Electronic Supplementary Information

Robustness of thioamide dimer synthon, carbon bonding and thioamide-thioamide stacking in ferrocene-based thiosemicarbazones

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Table of Contents

Characterization data of compounds 1-5.

4-Benzyl-1-(1-ferrocenylethyl)thiosemicarbazone (1)

Yield, 75%; mp, 140°C; IR (KBr), ν (cm^{-1}): 3342, 3222, 3067(NH), 1531(C=N), 1191(C=S). ^{1}H-NMR ($CDCl_3$), δ (ppm): 4.12(5H, s, Cp-ring C_{10}-H), 4.3(2H, m, Cp-ring $C_{3(4)}$-H), 4.51(2H, m, Cp-ring $C_{2(5)}$-H), 2.13(3H, s, CH_3-C=N), 4.94(2H, d, *J*= 4.5Hz, CH_2-N), 8.53(1H, s, CS-NH), 10.09 (1H, s, N-NH), 7.23-7.40(5H, m, Phenyl C_{2-6}), MS, m/z (rel. int.): 391 (M^+, 83), 284(100), 227(80), 184(61), 210(19), 129(27), 106(21), 91(74), 56(17).

4-(3-Chlorobenzyl)-1-(1-ferrocenylethyl)thiosemicarbazone (2)

Yield, 74%; mp, 175°C; IR (KBr), ν (cm^{-1}): 3338, 3263, 3084(NH), 1537(C=N), 1193(C=S). ^{1}H-NMR ($CDCl_3$), δ (ppm): 4.22(5H, s, Cp-ring C_{10}-H), 4.42(2H, m, Cp-ring C-$_{3(4)}$), 4.48(2H, m, Cp-ring C-$_{2(5)}$), 2.11(3H, s, CH_3-C=N), 4.88(2H, d, *J*= 5.64Hz, CH_2-N), 8.40(1H, s, CS-NH), 10.07(1H, s, N-NH), 7.74(1H, d, *J* =14.34Hz Phenyl C_2-H), 7.19-7.33(3H, m, Phenyl C_{4-6}-H), ^{13}C NMR (δppm) 126.07(C_5-Phenyl), 127.95(C_4-Phenyl), 127.79(C_6-Phenyl), 129.99(C_2-phenyl), 134.57(C_3-Phenyl), 139.93(C_1-Phenyl), 148.04(C=S), 149.7(C=N), 47.56(NH-CH_2), 24.24(CH_3-C=N), 82.15(C_1-Cpring), 69.38(C_{10}-Cpring), 69.87(C-$_{3(4)}$-Cpring), 70.45(C-$_{2(5)}$-Cpring). MS, m/z (rel. int.): 425(M^+, 66), 284(100), 227(60), 210(18), 185(57), 162(22), 140(10), 129(22), 121(35), 106(14), 91(74), 56(12).

4-(3-Methoxybenzyl)-1-(1-ferrocenylethyl)thiosemicarbazone (3)

Yield, 86%; mp, 140°C; IR (KBr), ν (cm^{-1}): 3338, 3238, 2914(NH), 1539(C=N), 1163(C=S). ^{1}H-NMR ($CDCl_3$), δ (ppm): 4.32(5H,s, Cp-ring C_{10}-H), 4.40(2H, m, Cp-ring $C_{3(4)}$-H), 4.46(2H, m, Cp-ring $C_{2(5)}$-H), 2.1 (3H,s, CH_3-C=N), 4.86 (2H, d, *J*= 5.52Hz CH_2-N), 7.78 (1H, s, CS-NH), 8.25(1H, s, N-NH), 3.75(3H, s, Phenyl C_3-OCH_3), 6.91 (2H, m, Phenyl $C_{2,4}$-H), 7.20(1H, dd, *J* =2.28Hz, Phenyl C_5-H), 6.78(1H, d, *J*= 7.8Hz, Phenyl C_6-H), ^{13}C NMR (δppm) 159.9(C_3-Phenyl), 139.40(C_1-Phenyl), 129.79(C_5-Phenyl), 120.02(C_4-Phenyl), 120.24(C_2-Phenyl), 113.63(C_6-Phenyl), 159.93(C_3-Phenyl), 148.04(C=S), 149.61(C=N), 48.3(CH_2), 24.2(CH_3-C=N), 55.31(O-CH_3), 82.18(C_1-Cpring), 69.86(C_{10}-Cpring), 70.37(C-$_{3(4)}$-Cpring), 70.76(C-$_{2(5)}$-Cpring). MS, m/z (rel. int.): 420 (M^+, 37), 283(93), 227(100), 185(80), 211(25), 136(30), 129(36), 121(79), 106(12), 91(19), 56(15).

4-(2-Fluorobenzyl)-1-(1-ferrocenylethyl)thiosemicarbazone (4)

Yield, 80%; mp, 188℃; IR (KBr), $\bar{\nu}$ (cm^{-1}): 3355, 3274, 3093(NH), 1531(C=N), 1207(C=S). ^{1}H-NMR ($CDCl_3$), δ (ppm): 4.35(s, 5H, Cp-ring C_{10}-H), 4.39(m, 2H, Cp-ring $C_{3(4)}$-H), 4.49(m, 2H, Cp-ring $C_{2(5)}$-H), 2.18(s, 3H,CH_3-C=N), 5.03(d, 2H, CH_2-N), 7.99(s, 1H, CS-NH), 8.27 (s, 1H, N-NH), 7.06-7.54(m, 4H, Phenyl $C_{3\text{-}6}$-H)) ^{13}C NMR (δppm) 162.72(C_2-Phenyl), 130.55(C_1-Phenyl), 129.47(C_6-Phenyl), 129.36(C_4-Phenyl), 124.35(C_5-Phenyl), 115.52(C_3-Phenyl), 148.3(C=S), 159.8(C=N), 41.9(CH_2), 24.2(CH_3-C=N), 82.13(C_1-Cpring), 69.86(C_{10}-Cpring), 70.40(C-$_{3(4)}$-Cpring), 70.75(C-$_{2(5)}$-Cpring), MS, m/z (rel. int.): 409 (M^+, 21), 374(41), 284(22), 227(100), 211(44), 185(42), 129(15), 121(49), 109(83), 56(13), 43(84).

4-(4-Fluorobenzyl)-1-(1-ferrocenylethyl)thiosemicarbazone (5)

Yield, 84%; mp, 141℃; IR (KBr), $\bar{\nu}$ (cm^{-1}): 3649, 3357, 3084(NH), 1531(C=N), 1191(C=S). ^{1}H-NMR ($CDCl_3$), δ (ppm): 4.06(5H, s, Cp-ring C_{10}-H), 4.3(2H, m, Cp-ring $C_{3(4)}$-H), 4.43(2H, m, Cp-ring $C_{2(5)}$-H), 2.08(3H, s, CH_3-C=N), 4.85(2H, d, *J*=3.2 Hz, CH_2-NH), 7.77(1H, s, CS-NH), 8.20 (1H, s, N-NH), 7.25(2H, d, Phenyl $C_{3,5}$-H)), 6.98(2H, d, Phenyl $C_{2,6}$-H)) ^{13}C NMR (δppm) 160.68(C_4-Phenyl), 133.66(C_1-Phenyl), 129.68($C_{2,6}$-Phenyl), 115.68($C_{3,5}$-Phenyl), 148.13(C=S), 149.83(C=N), 47.50(NH-CH_2), 24.26(CH_3-C=N), 82.12(C_1-Cpring), 69.86(C_{10}-Cpring), 70.41($C_{3(4)}$-Cpring), 70.80($C_{2(5)}$-Cpring). MS, m/z (rel. int.): 409(M^+, 29), 284(36), 227(90), 211(23), 185(38), 162(20), 129(15), 121(26), 109(100), 56(14).

Table S1. X-ray crystallographic data of **1-5**

Crystal data	**1**	**2**	**3**	**4**	**5**
CCDC	1041597	1041598	1041599	1041600	1041601
Chemical formula	$C_{20}H_{21}FeN_3S$	$C_{20}H_{20}ClFeN_3S$	$C_{21}H_{23}FeN_3OS$	$C_{20}H_{20}FFeN_3S$	$C_{20}H_{20}FFeN_3S$
M_r	391.31	425.75	421.33	409.30	409.30
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$	Monoclinic, $C2/c$
Temperature (K)	296	296	296	296	296
a, b, c (Å)	7.0680 (4), 10.3127 (5), 14.2953 (7)	19.7141 (14), 7.0263 (4), 28.099 (2)	7.1685 (3), 10.3397 (4), 14.5960 (6)	18.8634 (13), 7.1602 (5), 27.7613 (18)	19.0887 (9), 7.2037 (3), 27.4267 (12)
α, β, γ (°)	81.736 (3), 77.874 (2), 70.655 (2)	90.386 (2)	80.533 (2), 81.113 (1), 70.067 (2)	92.830 (4)	91.056 (2)
V (Å^3)	958.11 (9)	3892.1 (5)	997.53 (7)	3745.0 (4)	3770.8 (3)
Z	2	8	2	8	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.90	1.03	0.88	0.94	0.93
Crystal size (mm)	0.32 × 0.25 × 0.23	0.34 × 0.26 × 0.20	0.26 × 0.20 × 0.18	0.28 × 0.18 × 0.16	0.35 × 0.28 × 0.23
Data collection					
Diffractometer	Bruker Kappa APEXII CCD diffractometer	Bruker Kappa APEXII CCD diffractometer	Bruker Kappa APEXII CCD diffractometer	Bruker Kappa APEXII CCD diffractometer	Bruker Kappa APEXII CCD diffractometer
Absorption correction	Multi-scan (*SADABS*; Bruker, 2005)	Multi-scan (*SADABS*; Bruker, 2005)	Multi-scan (*SADABS*; Bruker, 2005)	Multi-scan (*SADABS*; Bruker, 2005)	Multi-scan (*SADABS*; Bruker, 2005)
T_{min}, T_{max}	0.763, 0.820	0.723, 0.822	0.806, 0.859	0.781, 0.864	0.739, 0.818
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14116, 3744, 3224	14496, 3821, 2799	14909, 3911, 3195	13585, 3682, 2678	14970, 3704, 2950
R_{int}	0.027	0.040	0.025	0.035	0.029
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617	0.617	0.617	0.617	0.617
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.079, 1.03	0.036, 0.090, 1.02	0.031, 0.080, 1.05	0.035, 0.083, 1.03	0.031, 0.078, 1.02
No. of reflections	3744	3821	3911	3682	3704
No. of parameters	227	236	246	236	236
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.21, -0.26	0.31, -0.40	0.29, -0.21	0.24, -0.21	0.20, -0.22