Supporting Information for

Energy-Resolved Collision-Induced Dissociation Studies of 1,10-Phenanthroline Complexes of the Late First-Row Divalent Transition Metal Cations: Determination of the Third Sequential Binding Energies

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Ref. 37 [Complete Reference]: **Gaussian 03**, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford, CT, **2004**.

Ref. 38 [Complete Reference]: **Gaussian 09**, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A, Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford, CT, **2009**.

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

Species	E_{vib} (eV)[a]	Vibrational frequencies (cm^{-1}) [b]
Phen	0.22 (0.03)	98, 108, 233, 235, 238, 402, 405, 434, 457, 497, 509, 550, 554, 603, 618, 702, 725, 739, 763, 801, 833, 844, 852, 879, 943, 946, 955, 971, 975, 1032, 1044, 1076, 1098, 1144, 1154, 1206, 1215, 1229, 1279, 1309, 1332, 1364, 1400, 1430, 1436, 1465, 1515, 1520, 1572, 1616, 1629, 1639, 3099(2), 3115, 3123(2), 3133, 3150(2)
Fe^{2+}(Phen)	0.26 (0.03)	71, 137, 142, 229, 239, 244, 280, 293, 399, 424, 437, 467, 500, 507, 522, 558, 598, 658, 701, 724, 729, 762, 784, 819, 858, 873, 904, 958, 962, 991, 1015, 1018, 1023, 1078, 1104, 1105, 1165, 1174, 1214, 1225, 1228, 1261, 1324, 1335, 1342, 1411, 1417, 1440, 1454, 1503, 1529, 1580, 1594, 1600, 1631, 3157, 3158, 3159, 3164(2), 3169, 3183(2)
$Fe^{2+}(Phen)_2$	0.56 (0.06)	18, 26, 26, 75(2), 124, 138, 140, 141(2), 232(2), 237(2), 248, 249, 267, 282, 291, 407(2), 425, 435(3), 475(2), 508(2), 510(2), 538, 539, 556, 558, 606, 607, 651(2), 719(2), 724(2), 730, 731, 781(2), 792, 794, 821, 822, 857(2), 869, 871, 904(2), 955(2), 958(2), 984(2), 1005(2), 1009(2), 1033(2), 1070(2), 1099(2), 1111, 1112, 1160(2), 1169(2), 1218, 1220, 1224, 1225, 1232(2), 1267(2), 1331, 1333, 1335(2) 1349, 1351, 1423, 1424, 1426 (2), 1440(2), 1463(2), 1508(2), 1536, 1537, 1594(2), 1603(2), 1613(2), 1638, 1639, 3151(2), 3152(4), 1349, 1351, 1423, 1424, 1426(2), 1440(2), 1463(2), 1508(2), 1536, 1537, 1594(2), 1603(2), 1613(2), 1638, 1639, 3151(2), 3152(4), 3155, 3156(3), 3164(2), 3180 (4)
$Fe^{2+}(Phen)_3$	0.82 (0.09)	27, 28, 44(2), 45(2), 85, 86, 93, 142, 164, 165(2), 166, 175, 176, 200(2), 230(2), 234, 280(2), 288, 289, 290, 306, 348, 361, 362, 427(3), 430, 431, 439, 458, 465(2), 490(2), 493, 509, 510(2), 530, 532(2), 541(2), 544, 557(3), 614(2), 619, 643(2), 644, 716, 718(2), 723(3), 731, 732, 737, 777(2), 778(2), 779, 780, 813, 814, 816, 852(2), 853, 872(2), 875, 908(3), 942, 943, 945, 946, 947, 950, 978(2), 979, 993(3), 997, 998(2), 1034, 1037, 1038, 1065, 1066(2), 1096(2), 1098, 1110(2), 1116, 1157(2), 1158, 1165(3), 1219, 1220(2), 1221, 1223, 1226, 1233(2), 1234, 1263, 1265, 1267, 1323(2), 1324, 1336, 1337(2), 1351, 1353, 1354, 1425, 1427(2), 1435, 1436(2), 1439(2), 1440, 1465, 1467(2), 1509, 1510(2), 1533, 1534(2), 1593, 1597(2), 1602(3), 1615(2), 1616, 1643(2), 1644, 3147, 3148(2), 3153(4), 3154(2), 3161(3), 3168, 3169(6), 3180(2), 3181, 3182(3)
$Fe^{2+}(Phen)_3$	*0.87 (0.09)*	*19, 21, 27, 30, 31, 34, 77(2), 79, 107, 109, 110, 134, 137, 142, 150, 152, 161, 206, 218, 226, 232, 233, 234, 249, 254, 256, 273, 277, 280, 407, 410, 411, 417, 419, 420, 437, 440, 449, 472, 473, 476, 507, 508(2), 509, 510(2), 542, 543, 545, 554, 555(2), 606(2), 608, 634, 639, 640, 719, 722(2), 723(3) 724, 725, 728, 779, 780, 781, 793(2), 802, 817, 818, 822, 855, 856, 857, 862, 864, 868, 894, 895, 897, 950, 951, 954, 956, 957, 959, 979(2), 980, 995, 996, 998, 1000, 1001, 1002, 1033, 1035, 1037, 1064(3), 1093, 1094, 1096, 1108, 1110, 1112, 1155, 1156(2), 1165, 1166(2), 1217, 1218(2), 1221, 1223, 1224, 1232, 1233, 1234, 1268(2), 1270, 1324, 1325, 1326, 1337(2), 1338, 1351, 1352, 1353, 1419(2), 1421, 1428, 1429(2), 1437, 1438(2), 1462, 1465, 1467, 1510, 1511(2), 1532, 1535, 1539, 1591, 1593(2), 1605, 1607, 1608, 1617(2), 1619, 1639, 1640, 1641, 3146(3), 3148, 3149(4), 3150, 3152(2), 3153(3), 3154, 3160(3), 3174(3), 3175(3)*
Co^{2+}(Phen)	0.26 (0.03)	79, 143, 147, 231, 247, 266, 267, 295, 402, 427, 440, 472, 503, 506, 522, 559, 600, 657, 702, 723, 737, 765, 784, 819, 857, 876, 908, 961, 964, 991, 1015, 1018, 1025, 1076, 1101, 1107, 1164, 1173, 1219, 1226, 1228, 1255, 1328, 1335, 1349, 1416, 1423, 1441, 1454, 1500, 1529, 1578, 1588, 1597, 1629, 3157, 3158, 3159, 3164(2), 3169, 3182(2)

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

Species	E_{vib} (eV)[a]	Vibrational frequencies (cm^{-1}) [b]
$Co^{2+}(Phen)_2$	0.56 (0.06)	18, 28, 28, 77(2), 126, 139, 146(3), 231(2), 248, 251(2), 254, 287(2), 309, 404, 411, 427, 437(2), 438, 477(2), 508(2), 509(2), 539, 540, 557, 559, 604, 608, 651(2), 717(2), 724(2), 733, 735, 780(2), 793, 795, 821, 822, 856(2), 871, 873, 907(2), 953(2), 955(2), 984(2), 1004(2), 1008(2), 1033(2), 1069, 1070, 1099(2), 1113, 1114, 1161(2), 1169(2), 1219, 1220, 1225, 1226, 1233(2), 1267(2), 1335(2), 1337(2), 1350, 1351, 1426(2),1427, 1428, 1440(2), 1464(2), 1508(2), 1537, 1538, 1597(2), 1604(2), 1614(2), 1639(2), 3151(2), 3154(4), 3157(4), 3164(2), 3180(4)
$Co^{2+}(Phen)_3$	0.87 (0.09)	21, 23, 31(2), 35, 35, 79, 80, 81, 108, 110, 116, 139, 142, 142, 158(2), 159, 188, 226, 228, 233, 234, 235, 253, 254, 264, 279, 283, 285, 409(2), 417, 418(2), 421, 438, 442, 443, 474, 475, 477, 508(2), 509(2), 510(2), 542(2), 544, 555(3) 605(2), 609, 637, 638, 639, 721, 722(2), 723(3), 724(2), 727, 779, 780(2), 794(2), 795, 818(2), 819, 855(2), 856, 864(2), 865, 896(2), 899, 952(2), 954, 955, 956, 958, 979(2), 980, 997(3), 1001(3), 1033, 1036(2), 1063, 1064(2), 1093(2), 1095, 1109(2), 1112, 1156(3), 1165(3), 1218(2), 1219, 1222, 1223, 1226, 1233(2), 1234, 1268, 1269, 1271, 1326(2), 1327, 1339(3), 1352, 1353, 1355, 1422(2), 1423, 1429, 1430(2), 1438(2), 1439, 1465(2), 1466, 1510, 1511(2), 1535(3), 1593, 1595(2), 1607(2), 1608, 1618, 1619(2), 1640(3), 3146(3), 3149(2), 3150(4), 3153, 3154(5), 3159(2), 3160, 3174(3), 3175(3)
$Ni^{2+}(Phen)$	0.26 (0.03)	81, 144, 152, 231, 247, 276, 281, 298, 402, 425, 442, 475, 502, 505(2), 561, 587, 660, 693, 723, 733, 737, 781, 814, 853, 880, 916, 957, 960, 990, 1014, 1017, 1023, 1073, 1099, 1107, 1166, 1173, 1220, 1227, 1229, 1255, 1323, 1338, 1353, 1417, 1426, 1440, 1456, 1499, 1524, 1574, 1584, 1593, 1630, 3157, 3159(2), 3165(2), 3169, 3182(2)
$Ni^{2+}(Phen)_2$	0.55 (0.06)	14, 33, 33, 88(2), 135, 146, 147, 166(2), 232(2), 251, 253, 263(2), 284, 294, 326, 408, 411, 429, 439, 445(2), 486(2), 507(2), 516(2), 539, 540, 558, 560, 604, 606, 655(2), 718(2), 723(2), 739(2), 781(2), 795, 798, 823, 824, 856(2), 873(2), 911(2), 953(2), 956(2), 983(2), 1004(2), 1008(2), 1034(2), 1067, 1068, 1097(2), 1114, 1116, 1161(2),1168(2), 1221, 1222, 1227, 1229, 1233(2),1264(2), 1338(2), 1341(2), 1351, 1353, 1426(2), 1435(2), 1441(2), 1466(2), 1506(2), 1537, 1538, 1597(2), 1603(2), 1614(2), 1639(2), 3152(2), 3154(4), 3157(4), 3164(2), 3180(4)
$Ni^{2+}(Phen)_3$	0.86 (0.09)	23, 24, 35, 36, 36, 38, 81, 82, 85, 117, 118, 122, 144, 147, 148, 160, 168, 169, 232(2), 234, 236, 239, 241, 259(2), 265, 283, 291, 292, 411, 412, 417, 420(2), 422, 441, 444, 445, 476, 477, 480, 509(3), 510, 511(2), 542(2), 544, 556(3), 606(2), 608, 638, 639, 640, 721(3), 723(2), 724(3), 730, 780(2), 781, 794(2), 795, 818(2), 819, 855(2), 856, 865(2), 867, 898(2), 901, 952(2), 955(2), 956, 959, 979, 980(2), 997(3), 1001(3), 1033, 1036(2), 1064(3), 1093, 1094, 1095, 1110, 1111, 1114, 1156, 1157(2), 1165(2), 1166, 1218, 1219, 1220, 1223, 1224, 1227, 1233, 1234, 1235, 1267, 1268, 1270, 1327, 1328(2), 1339(2), 1340, 1353, 1354, 1355, 1424(2), 1425, 1429, 1430(2), 1438(2), 1439, 1466, 1467(2), 1511(3), 1536(3), 1594, 1596, 1597, 1608(3), 1619(2), 1620, 1640(2), 1641, 3146(3), 3150(5), 3151, 3157, 3158(3), 3159(2), 3160(3), 3175(6)
$Cu^{2+}(Phen)$	0.27 (0.03)	72, 142, 146, 215, 227, 267, 271, 273, 300, 425, 432, 444, 478, 497, 504, 510, 562, 656, 681, 721, 727, 745, 759, 799, 834, 880, 915, 948, 950, 973, 1009, 1014, 1020, 1071, 1096, 1116, 1164, 1172, 1223, 1224, 1231, 1257, 1332, 1343, 1351, 1416, 1429, 1437, 1457, 1497, 1518, 1574, 1592, 1595, 1632, 3156, 3158(2), 3161(2), 3168, 3180(2)

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

Species	E_{vib} (eV)[a]	Vibrational frequencies (cm^{-1}) [b]
$Cu^{2+}(Phen)_2$	0.55 (0.06)	27, 39, 39, 90(2), 140, 141, 145, 159, 168, 196, 233, 238, 251, 261, 273, 281, 299, 318, 409, 415, 430, 435, 440, 445, 480, 488, 507, 508, 511, 513, 539, 543, 560(2), 603, 607, 648, 653, 719, 720, 722, 723, 738, 741, 781, 783, 792, 794, 822, 825, 856, 857, 874, 875, 907, 913, 954, 957, 961, 964, 984(2), 1004, 1005, 1008(2), 1033, 1034, 1067, 1069, 1096, 1098, 1115, 1118, 1160, 1161, 1168(2), 1222, 1223, 1226, 1229, 1233, 1235, 1263, 1266, 1339(2), 1341, 1342, 1350, 1354, 1426(2), 1435(2), 1440, 1442, 1465, 1467, 1507(2), 1537, 1538, 1597(2), 1603, 1604, 1613, 1614, 1639(2), 3153(2), 3156(4), 3160(2), 3162(2), 3165(2), 3180(4)
$Cu^{2+}(Phen)_3$	0.87 (0.09)	17, 21, 23, 31, 33, 35, 75, 76, 79, 82, 96, 113, 125, 126, 129, 149, 155, 159, 175, 231, 232, 235, 238, 238, 255, 259, 266, 271, 278, 296, 407, 409, 412, 416, 419, 424, 439, 442, 444, 471(2), 482, 507, 508(3), 510, 511, 541, 546, 548, 554(2), 557, 603, 606, 609, 635, 638, 642, 717, 718, 721, 723, 725, 726(2), 728, 732, 779, 780(2), 791, 805(2), 818, 822, 823, 854, 857(2), 861, 862, 869, 894, 897, 903, 952, 955, 957, 958, 959, 962, 979(2), 980, 997, 998(2), 1001, 1002(2), 1032, 1035, 1036, 1062, 1063, 1066, 1093, 1094, 1096, 1109, 1111, 1114, 1155, 1156, 1158, 1165(2), 1166, 1217(2), 1220, 1221, 1223, 1227, 1233(2), 1234, 1266, 1271, 1273, 1324, 1325, 1332, 1337(2), 1341, 1354, 1356, 1358, 1414(2), 1429(2), 1431, 1432, 1438(2), 1439, 1464(2), 1468, 1510, 1511(2), 1535(2), 1538, 1590, 1592, 1598, 1608, 1609(2), 1619, 1620, 1621, 1639(2), 1640, 3132(2), 3145(2), 3148, 3149, 3150(3), 3152(2), 3159(2), 3161, 3162, 3163, 3166(2), 3172(2), 3177(2), 3178(2)
$Zn^{2+}(Phen)$	0.26 (0.03)	80, 138, 154, 232, 244, 245, 288, 308, 398, 430, 439, 468, 496, 507, 515, 562, 595, 658, 699, 724, 731, 748, 785, 817, 860, 873, 912, 963, 967, 992, 1017, 1019, 1022, 1081, 1105, 1106, 1167, 1174, 1214, 1225, 1230, 1265, 1333, 1335, 1346, 1411, 1419, 1442, 1453, 1504, 1527, 1583, 1596, 1603, 1630, 3157, 3159, 3160, 3169, 3175 (2), 3185(2)
$Zn^{2+}(Phen)_2$	0.55 (0.06)	24, 27(2), 81(2), 129, 141, 147, 151, 152, 222(2), 233(2), 250, 256, 279, 294, 301, 406, 412, 428, 434, 441(2), 478(2), 509(2), 511(2), 543, 544, 559, 560, 607, 610, 652(2), 724(2), 725(2), 733, 735, 782(2), 804, 806, 829, 831, 859(2), 872, 873, 909(2), 958(2), 961(2), 985(2), 1006(2), 1010(2), 1035(2), 1072, 1073, 1101(2), 1115, 1117, 1162(2), 1169(2), 1220(2), 1227, 1229, 1235(2), 1270(2), 1335(2), 1340(2), 1353, 1355, 1426(2), 1430(2), 1442(2), 1464, 1465, 1509(2), 1538, 1540, 1600(2), 1606(2), 1616(2), 1639(2), 3151(2), 3155(4), 3159(4), 3164(2), 3180(4)
$Zn^{2+}(Phen)_3$	0.87 (0.08)	19, 21, 28, 29, 31, 33, 79(2), 80, 88, 89, 116, 134, 138, 139, 149, 155, 156, 160, 182, 186, 233(2), 236, 251, 252, 254, 280, 281, 282, 407, 408, 411, 417(2), 421, 438, 442, 443, 471, 472, 476, 508(3), 509, 510(2), 546, 547, 549, 555, 556(2), 607(2), 609, 637(2), 640, 721, 722, 723(2), 724, 728(4), 780(2), 781, 807(2), 808, 825, 826, 827, 857(2), 858, 863(2), 865, 894, 895, 898, 957(2), 959, 960, 961, 963, 980(3), 998(2), 999, 1002(3), 1034, 1036(2), 1065(3), 1093, 1094, 1095, 1110(2), 1113, 1156(3), 1165(3), 1217, 1218(2), 1223, 1224, 1227, 1234(2), 1235, 1268, 1269, 1272, 1327(3), 1340, 1341(2), 1354, 1355, 1357, 1419, 1420(2), 1431, 1432(2), 1438, 1439(2), 1466(2), 1467, 1511(3), 1536, 1537(2), 1593, 1595, 1596, 1609(2), 1610, 1620, 1621(2), 1639, 1640(2), 3146(3), 3149(6), 3153(6), 3159(2), 3160, 3174(2), 3175(4)

[a]Uncertainties listed in parentheses are determined as described in the text. [b]Vibrational frequencies scaled by 0.9804 obtained from vibrational analyses of the B3LYP/6-31G* geometry optimized structures. Degeneracies are indicated in parentheses. [c]Vibrational frequencies and average vibrational energies for singlet state $Fe^{2+}(Phen)_3$ are shown in standard font, while those for quintet state are shown in italics.

Table S2. Rotational Constants (in cm^{-1}) of $M^{2+}(Phen)_x$, where x = 1–3 and the corresponding PSL Transition States for Dissociation of $M^{2+}(Phen)_3$.

Complex	Energized Molecule		Transition State		
	1-D[a]	2-D[b]	1-D[c]	2-D[c]	2-D[d]
$Fe^{2+}(Phen)$	0.025	0.014	-	-	-
$Fe^{2+}(Phen)_2$	0.010	0.003	-	-	-
$Fe^{2+}(Phen)_3$	0.003	0.003	0.010, 0.054	0.003, 0.017	0.0004
$Co^{2+}(Phen)$	0.024	0.014	-	-	-
$Co^{2+}(Phen)_2$	0.010	0.004	-	-	-
$Co^{2+}(Phen)_3$	0.003	0.003	0.010, 0.054	0.004, 0.017	0.0004
$Ni^{2+}(Phen)$	0.025	0.015	-	-	-
$Ni^{2+}(Phen)_2$	0.010	0.004	-	-	-
$Ni^{2+}(Phen)_3$	0.003	0.003	0.010, 0.054	0.004, 0.017	0.0004
$Cu^{2+}(Phen)$	0.024	0.015	-	-	-
$Cu^{2+}(Phen)_2$	0.010	0.004	-	-	-
$Cu^{2+}(Phen)_3$	0.003	0.003	0.010, 0.054	0.004, 0.017	0.0003
$Zn^{2+}(Phen)$	0.024	0.014	-	-	-
$Zn^{2+}(Phen)_2$	0.010	0.004	-	-	-
$Zn^{2+}(Phen)_3$	0.003	0.003	0.010, 0.054	0.004, 0.017	0.0004

[a]Active external. [b]Inactive external. [c]Rotational constants of the PSL TS treated as free internal rotors. [d]Two-dimensional rotational constant of the PSL TS at threshold, treated variationally and statistically.

Table S3. Relative Energies between the various Spin States of a Given $M^{2+}(Phen)_x$ Complex in their Ground-State Conformations where $M^{2+} = Fe^{2+}$, Co^{2+}, and Ni^{2+} at 0 K in kJ/mol.

Complex	Multiplicity	B3LYP[a]	BHandHLYP[b]	M06[c]
Fe^{2+}	5	0.0	0.0	0.0
	3	241.3	263.6	260.2
	1	378.4	404.4	408.5
$Fe^{2+}(Phen)$	5	0.0	0.0	0.0
	3	71.1	104.3	95.2
	1	196.7	235.3	203.1
$Fe^{2+}(Phen)_2$	5	0.0	0.0	0.0
	3	49.9	105.8	92.9
	1	216.6	252.2	241.2
$Fe^{2+}(Phen)_3$	5	2.5	0.0	0.0
	3	49.9	106.2	92.9
	1	0.0	97.1	38.4
Co^{2+}	4	0.0	0.0	0.0
	2	252.6	273.5	304.6
$Co^{2+}(Phen)$	4	0.0	0.0	0.0
	2	45.6	110.2	28.4
$Co^{2+}(Phen)_2$	4	0.0	0.0	0.0
	2	50.5	110.2	24.0
$Co^{2+}(Phen)_3$	4	0.0	0.0	0.0
	2	25.9	94.6	10.9
Ni^{2+}	3	0.0	0.0	0.0
	1	297.0	317.3	234.6
$Ni^{2+}(Phen)$	3	0.0	0.0	0.0
	1	44.4	128.0	26.1
$Ni^{2+}(Phen)_2$	3	0.0	0.0	0.0
	1	24.6	107.4	65.7
$Ni^{2+}(Phen)_3$	3	0.0	0.0	0.0
	1	124.3	201.2	110.2

[a]Calculated at the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G* level of theory including ZPE corrections with frequencies scaled by 0.9804. [b]Calculated at the BHandHLYP/6-311+G(2d,2p)//BHandHLYP/6-31G* level of theory including ZPE corrections with frequencies scaled by 0.9472. [c]Calculated 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 Ground-State Structures of the Neutral Phen Ligand and $M^{2+}(Phen)_x$ Complexes[a]

	BHandHLYP					M06				
Complex	M^{2+}–N	∠NCCN	∠$NM^{2+}NC$	∠$NM^{2+}N^b$	∠$NM^{2+}N^c$	M^{2+}–N	∠NCCN	∠$NM^{2+}NC$	∠$NM^{2+}N^b$	∠$NM^{2+}N^c$
Phen		0.0					0.0			
$Fe^{2+}(Phen)$	1.987	0.0		88.8		1.971	0.0		88.1	
$Fe^{2+}(Phen)_2$	2.076	0.0	81.2	82.2	124.6	2.048	0.0	81.2	82.8	124.2 (4)
$Fe^{2+}(Phen)_3$	2.042	1.2	60.1	81.2	89.3 (3)	1.982	0.6 (2), 1.0	58.2	82.9	89.4 (3)
					94.9 (6)					93.9 (6)
					174.5 (3)					175.5 (3)
$Fe^{2+}(Phen)_3$	**2.213**	**1.2, 1.6 (2)**	**57.3**	**75.9**	**92.6 (2)**	**2.164**	**0.4, 1.2 (2)**	**57.2**	**77.7**	**92.8 (4)**
					95.3 (5)					**95.7 (5)**
					97.0 (2)					**169.7 (3)**
					167.7 (2)					
					169.6					
$Co^{2+}(Phen)$	1.956	0.0		88.3		1.926	0.0		89.6	
$Co^{2+}(Phen)_2$	2.044	1.3	81.2	83.4	104.7 (2)	2.007	1.3	81.2	84.3	109.1 (2)
					149.5 (2)					140.7 (2)
$Co^{2+}(Phen)_3$	2.174	1.3 (2), 1.4	60.9	76.9	89.9 (3)	2.132	0.7, 1.2 (2)	60.8	78.7	90.8 (2)
					96.9 (6)					94.9 (7)
					171.4 (3)					171.1 (3)
$Ni^{2+}(Phen)$	1.908	0.0	90.9			1.906	0.0		90.7	
$Ni^{2+}(Phen)_2$	2.018	0.0	82.0	82.7	124.3	1.985	0.0	82.2	83.5	123.8 (4)
$Ni^{2+}(Phen)_3$	2.130	1.5	59.8	78.5	91.5 (3)	2.089	1.1 (3)	59.6	80.2	90.7 (3)
					95.3 (6)					94.7 (6)
					171.2 (3)					172.9 (3)

Table S4. (continued) Geometrical Parameters of the Ground-State Structures of the Neutral Phen Ligand and $M^{2+}(Phen)_x$ Complexes[a]

	BHandHLYP					M06				
Complex	M^{2+}–N	∠NCCN	∠NM^{2+}NC	∠$NM^{2+}N^b$	∠$NM^{2+}N^c$	M^{2+}–N	∠NCCN	∠NM^{2+}NC	∠$NM^{2+}N^b$	∠$NM^{2+}N^c$
Cu^{2+}(Phen)	1.886	0.0		91.0		1.869	0.0		89.0	
$Cu^{2+}(Phen)_2$	1.994	1.1 (2)	49.3	83.8	104.2 (2)	1.970	1.0	49.2	84.8	103.3 (2)
					149.7 (2)					149.3 (2)
$Cu^{2+}(Phen)_3$	2.073 (4)	0.6, 2.1 (2)	57.1	76.0 (2)	91.8 (3)	2.028 (4)	0.1, 1.9 (2)	57.3	78.9	91.1 (4)
	2.339 (2)			80.3	94.7 (4)	2.336 (2)				94.0 (3)
					98.0 (2)					99.5 (2)
					170.1 (3)					171.2 (3)
Zn^{2+}(Phen)	1.912	0.0		93.5		1.905	0.0		94.3	
$Zn^{2+}(Phen)_2$	2.021	0.0	81.2	84.2	123.4	2.002	0.0	80.9	85.2	122.8
$Zn^{2+}(Phen)_3$	2.181	1.7	56.6	76.8	94.8 (9)	2.155	0.9, 1.2 (2)	56.7	78.0	94.3 (9)
					168.3 (3)					169.1 (3)

[a] Average values are given for similar bond distances or angles; degeneracies are listed in parentheses for values that differ sufficiently than more than one value is needed to describe the bond angle or bond distance. Geometrical parameters for the singlet ground-state $Fe^{2+}(Phen)_3$ are shown in normal font while those for excited quintet state are shown in bold. All bond angles (∠) are given in degrees (°) and M^{2+}–N bond lengths in angstroms (Å). [b] intra-ligand angles. [c] Inter-ligand angles.

Figure Captions

Figure S1. Cross sections for collision-induced dissociation of $M^{2+}(Phen)_3$ complexes, where $M^{2+} = Fe^{2+}$, Co^{2+}, and Ni^{2+}, parts a–c, respectively, with Xe as a function of kinetic energy in the center-of-mass frame (lower *x*-axis) and laboratory frame (upper *x*-axis). Data are shown for a Xe pressure of ~0.2 mTorr.

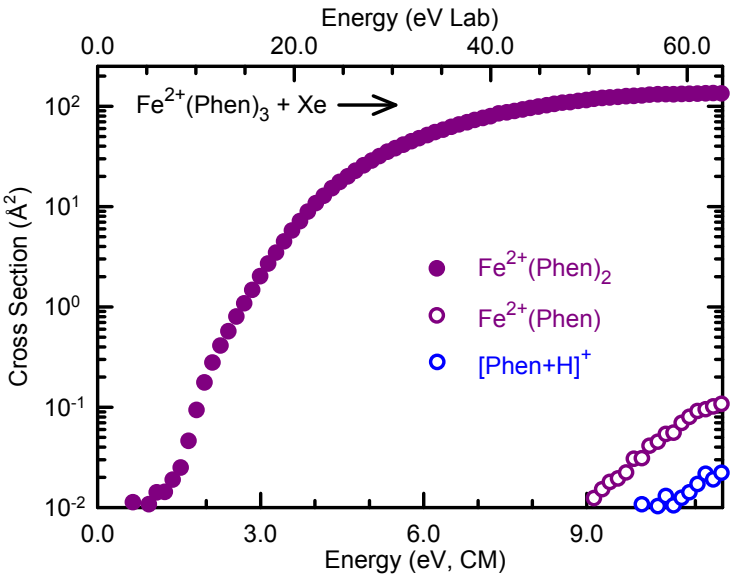
Figure S2. Zero-pressure-extrapolated cross sections for collision-induced dissociation of $M^{2+}(Phen)_3$ complexes, where $M^{2+} = Fe^{2+}$, Co^{2+}, and Ni^{2+}, parts a–c, respectively, with Xe in the threshold region as a function of kinetic energy in the center-of-mass frame (lower *x*-axis) and laboratory frame (upper *x*-axis). Solid lines show the best fits to the data using eq 1 convoluted over the kinetic and internal energy distributions of the reactants. Dotted lines show the model cross sections in the absence of experimental kinetic energy broadening for reactants with an internal energy corresponding to 0 K.

Figure S3. Variation in the average M^{2+}–N bond distances in B3LYP/6-31G* optimized $M^{2+}(Phen)_x$, $x = 1–3$ complexes as a function of the metal cation, M^{2+}, where $M^{2+} = Fe^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. The ionic radii of the bare metal cation; M^{2+} are also shown. Ionic radii of M^{2+} are taken from Refs 54 and 55.

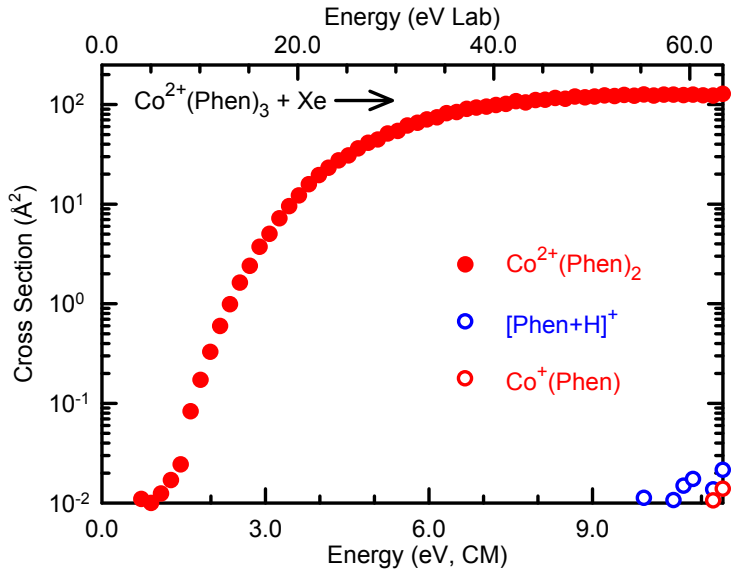
Figure S4. B3LYP/6-31G* optimized geometries of $M^{2+}(Phen)_x$, $x = 1–3$ complexes, where $M^{2+} = Fe^{2+}$, Co^{2+}, and Ni^{2+}.

Figure S1.

a.



b.



c.

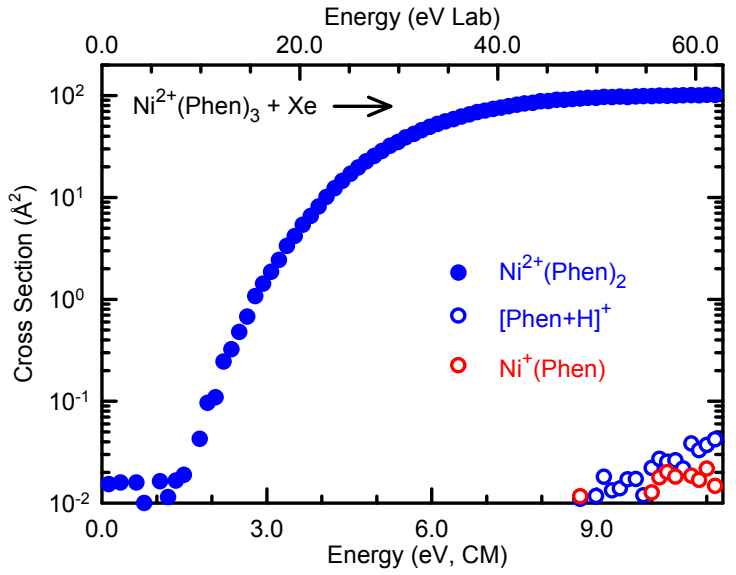


Figure S2.

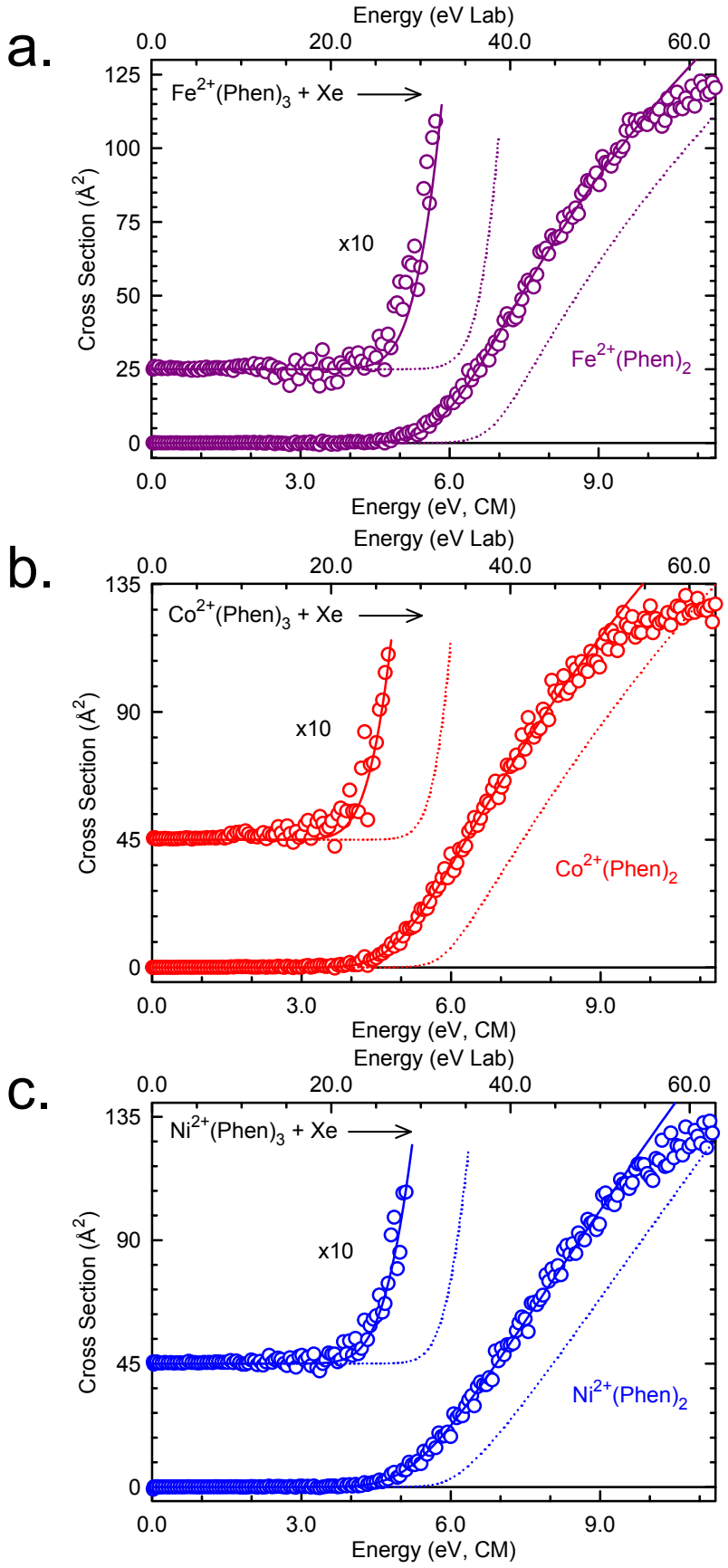

a.
Energy (eV Lab)
0.0
20.0
40.0
60.0
125
100
75
50
25
0
Fe2+(Phen)3 + Xe
x10
Fe2+(Phen)2
Cross Section (Å2)
0.0
3.0
6.0
9.0
Energy (eV, CM)
b.
Energy (eV Lab)
135
90
45
0
Co2+(Phen)3 + Xe
x10
Co2+(Phen)2
Cross Section (Å2)
Energy (eV, CM)
c.
Energy (eV Lab)
Ni2+(Phen)3 + Xe
x10
Ni2+(Phen)2
Cross Section (Å2)
Energy (eV, CM)

Figure S3.

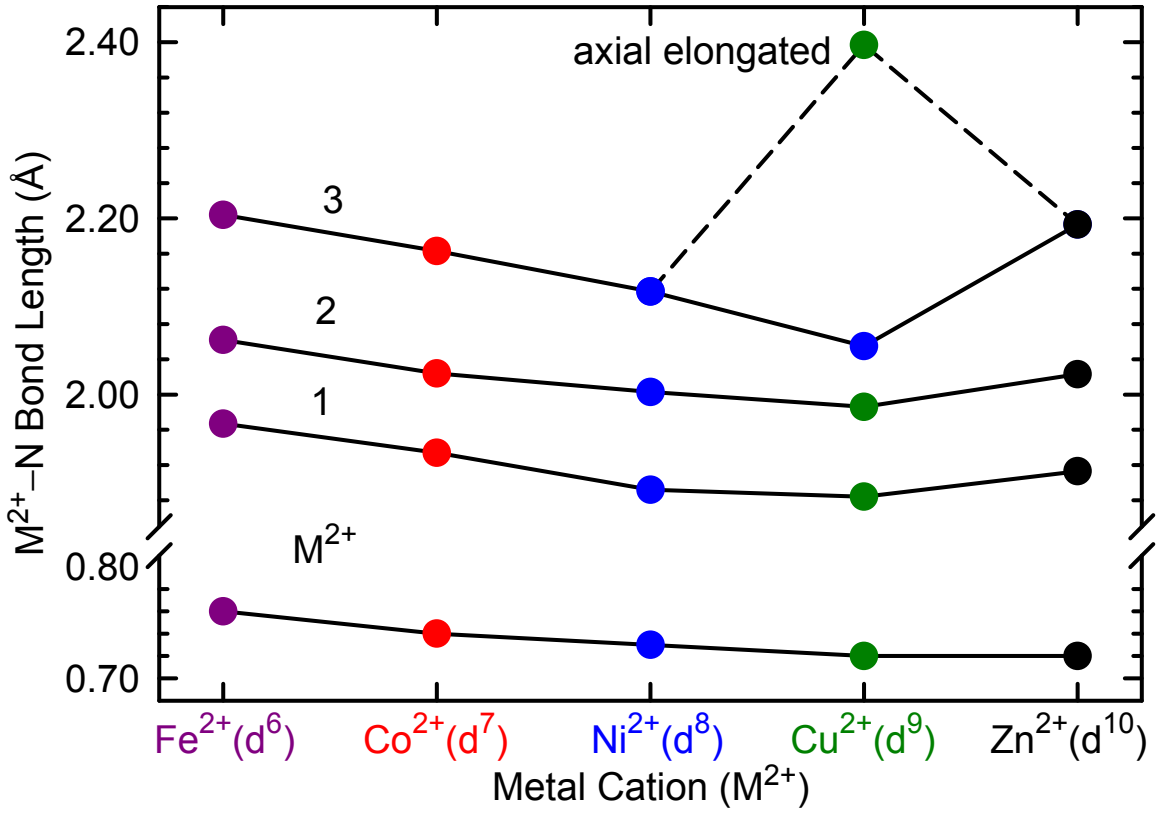
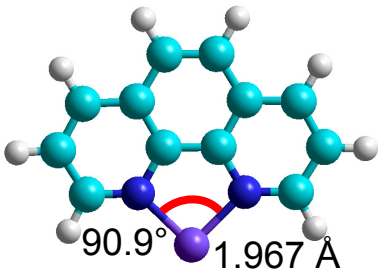
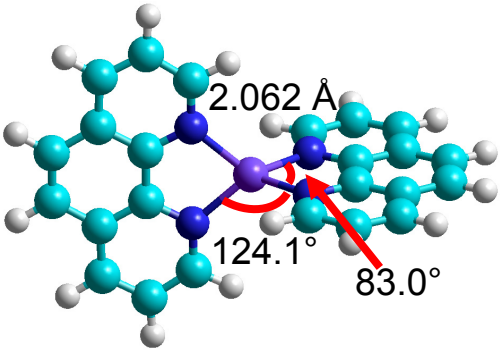

axial elongated
3
2
1
M2+
2.40
2.20
2.00
0.80
0.70
M2+–N Bond Length (Å)
Fe2+(d6)
Co2+(d7)
Ni2+(d8)
Cu2+(d9)
Zn2+(d10)
Metal Cation (M2+)

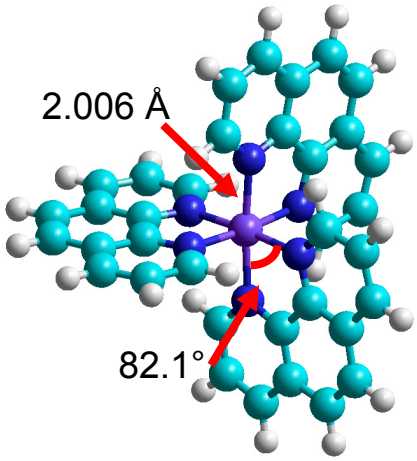
Figure S4.



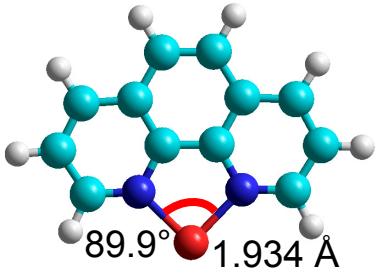
$Fe^{2+}(Phen)$



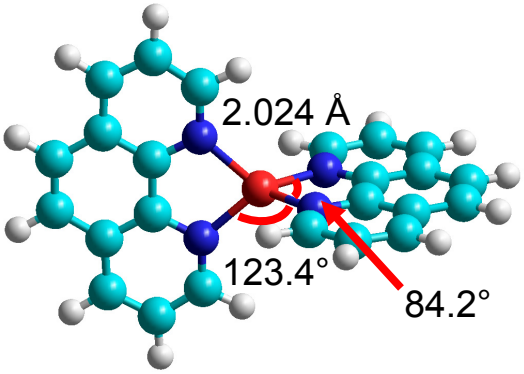
$Fe^{2+}(Phen)_2$



$Fe^{2+}(Phen)_3$



$Co^{2+}(Phen)$



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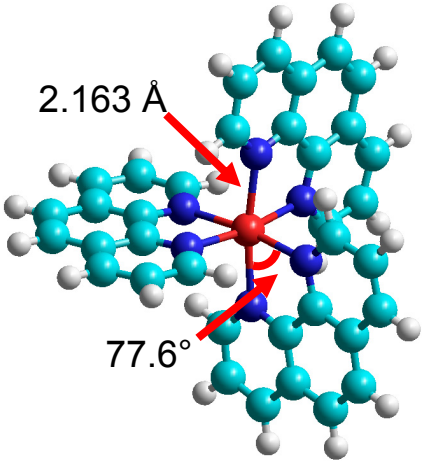
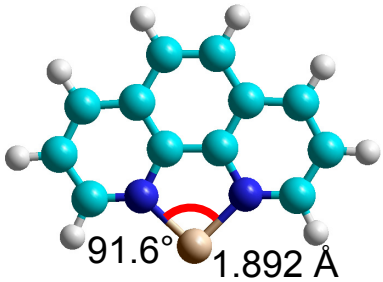
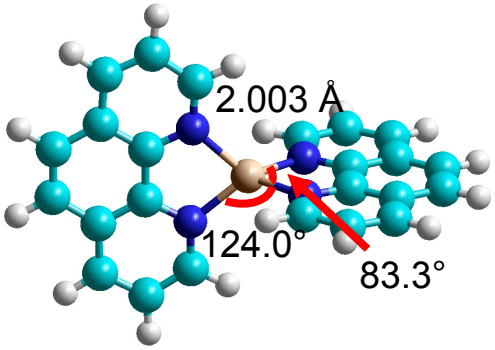


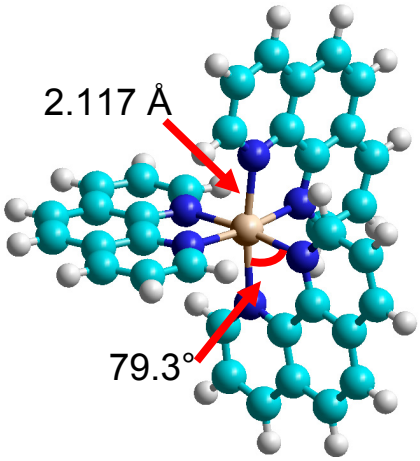
$Co^{2+}(Phen)_3$



$Ni^{2+}(Phen)$



$Ni^{2+}(Phen)_2$



$Ni^{2+}(Phen)_3$