

Supplementary material

Spectroscopic data of the ligands and complexes

N,N'-bis(2-pyrimidyl)-1,2-ethylenediamine (pyr₂C₂) I. Selected IR bands ($\bar{\nu}_{\max}/\text{cm}^{-1}$): 3267s, 1593vs, 1538vs, 1454s, 1421vs, 1359s, 1304m, 1284m, 1254m, 1223m, 1176w, 1126w, 1089w, 1074w, 988w, 799s, 731m, 664s, 494s; \square_{H} (DMSO-*d*₆) 8.25 [4H, br d, J_{est} 4.8 Hz, H(4)/H(6)/H(4')/H(6')], 7.17 [2H, br s, N-H], 6.55 [2H, br t, J_{est} 4.8 Hz, H(5)/H(5')], 3.43 [4H, br d, H(7)/H(7')]; \square_{C} (DMSO-*d*₆) 162.3 [C(2)/C(2')], 158.0 [C(4)/C(6)/C(4')/C(6')], 110.1 [C(5)/C(5')], 40.3 [C(7)/C(7')]. [(H-pyr)₂C₂](NO₃) (**Ia**). Selected IR bands ($\bar{\nu}_{\max}/\text{cm}^{-1}$): 3246m, 3091s, 1644vs, 1544m, 1473m, 1398vs, 1354vs, 1315vs, 1290s, 1219s, 1132m, 1088s, 1057m, 1042s, 988m, 825s, 811s, 775m, 631m, 506w, 484w. \square_{H} (DMSO-*d*₆) 8.50 [4H, br d, J_{est} 5.1 Hz, H(4)/H(6)/H(4')/H(6')], 6.85 [2H, br t, H(5)/H(5')], 3.57 [4H, br s, H(7)/H(7')]; \square_{C} (DMSO-*d*₆): *ca* 160 broad peak [C(2)/C(2')], 157.0 [C(4)/C(6)/C(4')/C(6')], 110.5 [C(5)/C(5')], 40.4 [C(7)/C(7')].

N,N'-bis(2-pyrimidyl)-1,3-trimethylenediamine dihydrate (pyr₂C₃·2H₂O) II. Selected IR bands ($\bar{\nu}_{\max}/\text{cm}^{-1}$): 3261s, 2939s, 2880m, 1597vs, 1536vs, 1475vs, 1454s, 1416vs, 1361s, 1330s, 1264s, 1230m, 1178m, 1144m, 1078w, 1031w, 993w, 799vs, 666m, 642s, 473m; \square_{H} (DMSO-*d*₆) 8.24 [4H, d, J 4.8 Hz, H(4)/H(6)/H(4')/H(6')], 7.13 [2H, br t, N-H], 6.52 [2H, t, J 4.8 Hz H(5)/H(5')], 3.30 [4H, br q, J_{est} 6.6 Hz, H(7)/H(7')], 1.75 [2H, br quint, J_{est} 6.6 Hz H(8)]; \square_{C} (DMSO-*d*₆) 162.3 [C(2)/C(2')], 157.9 [C(4)/C(6)/C(4')/C(6')], 109.8 [C(5)/C(5')], 38.3 [C(7)/C(7')], 28.8 [C(8)].

N,N'-bis(2-pyrimidyl)-1,4-tetramethylenediamine (pyr₂C₄) III. Selected IR bands ($\bar{\nu}_{\max}/\text{cm}^{-1}$): 3257s, 2939s, 1599vs, 1542vs, 1463vs, 1416vs, 1369s, 1347s, 1278m, 1229m, 1183m, 1113w, 1088w, 1071w, 993w, 802m, 735m, 642w, 617w; \square_{H} (DMSO-*d*₆) 8.23 [4H, d, J 4.8 Hz, H(4)/H(6)/H(4')/H(6')], 7.12 [2H, br t, N-H], 6.51 [2H, t, J_{est} 4.8 Hz, H(5)/H(5')], 3.25 [4H, m, H(7)/H(7')], 1.54 [4H, br m, H(8)/H(8')]; \square_{C} (DMSO-*d*₆) 162.3 [C(2)/C(2')], 157.9 [C(4)/C(6)/C(4')/C(6')], 109.6 [C(5)/C(5')], 40.4

[C(7)/C(7')], 26.5 [C(8)/C(8')]. [(H-pyr)₂C₄](NO₃) (**IIIa**) Selected IR bands ($\bar{\nu}_{\text{max}}/\text{cm}^{-1}$): 3253m, 2930-2700s, 1652vs, 1615vs, 1571m, 1545w, 1466s, 1383vs, 1329vs, 1209s, 1108m, 1093m, 1063m, 1039m, 986s, 950m, 874w, 840w, 824m, 809m, 792s, 685m, 597w, 511w; δ_{H} (DMSO-*d*₆) 8.55 [4H, d, J_{est} 5.1 Hz, H(4)/H(6)/H(4')/H(6')], 6.88 [2H, t, J_{est} 5.1 Hz, H(5)/H(5')], 3.38 [4H, br s, H(7)/H(7')], 1.62 [4H, br s, H(8)/H(8')]; δ_{C} (DMSO-*d*₆) 157.1 broad peak [C(2)/C(2')], 156.2 [C(4)/C(6)/C(4')/C(6')], 109.5 [C(5)/C(5')], 40.6 [C(7)/C(7')], 25.6 [C(8)/C(8')].

N,N'-bis(2-pyrimidyl)-1,5-pentamethylenediamine (pyr₂C₅) IV. Selected IR bands ($\bar{\nu}_{\text{max}}/\text{cm}^{-1}$): 3264s, 2934s, 2858w, 1594vs, 1538vs, 1457s, 1415m, 1366s, 1321w, 1294w, 1262w, 1246w, 1223w, 1178w, 1136w, 1088w, 803m, 779w, 699w, 642m, 524w; δ_{H} (DMSO-*d*₆) 8.23 [4H, br d, J_{est} 4.8 Hz, H(4)/H(6)/H(4')/H(6')], 7.10 [2H, br t, N-H], 6.51 [2H, br t, J_{est} 4.8 Hz, H(5)/H(5')], 3.23 [4H, br q, J_{est} 6.9 Hz, H(7)/H(7')], 1.52 [4H, br quint, J_{est} 6.9 Hz, H(8)/H(8')], 1.34 [2H, m, H(9)]; δ_{C} (DMSO-*d*₆) 162.3 [C(2)/C(2')], 157.8 [C(4)/C(6)/C(4')/C(6')], 110.5 [C(5)/C(5')], 40.5 [C(7)/C(7')], 28.7 [C(8)/C(8')], 24.0 [C(9)].

N,N'-bis(2-pyrimidyl)-1,6-hexamethylenediamine (pyr₂C₆) V. Selected IR bands ($\bar{\nu}_{\text{max}}/\text{cm}^{-1}$): 3268vs, 2935vs, 2867s, 1588vs, 1533vs, 1487s, 1454vs, 1441vs, 1419vs, 1374vs, 1355s, 1320s, 1294w, 1267vs, 1219m, 1177m, 1118s, 1091m, 1076m, 1022w, 984w, 815s, 799s, 736w, 666m, 641m, 553m; δ_{H} (DMSO-*d*₆) 8.13 [4H, br d, J_{est} 4.8 Hz H(4)/H(6)/H(4')/H(6')], 7.00 [2H, br t, N-H], 6.41 [2H, br t, J_{est} 4.8 Hz H(5)/H(5')], 3.11 [4H, br q, H(7)/H(7')], 1.40 [4H, m, H(8)/H(8')], 1.21 [4H, m, H(9)/H(9')]; δ_{C} (DMSO-*d*₆) 162.3 [C(2)/C(2')], 157.8 [C(4)/C(6)/C(4')/C(6')], 109.6 [C(5)/C(5')], 40.5 [C(7)/C(7')], 28.9 [C(8)/C(8')], 26.3 [C(9)/C(9')].

2-(butylamino)pyrimidine (pyrBu) VI.¹² δ_{H} (DMSO-*d*₆) 8.23 [4H, br d, J_{est} 4.8 Hz, H(4)/H(6)], 7.09 [2H, br t, N-H], 6.50 [2H, br t, J_{est} 4.8 Hz, H(5)], 3.23 bq [2H, br q, J_{est} 7.2 Hz, H(7)], 1.48 [2H, br quint, J_{est} 7.2 Hz, H(8)], 1.31 [2H, br hex, J_{est} 7.2 Hz, H(9)],

0.88 [3H, t, J 7.2 Hz, H(10)]; δ_{C} (DMSO- d_6) 162.3 [C(2)], 157.8 [C(4)/C(6)], 109.6 [C(5)], 40.2 [C(7)], 31.1 [C(8)], 19.6 [C(9)], 13.8 [C(10)].

[Ag(pyr₂C₂)(NO₃)₂ 1. Selected IR bands ($\bar{\nu}_{\text{max}}/\text{cm}^{-1}$): 3385m, 3302s, 1597vs, 1572vs, 1531vs, 1460s, 1386vs, 1363vs, 1292vs, 1251s, 1223s, 1177m, 1133m, 1077w, 1032w, 792s, 667w, 649w, 546w, 472w; δ_{H} (DMSO- d_6) 8.30 [4H, br d, J_{est} 4.8 Hz, H(4)/H(6)/H(4')/H(6')], 7.30 [2H, br s, N-H], 6.60 [2H, br t, J_{est} 4.8 Hz, H(5)/H(5')], 3.46 [4H, br s, H(7)/H(7')]; δ_{C} (DMSO- d_6) 161.8 [C(2)/C(2')], 158.5 [C(4)/C(6)/C(4')/C(6')], 110.1 [C(5)/C(5')], 40.2 [C(7)/C(7')].

pyr₂C₃·AgNO₃ 2 Selected IR bands ($\bar{\nu}_{\text{max}}/\text{cm}^{-1}$): 3267s, 2940m, 1600vs, 1570vs, 1541vs, 1456s, 1418vs, 1364vs, 1267vs, 1223s, 1174m, 1130m, 1084m, 1038w, 955m, 796s, 649m; δ_{H} (DMSO- d_6) 8.29 [4H, br d, J_{est} 4.8 Hz, H(4)/H(6)/H(4')/H(6')], 7.24 [2H, br t, J_{est} 5.7 Hz, N-H], 6.59 [2H, br t, J_{est} 4.8 Hz, H(5)/H(5')], 3.33 [4H, br q, H(7)/H(7')], 1.78 [2H, br quint, J_{est} 6.9 Hz, H(8)]; δ_{C} (DMSO- d_6) 161.8 [C(2)/C(2')], 158.5 [C(4)/C(6)/C(4')/C(6')], 109.9 [C(5)/C(5')], 38.5 [C(7)/C(7')], 28.6 [C(8)].

pyr₂C₄·AgNO₃ 3 Selected IR ($\bar{\nu}_{\text{max}}/\text{cm}^{-1}$): 3279s, 2955m, 2938m, 1596vs, 1573vs, 1538vs, 1462vs, 1415vs, 1364vs, 1297vs, 1278vs, 1236s, 1174m, 1134m, 1112m, 1085w, 1072w, 1037m, 996w, 792s, 778m, 745w, 645w, 617w, 516w; δ_{H} (DMSO- d_6) 8.27 [4H, d, J 4.8 Hz, H(4)/H(6)/H(4')/H(6')], 7.20 [2H, t, J_{est} 5.7 Hz, N-H], 6.56 [2H, t, J 4.8 Hz, H(5)/H(5')], 3.28 [4H, br dt, J_{est} 5.7 Hz, H(7)/H(7')], 1.56 [4H, br m, H(8)/H(8')]; δ_{C} (DMSO- d_6) 162.4 [C(2)/C(2')], 158.8 [C(4)/C(6)/C(4')/C(6')], 110.2 [C(5)/C(5')], 40.9 [C(7)/C(7')], 26.9 [C(8)/C(8')].

[Ag(Hpyr₂C₄)(NO₃)₂ 4. Selected IR ($\bar{\nu}_{\text{max}}/\text{cm}^{-1}$): 3257s, 2940s, 1670s, 1600vs, 1578vs, 1543vs, 1464s, 1383vs, 1346vs, 1278s, 1230s, 1112s, 1088m, 1071m, 1052w, 991w, 944w, 825m, 802s, 789s, 735s, 642m, 617m, 510w); δ_{H} (DMSO- d_6): The spectrum shows that the two pyrimidine rings are not completely equivalent: 8.39 [4H, br m,

H(4)/H(6)/H(4')/H(6')], 7.80 [2H, br s, N-H], 6.70 [2H, br m, H(5)/H(5')], 3.31 [4H, br s, H(7)/H(7')], 1.58 [4H, br s, H(8)/H(8')]; δ_{c} (DMSO- d_6) 159.0 [C(2)/C(2')], 157.7 [C(4)/C(6)/C(4')/C(6')], 109.6 [C(5)/C(5')], 40.5 [C(7)/C(7')], 26.0 [C(8)/C(8')].