 (2), 148.4	1.893 (2), 1.918	103.3 (2), 153.5
$\text{Cu}^{2+}(\text{Pyr})_4$	2.013	94.9, 97.5, 99.1 (2), 137.2 (2)	1.976	93.9, 97.1 (3), 141.3 (2)
$\text{Cu}^{2+}(\text{Pyr})_5$	2.075 (4), 2.247	86.8 (2), 90.1 (2), 96.4 (2), 104.3 (2), 159.4 (2)	2.044 (4), 2.156	86.3 (2), 92.2 (4), 112.8 (2), 134.4, 174.5
$\text{Cu}^{2+}(\text{Pyr})_6$	2.063 (4), 2.815 (2)	89.9, 90.0 (11), 179.9 (3)	2.032 (4), 2.409 (2)	85.6 (8), 97.9 (4), 169.7 (3)
$\text{Zn}^{2+}(\text{Pyr})$	1.865	–	1.858	–
$\text{Zn}^{2+}(\text{Pyr})_2$	1.879	180.0	1.872	180.0
$\text{Zn}^{2+}(\text{Pyr})_3$	1.956	120.0	1.936	120.0
$\text{Zn}^{2+}(\text{Pyr})_4$	2.027	106.1 (2), 111.2 (4)	2.001	107.2 (2), 110.6 (4)
$\text{Zn}^{2+}(\text{Pyr})_5$	2.092 (3), 2.226 (2)	88.1 (3), 92.0 (3), 118.4, 120.8 (2), 177.4	2.057 (3), 2.201 (2)	86.2 (2), 90.3 (2), 94.0 (2), 116.6 (2), 126.9, 172.1
$\text{Zn}^{2+}(\text{Pyr})_6$	2.267	89.9 (3), 90.0 (9), 179.9 (3)	2.226	89.6 (6), 90.4 (6), 179.4 (3)

^a The spin states of $\text{Fe}^{2+}(\text{Pyr})_x$, $\text{Co}^{2+}(\text{Pyr})_x$, $\text{Ni}^{2+}(\text{Pyr})_x$, $\text{Cu}^{2+}(\text{Pyr})_x$, and $\text{Zn}^{2+}(\text{Pyr})_x$ complexes are quintet, quartet, triplet, doublet, and singlet, respectively, for all values of x . Average values are given for similar bond distances or angles; degeneracies are listed in parentheses for values that differ sufficiently such that more than one value is needed to describe the bond angle or bond distance. All bond angles (\angle) are given in degrees ($^\circ$) and $M^{2+}-N$ bond lengths in angstroms (\AA).

Table S5. Sequential and Total BDEs of Ground-State $M^{2+}(\text{Pyr})_x$ Complexes at 0 K in kJ/mol

Complex	Spin	Theory								
		B3LYP ^a			BHandHLYP ^b			M06 ^c		
		D_0	$D_{0,\text{BSSE}}^d$	Total ^d	D_0	$D_{0,\text{BSSE}}^d$	Total ^d	D_0	$D_{0,\text{BSSE}}^d$	Total ^d
Fe ²⁺ (Pyr)	5	343.8	343.1	343.1	319.3	317.6	317.6	370.4	369.6	369.6
Fe ²⁺ (Pyr) ₂	5	487.2	484.6	827.7	480.5	478.0	795.6	481.9	478.8	848.4
Fe ²⁺ (Pyr) ₃	5	322.5	319.9	1147.6	319.4	317.1	1112.7	361.2	357.9	1206.3
Fe ²⁺ (Pyr) ₄	5	203.8	199.4	1347.0	202.3	199.3	1312.0	237.0	222.9	1429.2
Fe ²⁺ (Pyr) ₅	5	87.2	83.4	1430.4	100.7	97.1	1409.1	133.1	127.7	1556.9
Fe ²⁺ (Pyr) ₆	5	62.5	58.4	1488.8	78.8	75.4	1484.5	112.1	106.2	1663.1
Co ²⁺ (Pyr)	4	323.8	321.9	321.9	280.7	278.8	278.8	398.1	398.0	398.0
Co ²⁺ (Pyr) ₂	4	454.0	450.5	772.4	457.9	455.5	734.3	497.4	494.6	892.6
Co ²⁺ (Pyr) ₃	4	374.0	370.0	1142.4	370.0	367.4	1101.7	332.5	329.1	1221.7
Co ²⁺ (Pyr) ₄	4	227.2	224.0	1366.4	234.5	231.3	1333.0	237.6	232.8	1454.5
Co ²⁺ (Pyr) ₅	4	127.2	123.2	1489.6	167.4	163.5	1496.5	124.9	118.8	1573.3
Co ²⁺ (Pyr) ₆	4	71.2	66.9	1556.5	94.6	92.1	1588.6	86.9	84.0	1657.3
Ni ²⁺ (Pyr)	3	351.3	349.3	349.3	301.2	299.3	299.3	461.5	452.7	452.7
Ni ²⁺ (Pyr) ₂	3	473.4	470.3	819.6	486.9	484.4	783.7	483.9	480.9	933.6
Ni ²⁺ (Pyr) ₃	3	330.1	327.2	1146.8	311.9	309.1	1092.8	332.1	330.9	1264.5
Ni ²⁺ (Pyr) ₄	3	209.0	205.3	1352.1	193.5	190.3	1283.1	198.5	193.3	1457.8
Ni ²⁺ (Pyr) ₅	3	106.9	102.9	1455.0	149.8	149.2	1432.3	183.7	177.8	1635.6
Ni ²⁺ (Pyr) ₆	3	53.4	48.5	1503.5	70.4	65.7	1498.0	102.0	95.9	1731.5
Cu ²⁺ (Pyr)	2	318.4	316.4	316.4	262.5	260.3	260.3	401.0	398.7	398.7
Cu ²⁺ (Pyr) ₂	2	496.5	493.0	809.4	508.5	506.0	766.3	461.3	457.9	856.6
Cu ²⁺ (Pyr) ₃	2	326.6	312.6	1122.0	311.3	308.0	1074.3	347.8	343.4	1200.0
Cu ²⁺ (Pyr) ₄	2	186.4	182.7	1304.7	196.2	192.3	1266.6	215.2	210.2	1410.2
Cu ²⁺ (Pyr) ₅	2	89.2	89.2	1393.9	102.7	98.7	1365.3	132.5	127.0	1537.2
Cu ²⁺ (Pyr) ₆	2	46.7	43.7	1437.6	48.2	44.8	1410.1	79.7	75.9	1613.1
Zn ²⁺ (Pyr)	1	183.9	182.3	182.3	174.1	172.4	172.4	254.2	252.5	252.5
Zn ²⁺ (Pyr) ₂	1	528.6	525.1	707.4	522.5	519.4	691.8	537.1	532.8	785.3
Zn ²⁺ (Pyr) ₃	1	289.3	286.8	994.2	297.3	294.7	986.5	310.2	305.2	1090.5
Zn ²⁺ (Pyr) ₄	1	202.2	198.6	1192.8	210.9	207.3	1193.8	229.4	225.1	1540.7
Zn ²⁺ (Pyr) ₅	1	57.5	53.0	1245.8	68.3	64.0	1257.8	99.0	93.2	1633.9
Zn ²⁺ (Pyr) ₆	1	37.5	32.3	1278.1	48.8	43.6	1301.4	87.2	80.9	1714.8

^aCalculated at the B3LYP/6-31G**/B3LYP/6-31G* level of theory including ZPE corrections with frequencies scaled by 0.9804. ^bCalculated at the BHandHLYP/6-31G**/BHandHLYP/6-31G* level of theory including ZPE corrections with frequencies scaled by 0.9472. ^cCalculated at the M06/6-31G**/M06/6-31G* level of theory including ZPE corrections with frequencies scaled by 0.9940. ^dAlso includes BSSE corrections.

Table S6. Natural Charges and 4s and 3d Populations of $M^{2+}(\text{Pyr})_x$ Complexes

Complex	x	BLYP/6-31G*		BLYP/6-31G*		B3LYP/6-311+G(2d,2p)	
		$q_{M^{2+}}$	q_N	4s	3d	4s	3d
Pyr			-0.406				
Fe^{2+}		2.000		0.00	6.00	0.00	6.00
$\text{Fe}^{2+}(\text{Pyr})_x$	1	1.482	-0.662	0.22	6.10	0.16	6.21
	2	1.278	-0.668	0.36	6.03	0.31	6.12
	3	1.181	-0.651	0.29	6.12	0.27	6.22
	4	1.177	-0.624	0.28	6.11	0.25	6.24
	5	1.193	-0.588	0.28	6.09	0.23	6.24
	6	1.192	-0.570	0.26	6.08	0.21	6.25
Co^{2+}		2.000		0.00	7.00	0.00	7.00
$\text{Co}^{2+}(\text{Pyr})_x$	1	1.370	-0.640	0.21	7.23	0.13	7.51
	2	1.215	-0.635	0.36	7.03	0.27	7.21
	3	1.069	-0.627	0.30	7.16	0.26	7.31
	4	1.053	-0.600	0.29	7.14	0.26	7.31
	5	1.057	-0.562	0.28	7.13	0.24	7.31
	6	1.070	-0.547	0.26	7.10	0.23	7.32
Ni^{2+}		2.000		0.00	8.00	0.00	8.00
$\text{Ni}^{2+}(\text{Pyr})_x$	1	1.397	-0.653	0.19	8.21	0.14	8.34
	2	0.776	-0.581	0.70	8.22	0.28	8.19
	3	1.008	-0.616	0.37	8.15	0.31	8.33
	4	0.992	-0.586	0.31	8.13	0.27	8.31
	5	1.011	-0.550	0.29	8.14	0.24	8.34
	6	1.036	-0.539	0.26	8.14	0.23	8.35
Cu^{2+}		2.000		0.00	9.00	0.00	9.00
$\text{Cu}^{2+}(\text{Pyr})_x$	1	1.224	-0.633	0.20	9.40	0.19	9.84
	2	0.853	-0.594	0.61	9.20	0.30	9.43
	3	0.917	-0.587	0.40	9.17	0.34	9.35
	4	0.854	-0.560	0.36	9.15	0.30	9.33
	5	0.910	-0.533	0.32	9.15	0.27	9.33
	6	0.901	-0.518	0.34	9.17	0.28	9.35
Zn^{2+}		2.000		0.00	10.0	0.00	10.00
$\text{Zn}^{2+}(\text{Pyr})_x$	1	1.362	-0.640	0.44	9.94	0.38	9.98
	2	1.090	-0.630	0.57	9.87	0.49	9.94
	3	1.004	-0.606	0.45	9.90	0.40	9.96
	4	0.966	-0.581	0.39	9.90	0.34	9.97
	5	1.004	-0.541	0.36	9.92	0.33	9.98
	6	1.038	-0.530	0.34	9.95	0.32	9.99

Figure Captions

Figure S1. B3LYP/6-31G* optimized geometries of $\text{Co}^{2+}(\text{Pyr})_x$ complexes, where $x = 1-6$.

Figure S2. B3LYP/6-31G* optimized geometries of $\text{Ni}^{2+}(\text{Pyr})_x$ complexes, where $x = 1-6$.

Figure S3. B3LYP/6-31G* optimized geometries of $\text{Zn}^{2+}(\text{Pyr})_x$ complexes, where $x = 1-6$.

Figure S4. B3LYP/6-31G* optimized geometries of $\text{Ca}^{2+}(\text{Pyr})_x$ complexes, where $x = 1-6$.

Figure S5. Theoretical $(\text{Pyr})_{x-1}\text{M}^{2+}-\text{Pyr}$ BDEs at 0 K (in kJ/mol) where $\text{M}^{2+} = \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+},$ and Zn^{2+} as a function of the number of ligands (x) and the metal cation determined at the B3LYP level of theory using 6-311+G(2d,2p) and 6-31G* basis sets. All values include ZPE and BSSE corrections and taken from Tables 2 and S5 of the Supporting Information.

Figure S6. Trends in the total enthalpies and free energies of binding of the $\text{M}^{2+}(\text{N-L})_x$ complexes at 298 K (in kJ/mol) where $\text{M}^{2+} = \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+},$ and Zn^{2+} , parts a–d, respectively, and $\text{N-L} = \text{Pyr}, \text{Bpy},$ and Phen as a function of the number of N -donor interactions. Energies are determined from calculations at B3LYP/6-311+G(2d,2p) level of theory including ZPE and BSSE corrections. Values for Pyr are taken from Table 3. Values for Bpy and Phen complexes are taken from references 21–22. Values for M^+ complexes are taken from references 13–16. All values are taken at 298 K.

Figure S1.

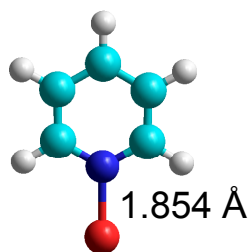
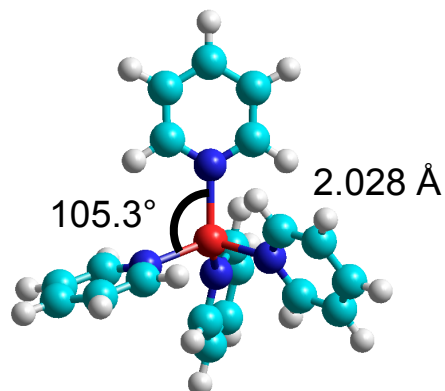
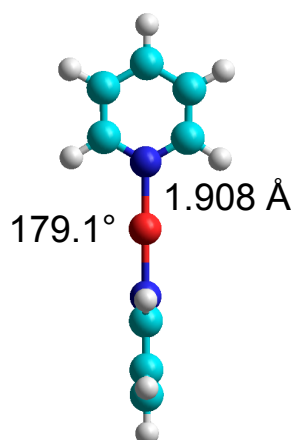
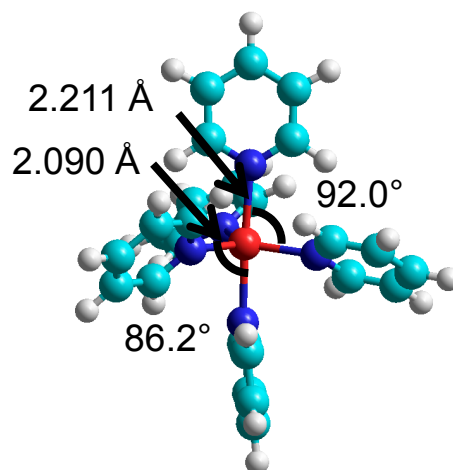
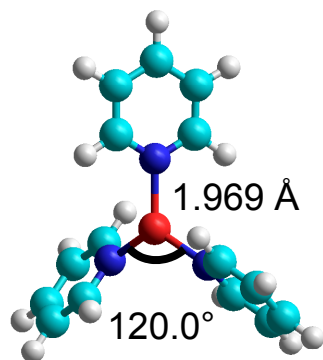
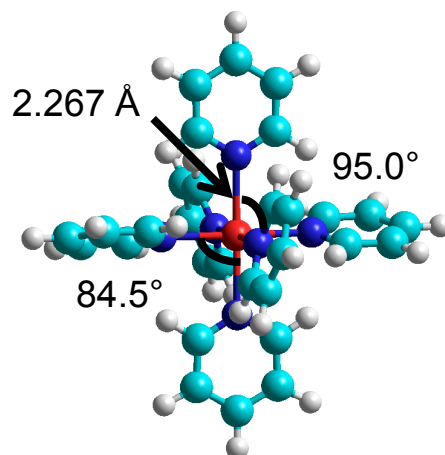
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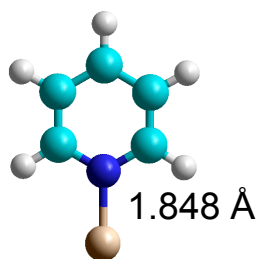
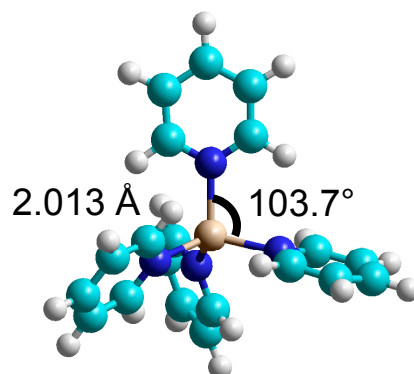
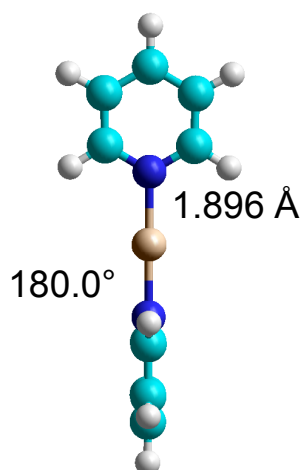
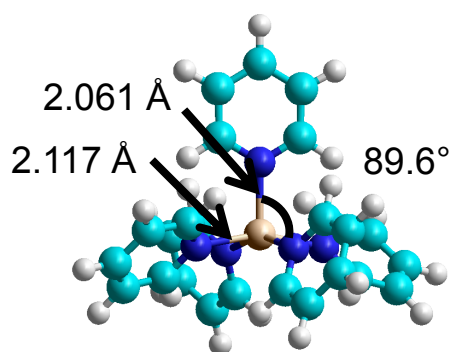
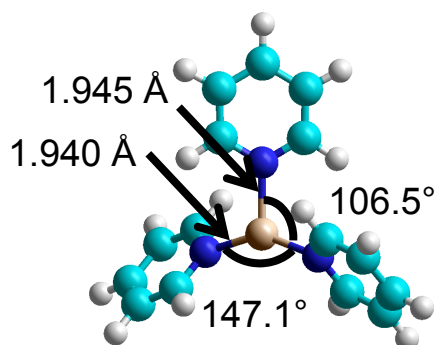
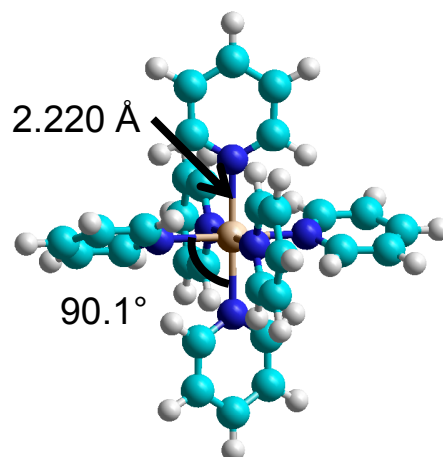
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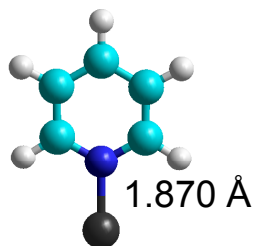
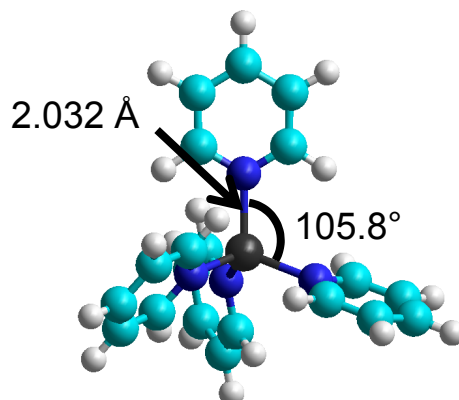
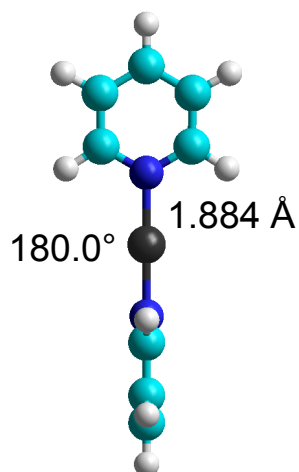
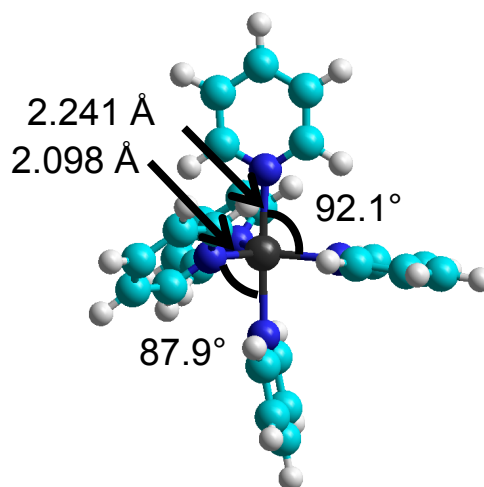
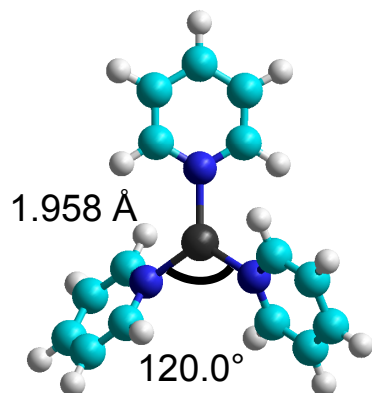
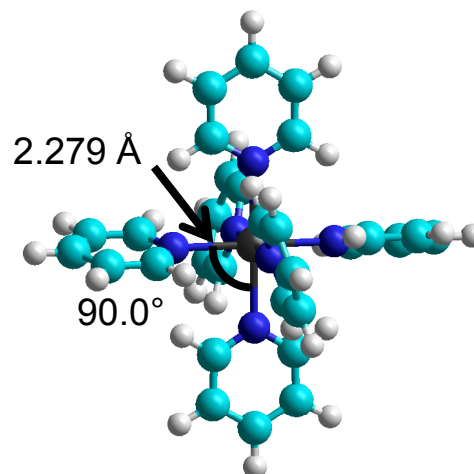
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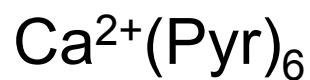
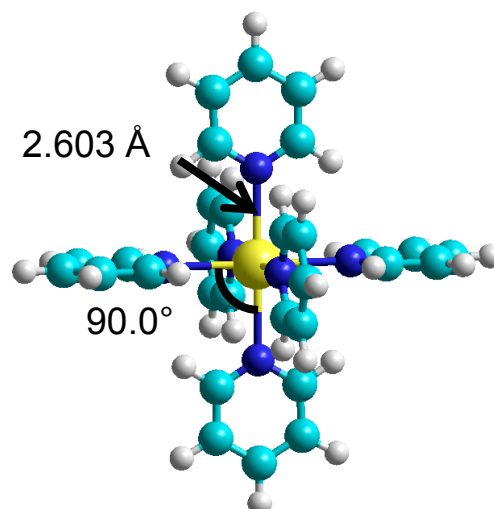
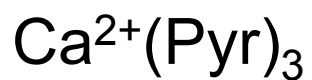
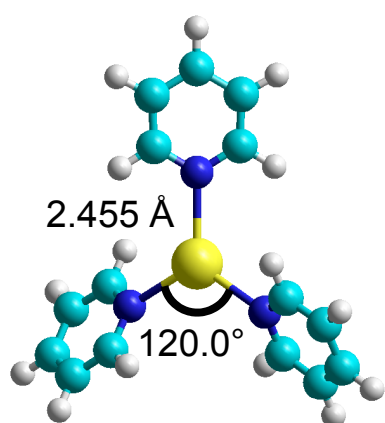
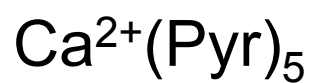
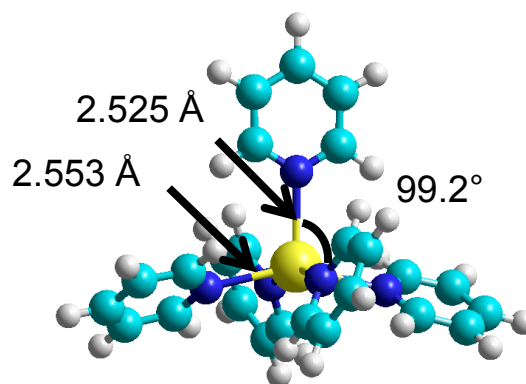
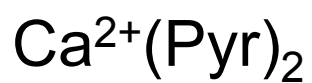
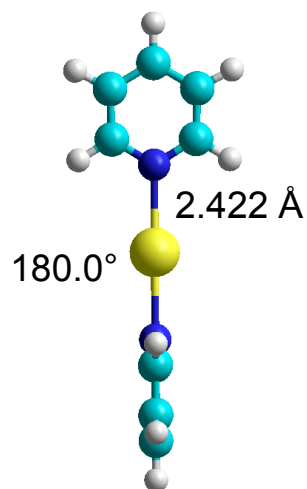
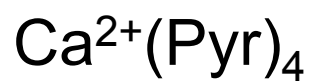
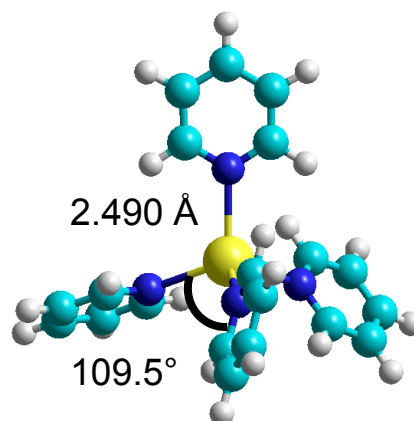
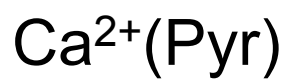
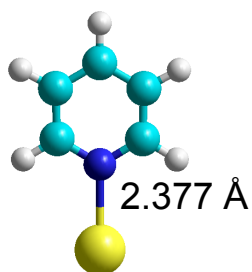


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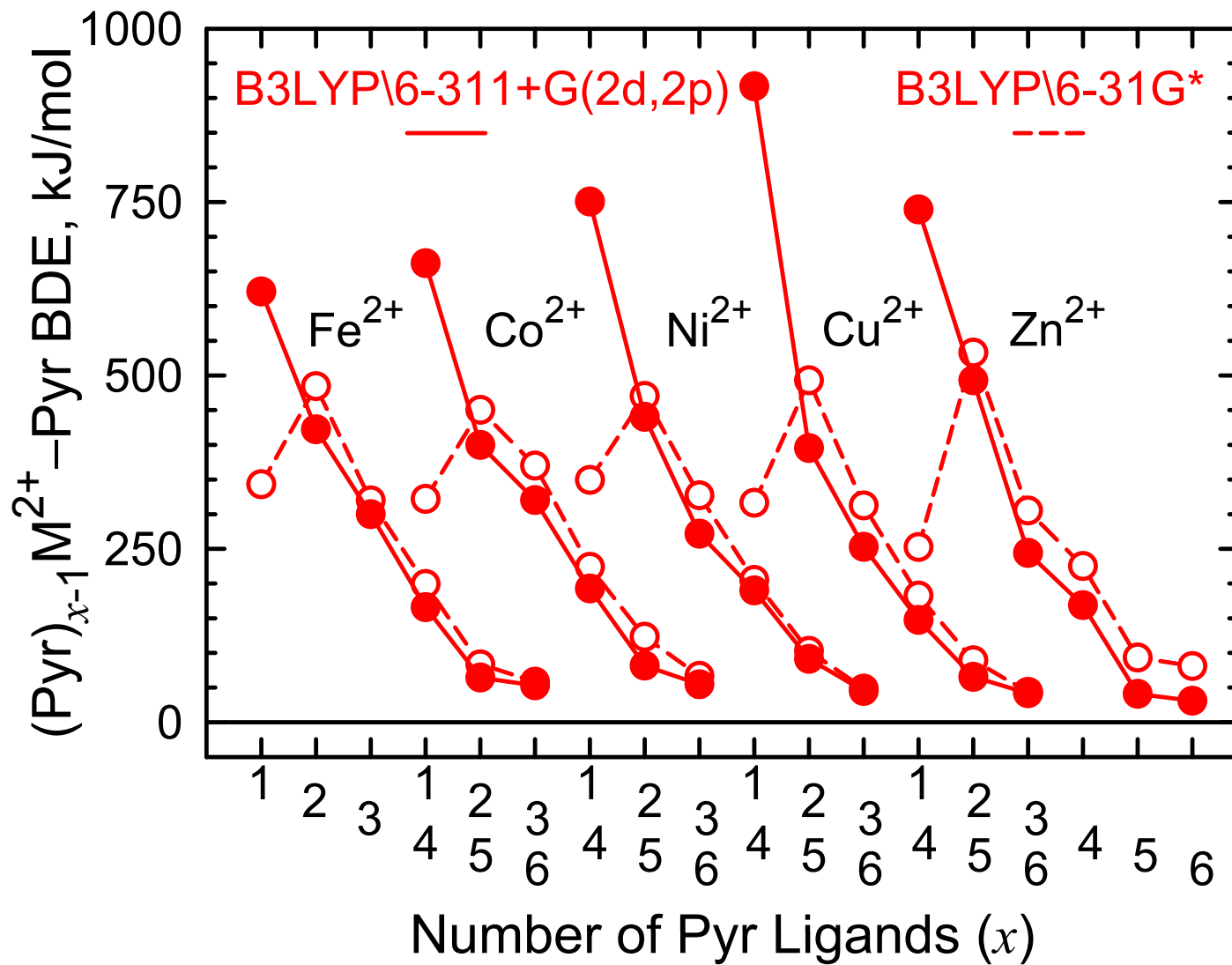


Figure S6.

