Solution processible Co(III) quinoline-thiosemicarbazone complexes: synthesis, structure extension and Langmuir-Blodgett deposition studies

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Abstract

Seven readily synthesised 8-Quinoline-4-**R**-3-thiosemicarbazone ligands [where R = phenyl (**L_1H**), 4-fluorophenyl (**L_2H**), 4-iodophenyl (**L_3H**), 4-nitrophenyl (**L_4H**), 4-carboxyphenyl (**L_5H**), 3-picolyl (**L_6H**), and octadecyl (**L_7H**)] and their corresponding Co(III) coordination complexes, $[Co(\mathbf{L})_2]BF_4$, have been synthesised and fully characterised. Crystallographic analysis of the complexes revealed that the substituents significantly alter solid-state supramolecular network topologies. The solution processability of these complexes was confirmed by incorporating a long carbon alkyl-chain into the ligand (**L_7H**) and immobilising the complex onto quartz slides using Langmuir-Blodgett deposition. The facile and modular synthesis of these thiosemicarbazone-based ligands coupled with the potential to exploit multiple applications makes these compounds excellent candidates for functional supramolecular materials.

Keywords: Thiosemicarbazone; Cobalt(III); Supramolecular Materials; Langmuir-Blodgett; Structure Extension

1. Introduction

The preparation of metallosupramolecular materials is a rapidly advancing and highly topical area of modern chemical and materials science.[1-9] By incorporating metal based-functionalities (magnetically interesting systems, redox labile systems, luminescent complexes, catalysts *etc.*) and structure directing components into coordination complexes it is possible to assemble the compounds into larger macroscopic materials (*e.g.* thin films, crystalline materials, frameworks, Langmuir-Blodgett films, Gels, polymers etc.).[10-17]

When designing supramolecular materials containing transition metals, the ligand coordination pocket must be considered *in addition* to the functional and structure directing groups. The correct donor atoms and denticity must be chosen to give a stable complex, with the metal binding at the desired site rather than interacting with the structure directing group. The binding pocket should also be remote enough from the structure directing group to ensure intermolecular interactions are enhanced. Additionally, the field strength of the ligands must also be carefully considered so that the desired metal-based functionality is achieved. Ideally, ligand synthesis should be modular so that a variety of structure directing groups can be introduced to the ligand scaffold with minimal synthetic effort.

To meet these requirements, we have chosen to develop transition-metal systems containing quinoline thiosemicarbazone ligands (Figure 1). These ligands can be prepared in a modular fashion from quinoline carbaldehyde and a functional thiosemicarbazide, thus allowing for the incorporation of a wide range of structure directing groups via commercially available thiosemicarbazides. The tridentate N_2S metal co-ordination pocket imparts stability toward a number of different transition metals (*e.g.* Co, Fe, Ru, Cu, Pt).[18-21] Lastly, transition metal complexes of thiosemicarbazone-based

ligands have found applications in many areas of chemistry, including catalysts[22-24], luminescent compounds[25-27], anti-cancer agents[28, 29], and spin and redox labile complexes.[30-36]

In this contribution, we describe the synthesis of seven thiosemicarbazone ligands and their Co(III) complexes. A range of structure directing groups have been incorporated into the structure with the aim of altering the ordering in the materials. Additionally, we have introduced a pendant 2-pyridyl group to extend the structure via coordination to other metal centres, and a long alkyl (C-18) chain to assess the ability of such materials to form Langmuir-Blodgett films.

2. Experimental

2.1 Materials and Instrumentation

All chemicals were purchased from commercial sources and used as received. Solvents were HPLC grade and were used without further purification. Infrared spectra were recorded on a Thermo Scientific Nicolet iS10 spectrometer with Smart ITR accessory between 400-4000 cm^{-1}. UV-visible spectra were recorded on a Perkin Elmer Lambda 265 spectrophotometer. NMR spectra were recorded on a Bruker DPX400 NMR spectrometer at 300 K. Chemical shifts are reported in parts per million and referenced to the residual solvent peak ($(CD_3)_2SO$: ^1H δ 2.50 ppm, ^{13}C δ 39.52 ppm). Standard conventions indicating multiplicity were used: m = multiplet, t = triplet, d = doublet, s = singlet. Mass spectrometry samples were analysed using a MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight (TOF) analyser. Samples were introduced to the mass spectrometer via a Dionex Ultimate 3000 auto-sampler and uHPLC pump [Gradient 20% MeCN (0.2% formic acid) to 100% MeCN (0.2% formic acid) in five minutes at 0.6 mL min^{-1}; Column: Acquity UPLC BEH C18 (Waters) 1.7 micron 50 x 2.1 mm]. High-resolution mass spectra were recorded using positive/negative ion electrospray ionization. Crystallography: Single-crystal X-ray diffraction data was collected at 100 K on either a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn 724+ detector mounted at the window of an FR-E+ Superbright Mo-K_α rotating anode generator (λ = 0.71075 Å) with HF or VHF varimax optics, or a Rigaku 007 HF diffractometer equipped with an enhanced sensitivity Saturn 944+ detector with a Cu-Kα rotating anode generator (λ = 1.5418 Å) with HF varimax optics.[37] Unit cell parameters were refined against all data and an empirical absorption correction applied in either CrystalClear[38] or CrysalisPro.[39] All structures were solved by direct methods using SHELXS-2017 and refined on F_O^2 by SHELXL-2017 using Olex2.[40-42] H-atoms were positioned geometrically and refined using a riding model. Unit cell parameters, collection and refinement data for ligands and complexes are presented in Tables S1 and S2 (in ESI). CCDC 1999846-1999851 (ligands) and 1999878-1999884 (complexes) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Langmuir-Blodgett measurements: Surface-pressure isotherms were measured at 25 °C on a KSV Micro Trough G2 Langmuir−Blodgett trough (KSV, Finland). Water was purified with a Milli-Q Integral system (Millipore), and its resistivity was measured to be higher than 18 MΩ cm. A 50:1 mixture of DCM/hexane was used as the spreading solvent. Typically drops (~30 μL) of L_7H or $[Co(L_7)_2]BF_4$ solution (0.5 mg mL^{-1}) were deposited using a microsyringe on the water sub-phase. After leaving to evaporate for 20 min, the barriers were compressed at 10 mm min^{-1} and the surface pressure was monitored using a platinum probe. Deposition studies were carried out using quartz slides (25 x 25 mm) that had been treated initially with conc. nitric acid and then piranha solution. The slides were thoroughly rinsed with, and then stored in Milli-Q water. Deposition studies were set up for hydrophilic surfaces by placing the slides in the water sub-phase to a depth of 15 mm. The monolayer was then formed (as described above) with compression to a constant pressure of 40 mNm^{-1}. The slide was then slowly drawn out of the sub-phase at 10 mm min^{-1} while monitoring the change in area. Multi-layering experiments were set up in the same way however after emersion of the slide it was then immersed at 10 mm min^{-1} – this process was repeated until no transfer or film delamination was observed (based on transfer ratios).

2.2 Synthesis of Ligands

General procedure for the synthesis of ligands L_1H – L_7H: Quinoline-8-carbaldehyde (1.1 equiv.) and the appropriate thiosemicarbazide (1.0 equiv.) were refluxed in methanol (15 – 40 mL) for 2 h during which time solids formed. The solution was cooled to room temperature and the solid collected by filtration, washed with diethyl ether (2 × 10 mL), and dried in vacuo to give the thiosemicarbazone ligands as off-white to pale yellow solids which were used without further purification. L_1H 83%; L_2H 63%; L_3H 84%; L_4H 93%; L_5H 59%; L_6H 78%; L_7H 75%.

8-Quinoline 4-phenyl-3-thiosemicarbazone (L_1H): Using the general procedure, quinoline-8-carbaldehyde (816 mg, 5.19 mmol, 1.1 equiv) and 4-phenylthiosemicarbazide (787 mg, 4.71 mmol, 1.0 equiv) in methanol (15 mL) yielded L_1H (1.2 g, 83%) as a yellow powder. Mass Spec. (HR, ESI^+) m/z: 307.1011 ($[M+H]^+$, calc for $C_{17}H_{15}N_4S$ 307.1012), 329.0830 ($[M+Na]^+$, calc for $C_{17}H_{14}N_4SNa$ 329.0831); FTIR (ATR): ν (cm^{-1}): 3288 (N-H), 3048 (N-H), 2901 (C-H), 1591 (N=C), 1088 (C=S) cm^{-1}; UV/vis (MeOH): λ_{max} 236 (ε = 23,800 L mol^{-1} cm^{-1}), 346 (ε = 21,500 L mol^{-1} cm^{-1}) nm. ^1H NMR (DMSO-d_6, 400 MHz) δ ppm: 12.14 (s, 1H, N*H*), 10.29 (s, 1H, NN*H*), 9.52 (s, 1H, C*H*=N), 8.98 (dd, J = 4.2, 1.8 Hz, 1H, Ar-*H*), 8.83 (dd, J = 7.4, 1.4 Hz, 1H, Ar-*H*), 8.39 (dd, J = 8.4, 1.8 Hz, 1H, Ar-*H*), 8.04 (dd, J = 8.2, 1.4 Hz, 1H, Ar-*H*), 7.69-7.63 (m, 3H, Ar-*H*), 7.57 (dd, J = 8.3, 4.2 Hz, 1H, Ar-*H*), 7.41 – 7.37 (m, 2H, Ar-*H*), 7.20 (m, 1H, Ar-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 101 MHz) δ ppm: 176.1 (C=S), 150.3 (C_{Ar}), 145.5 (C_{Ar}), 139.8 (CH=N), 139.1 (C_{Ar}), 136.6 (C_{Ar}), 130.9 (C_{Ar}), 130.0 (C_{Ar}), 128.0 (C_{Ar}), 127.9 (C_{Ar}), 126.6 (C_{Ar}), 126.3 (C_{Ar}), 125.9 (C_{Ar}), 125.31 (C_{Ar}), 121.76 (C_{Ar}). Single crystals of L_1H were obtained as large yellow blocks by recrystalisation from ethanol.

8-Quinoline 4-(4-fluorophenyl)-3-thiosemicarbazone (L_2H): Using the general procedure, quinoline-8-carbaldehyde (436 mg, 2.77 mmol, 1.1 equiv.) and 4-(4-fluorophenyl)-3-thiosemicarbazide (470 mg, 2.54 mmol, 1 equiv.) in methanol (15 mL) gave L_2H as a yellow crystalline solid (515 mg, 63%). Mass Spec. (HR, ESI^+) m/z: 325.0924 ($[M+H]^+$, calc for $C_{17}H_{14}FN_4S$ 325.0918); FTIR (ATR): ν (cm^{-1}): 3288 (N-H), 3144 (N-H), 2988 (C-H), 1607 (N=C), 1096 (C=S) cm^{-1}; UV/vis (MeOH): λ_{max} 235 (ε = 22,000 L mol^{-1} cm^{-1}), 346 (ε = 19,900 L mol^{-1} cm^{-1}) nm. ^1H NMR (DMSO-d_6, 400 MHz) δ ppm: 12.11 (s, 1H, N*H*), 10.26 (s, 1H, NN*H*), 9.47 (s, 1H, C*H*=N), 8.99 (dd, J = 4.2, 1.8 Hz, 1H, Ar-*H*), 8.81 (dd, J = 7.4, 1.4 Hz, 1H, Ar-*H*), 8.43 (dd, J = 8.4, 1.8 Hz, 1H, Ar-*H*), 8.07 (dd, J = 8.2, 1.4 Hz, 1H, Ar-*H*), 7.69 (t, J = 7.8 Hz, 1H, Ar-*H*), 7.62 – 7.57 (m, 3H, Ar-*H*), 7.22 (m, 2H, Ar-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 101 MHz) δ ppm: 176.5 (C=S), 159.7 (d, J = 242.1 Hz, C_{Ar}), 150.4 (C_{Ar}), 145.4 (C_{Ar}), 139.9 (C_{Ar}), 136.6 (C_{Ar}), 135.5 (d, J = 2.8 Hz, C_{Ar}), 130.9 (C_{Ar}), 130.0 (C_{Ar}), 128.2 (d, J = 8.3 Hz, C_{Ar}), 127.9 (C_{Ar}), 126.6 (C_{Ar}), 126.3 (C_{Ar}), 121.8 (C_{Ar}), 114.7 (d, J = 22.5 Hz, C_{Ar}). $^{19}F\{^1H\}$ NMR (376 MHz, DMSO-d_6, 376 MHz) δ ppm: -116.83 (s, 1F, C-*F*). Single crystals of L_2H were obtained as large yellow blocks by recrystalisation from ethanol.

8-Quinoline 4-(4-iodophenyl)-3-thiosemicarbazone (L_3H): Using the general procedure, quinoline-8-carbaldehyde (296 mg, 1.88 mmol, 1.1 equiv) and 4-(4-iodophenyl)-3-thiosemicarbazide (500 mg, 1.71 mmol, 1 equiv.) in methanol (20 mL) yielded L_3H as a yellow powder (617 mg, 84%). Mass Spec. (HR, ESI^+) m/z: 432.9988 ($[M+H]_+$, calc for $C_{17}H_{14}IN_4S$ 432.9978); FTIR (ATR): ν (cm^{-1}): 3315 (N-H), 3101 (N-H), 2957 (C-H), 1615 (N=C), 1085 (C=S) cm^{-1}; UV/vis (MeOH): λ_{max} 237 (ε = 14,500 L mol^{-1} cm^{-1}), 348 (ε = 12,000 L mol^{-1} cm^{-1}) nm; ^1H NMR (DMSO-d_6, 400 MHz) δ ppm: 12.18 (s, 1H, N*H*), 10.27 (s, 1H, NN*H*), 9.50 (s, 1H, C*H*=N), 8.97 (dd, J = 4.2, 1.8 Hz, 1H, Ar-*H*), 8.79 (dd, J = 7.4, 1.4 Hz, 1H, Ar-*H*), 8.39 (dd, J = 8.4, 1.8 Hz, 1H, Ar-*H*), 8.04 (dd, J = 8.2, 1.4 Hz, 1H, Ar-*H*), 7.73-7.71 (m, 3H, Ar-*H*), 7.68 – 7.65 (m, 1H, Ar-*H*), 7.57 (dd, J = 8.3, 4.2 Hz, 1H, Ar-*H*), 7.52 (d, J = 8.6 Hz, 2H, Ar-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 101 MHz) δ ppm: 175.9 (C=S), 150.3 (C_{Ar}), 145.4 (C_{Ar}), 140.2 (C_{Ar}), 139.0 (C_{Ar}), 136.7 (C_{Ar}), 136.6 (C_{Ar}), 130.8 (C_{Ar}), 130.1 (C_{Ar}), 127.9 (C_{Ar}), 127.9 (C_{Ar}), 126.6 (C_{Ar}), 126.3 (C_{Ar}), 121.8 (C_{Ar}), 89.9 (C_{Ar}). Single crystals of L_3H were obtained as large yellow blocks by diffusion of diethylether into acetonitrile.

8-Quinoline 4-(4-nitrophenyl)-3-thiosemicarbazone (L_4H): Using the general procedure, quinoline-8-carbaldehyde (144 mg, 0.92 mmol, 1.1 equiv) and 4-(4-nitrophenyl)-3-thiosemicarbazide (177 mg, 0.83 mmol, 1 equiv.) in methanol (15 mL) gave L_4H as a dark yellow powder (1.08 g, 93%). Mass Spec. (HR, ESI^+) m/z: 352.0865 ($[M+H]^+$, calcd for $C_{17}H_{14}N_5O_2S$ 352.0864); FTIR (ATR): ν (cm^{-1}): 3269 (N-H), 3074 (N-H), 2869 (C-H), 1600 (N=C), 1488 (N=O), 1323 (N=O), 1083 (C=S) cm^{-1}; UV/vis (MeOH): λ_{max} 234 (ε = 2,900 L mol^{-1} cm^{-1}), 351 (ε = 3,300 L mol^{-1} cm^{-1}) nm; ^1H NMR (DMSO-d_6, 400 MHz) δ ppm: 12.42 (s, 1H, N*H*), 10.56 (s, 1H, NN*H*), 9.53 (s, 1H, C*H*=N), 8.99 (dd, J = 4.2, 1.8 Hz, 1H, Ar-*H*), 8.78 (dd, J = 7.4, 1.4 Hz, 1H, Ar-*H*), 8.42 (dd, J = 8.3, 1.8 Hz, 1H, Ar-*H*), 8.27-8.23 (m, 2H, Ar-*H*), 8.14-8.11 (m, 2H, Ar-*H*), 8.09 (dd, J = 8.2, 1.5 Hz, 1H, Ar-*H*), 7.71 (t, J = 7.7 Hz, 1H, Ar-*H*), 7.60 (dd, J = 8.3, 4.2 Hz, 1H, Ar-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 101 MHz) δ ppm: 175.4 (C=S), 150.5 (C_{Ar}), 145.5 (C_{Ar}), 145.4 (C_{Ar}), 143.4 (C_{Ar}), 141.1 (C_{Ar}), 136.6 (C_{Ar}), 130.6 (C_{Ar}), 130.4 (C_{Ar}), 127.9 (C_{Ar}), 126.8 (C_{Ar}), 126.3 (C_{Ar}), 124.4 (C_{Ar}), 123.7 (C_{Ar}), 121.9 (C_{Ar}). Single crystals of $L_4H \cdot H_2O$ were obtained as large yellow blocks by recrystalisation from ethanol.

8-Quinoline 4-(4-carboxyphenyl)-3-thiosemicarbazone (L_5H): Following the general procedure, quinoline-8-carbaldehyde (868 mg, 5.52 mmol, 1.1 equiv.) 4-(4-carboxyphenyl)-3-thiosemicarbazide (1060 mg, 5.07 mmol, 1 equiv.) in methanol (40 mL) gave L_5H as an off white powder (1.03 g, 59%). Mass Spec. (HR, ESI^+) m/z: 351.0909 ($[(M+H)^+$, calc. for $C_{18}H_{17}N_4O_3S$ 351.0910); FTIR (ATR): ν (cm^{-1}): 3290 (N-H), 3149 (N-H), 2991 (C-H), 1690 (C=O), 1610 (N=C), 1084 (C=S) cm^{-1}; UV/vis (MeOH): λ_{max} 235 (ε = 14,200 L mol^{-1} cm^{-1}), 282 (ε = 12,600 L mol^{-1} cm^{-1}), 348 (ε = 12,500 L mol^{-1} cm^{-1}) nm. ^1H NMR (DMSO-d_6, 400 MHz) δ ppm: 12.24 (s, 1H, N*H*), 10.40 (s, 1H, NN*H*), 9.49 (s, 1H, H1, C*H*=N), 9.00 (dd, J = 4.2, 1.8 Hz, 1H, Ar-*H*), 8.80 (dd, J = 7.4, 1.4 Hz, 1H, Ar-*H*), 8.44 (dd, J = 8.3, 1.8 Hz, 1H, Ar-*H*), 8.09 (dd, J = 8.2, 1.4 Hz, 1H, Ar-*H*), 7.97-7.94 (m, 2H, Ar-*H*), 7.88-7.86 (m, 2H, Ar-*H*), 7.70 (t, J = 7.7 Hz, 1H, Ar-*H*), 7.61 (dd, J = 8.3 Hz, 1H, Ar-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 101 MHz) δ ppm: 175.7 (C=S), 167.0 (C=O), 150.5 (C_{Ar}), 145.5 (C_{Ar}), 143.2 (C_{Ar}), 140.5 (C_{Ar}), 136.7 (C_{Ar}), 130.8 (C_{Ar}), 130.2 (C_{Ar}), 129.4 (C_{Ar}), 127.9 (C_{Ar}), 126.9 (C_{Ar}), 126.7 (C_{Ar}), 126.4 (C_{Ar}), 124.6 (C_{Ar}), 121.9 (C_{Ar}). Single crystals of $L_5H \cdot H_2O$ were obtained as large yellow blocks by recrystalisation from ethanol.

8-Quinoline 4-(3-picolyl)-3-thiosemicarbazone (L_6H): Using the general procedure, quinoline-8-carbaldehyde (364 mg, 2.32 mmol, 1.1 equiv.) and 4-(3-picolyl)-3-thiosemicarbazide (396 mg, 2.17 mmol, 1 equiv.) in methanol (20 mL) gave yielded L_6H as off-white powder (546 mg, 78%). Mass Spec. (HR, ESI^+) m/z: 322.1118 ($[(M+H)^+$, calc. for $C_{17}H_{16}N_2S$ 322.1210), 344.0940 ($[M+Na]^+$ calc. for $C_{17}H_{15}N_2SNa$ 344.0943); FTIR (ATR): ν (cm^{-1}): 3251 (N-H), 3122 (N-H), 2903 (C-H), 1523 (N=C), 1043 (C=S) cm^{-1}; UV/vis (MeOH): λ_{max} 234 (ε = 18,400 L mol^{-1} cm^{-1}), 344 (ε = 15,700 L mol^{-1} cm^{-1}) nm. ^1H NMR (DMSO-d_6, 400 MHz) δ ppm: 11.90 (s, 1H, NN*H*), 9.38 (s, 1H, C*H*=N), 9.28 (t, J = 6.3 Hz, 1H, N*H*), 8.98 (dd, J = 4.2, 1.8 Hz, 1H, Ar-*H*), 8.65 (dd, J = 7.4, 1.4 Hz, 1H, Ar-*H*), 8.61 (d, J = 2.2 Hz, 1H, Ar-*H*), 8.46 (dd, J = 4.8, 1.7 Hz, 1H, Ar-*H*), 8.43 (dd, J = 8.4, 1.8 Hz, 1H, Ar-*H*), 8.06 (dd, J = 8.1, 1.4 Hz, 1H, Ar-*H*), 7.80 (dt, J = 7.9, 2.0 Hz, 1H, Ar-*H*), 7.68 (t, J = 7.7 Hz, 1H, Ar-*H*), 7.61 (dd, J = 8.3, 4.2 Hz, 1H, Ar-*H*), 7.36 (ddd, J = 7.8, 4.8, 0.9 Hz, 1H, Ar-*H*), 4.90 (d, J = 6.2 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 101 MHz) δ ppm: 177.8 (C=S), 150.4 (C_{Ar}), 148.9 (C_{Ar}), 148.0 (C_{Ar}), 145.3 (C_{Ar}), 139.4 (CH=N), 136.6 (C_{Ar}), 135.1 (C_{Ar}), 134.9 (C_{Ar}), 131.1 (C_{Ar}), 129.8 (C_{Ar}), 127.9 (C_{Ar}), 126.3 (C_{Ar}), 126.1 (C_{Ar}), 123.4 (C_{Ar}), 121.8 (C_{Ar}), 44.3 (CH_2). Single crystals of $L_6H \cdot$ ¼MeOH were obtained as yellow plates by evaporation from methanol.

8-Quinoline octadecyl-3-thiosemicarbazone (L_7H): Using the general procedure, quinoline-8-carbaldehyde (105 mg, 0.67 mmol, 1.1 equiv.) and octadecyl-3-thiosemicarbazide (204 mg, 0.59 mmol, 1.1 equiv.) in methanol (20 mL) gave L_7H as a dark yellow crystalline solid (215 mg, 75%). Mass Spec. (HR, ESI^+) m/z: 483.3527 ($[(M+H)^+]$, calc. for $C_{29}H_{47}N_4S$ 483.3516); FTIR (ATR): ν (cm^{-1}): 3341 (N-H), 3142 (N-H), 3090 (C-H), 1590 (N=C), 1493 (C=C), 1040 (C=S) cm^{-1}; UV/vis (MeOH): λ_{max} 234 (ε = 16,400 L mol^{-1} cm^{-1}), 343 (ε = 14,800 L mol^{-1} cm^{-1}) nm; ^1H NMR (DMSO-d_6, 400 MHz) δ ppm: 11.65 (s, 1H, N*H*), 9.33 (s, 1H, C*H*=N), 8.97 (dd, J = 4.2, 1.8 Hz, 1H, NN*H*), 8.67 – 8.56 (m, 2H, Ar-*H*), 8.42 (dd, J = 8.4, 1.8 Hz, 1H, Ar-*H*), 8.04 (dd, J = 8.1, 1.4 Hz, 1H, Ar-*H*), 7.67 (t, J

= 7.7 Hz, 1H, Ar-*H*), 7.60 (dd, J = 8.3, 4.2 Hz, 1H, Ar-*H*), 3.60 – 3.55 (m, 2H, NHCH_2), 1.62 – 1.59 (m, 2H, CH_2), 1.29 – 1.19 (m, 30H, CH_2), 0.85 – 0.82 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 101 MHz) δ ppm: 177.0 (C=S), 150.3 ($\underline{C}_{Ar}$), 145.3 ($\underline{C}_{Ar}$), 138.6 ($\underline{C}$H=N), 136.6 ($\underline{C}_{Ar}$), 131.3 ($\underline{C}_{Ar}$), 129.6 ($\underline{C}_{Ar}$), 127.9 ($\underline{C}_{Ar}$), 126.3 ($\underline{C}_{Ar}$), 125.9 ($\underline{C}_{Ar}$), 121.8 ($\underline{C}_{Ar}$), 43.5 (NH$\underline{C}H_2$), 31.3 ($\underline{C}H_2$), 29.01 – 28.98 (m, $\underline{C}H_2$), 28.8 ($\underline{C}H_2$), 28.7 ($\underline{C}H_2$), 26.4 ($\underline{C}H_2$), 22.1 ($\underline{C}H_2$), 13.9 ($\underline{C}H_3$). Single crystals of L_7H were obtained as large yellow blocks by recrystalisation from ethanol.

2.2 Synthesis of Complexes

General procedure for the synthesis of complexes $[Co(L_1)_2]BF_4$ - $[Co(L_7)_2]BF_4$: $Co(BF_4)_2{\cdot}6H_2O$ (1 equiv.) and the desired ligand L_1 – L_7 (2 equiv.) were stirred in methanol (3-20 mL) for 1 h. The resulting precipitates were collected by filtration and washed with additional methanol (2 x 10 mL) and diethyl ether (2 x 10 mL) and dried *in vaccuo* to give the coordination complexes as orange solids. $[Co(L_1)_2]BF_4$ 48%; $[Co(L_2)_2]BF_4$ 46%; $[Co(L_3)_2]BF_4$ 44%; $[Co(L_4)_2]BF_4$ 48%; $[Co(L_5)_2]BF_4$ 34%; $[Co(L_6)_2]BF_4$ 44%; $[Co(L_7)_2]BF_4$ 39%.

$[Co(L_1)_2]BF_4$: L_1H (99.5 mg, 0.325 mmol, 2 equiv.) and $Co(BF_4)_2{\cdot}6H_2O$ (59.6 mg, 0.175 mmol, 1 equiv.) in methanol (3 mL) gave $[Co(L_1)_2]BF_4$ (117.1 mg, 48%) as an orange powder. Mass Spec. (HR, ESI^+) m/z: 669.1043 ([M]+, calc. for $C_{34}H_{26}CoN_8S_2$ 669.1048); FTIR (ATR): ν (cm^{-1}): 3341 (N-H), 3090 (C-H), 1590 (N=C), 1493 (C=C), 1438 (C=C), 1040 (B-F), 744 (C-S) cm^{-1}; UV/vis (MeOH): λ_{max} 259 (ε = 19,800 L mol^{-1} cm^{-1}), 303 (ε = 9,800 L mol^{-1} cm^{-1}), 408 (ε = 7,800 L mol^{-1} cm^{-1}) nm. ^1H NMR (DMSO-d_6, 400 MHz) δ ppm: 9.76 (s, 2H, N*H*), 9.46 (s, 2H, C*H*=N), 8.86 (d, J = 5.4 Hz, 2H, Ar-*H*), 8.72 (d, J = 8.1 Hz, 2H, Ar-*H*), 8.64 (d, J = 7.4 Hz, 2H, Ar-*H*), 8.41 (d, J = 8.2 Hz, 2H, Ar-*H*), 8.04 (t, J = 7.8 Hz, 2H, Ar-*H*), 7.73 – 7.48 (m, 6H, Ar-*H*), 7.28 (t, J = 7.7 Hz, 4H, Ar-*H*), 6.99 (t, J = 7.4 Hz, 2H, Ar-*H*). Single crystals of $[Co(L_1)_2]BF_4{\cdot}2DMF$ were obtained as orange plates by slow diffusion of diethyl ether into a solution of the complex dissolved in dimethylformamide.

$[Co(L_2)_2]BF_4$: L_2H (200.0 mg, 0.617 mmol, 2 equiv.) and $Co(BF_4)_2{\cdot}6H_2O$ (113.3 mg, 0.333 mmol, 1 equiv.) in methanol (3 mL) gave $[Co(L_2)_2]BF_4$ (227.1 mg, 46%) as an orange solid. Mass Spec. (HR, ESI^+) m/z: 705.0850 ($[M]^{+\cdot}$ calc. for $C_{34}H_{24}CoF_2N_8S_2$ 705.0860); FTIR (ATR): ν (cm^{-1}): 3346 (N-H), 3088 (C-H), 1591 (N=C), 1493 (C=C), 1406 (C=C), 1050 (B-F), 775 (C-S) cm^{-1}; UV/vis (MeOH): λ_{max} 257 (ε = 33,800 L mol^{-1} cm^{-1}), 407 (ε = 13,000 L mol^{-1} cm^{-1}) nm; ^1H NMR (DMSO-d_6, 400 MHz) δ ppm: 9.79 (s, 2H, N*H*), 9.44 (s, 2H, N=C*H*), 8.85 (s, 2H, Ar-*H*), 8.73 (s, 2H, Ar-*H*), 8.62 (s, 2H, Ar-*H*), 8.42 (s, 2H, Ar-*H*), 8.04 (s, 2H, Ar-*H*), 7.63 (s, 6H, Ar-*H*), 7.12 (s, 4H, Ar-*H*). $^{19}F\{^1H\}$ NMR (DMSO-d_6, 376 MHz) δ ppm: -119.81 (C-*F*). Single crystals of $[Co(L_2)_2]BF_4{\cdot}2DMF{\cdot}\ \frac{1}{3}H_2O$ were obtained as orange plates by slow diffusion of diethyl ether into a solution of the complex dissolved in dimethylformamide.

$[Co(L_3)_2]BF_4$: L_3H (347.3 mg, 0.803 mmol, 2 equiv.) and $Co(BF_4)_2{\cdot}6H_2O$ (147.2 mg, 0.432 mmol, 1 equiv.) in methanol (5 mL) yielded $[Co(L_3)_2]BF_4$ (356.4 mg, 44%) as an orange solid. Mass Spec. (HR, ESI^+) m/z: 920.8966 ($[M]^{+\cdot}$ calc. for $C_{34}H_{24}CoI_2N_8S_2$ 920.8981); FTIR (ATR): ν (cm^{-1}): 3342 (N-H), 3077 (C-H), 1583 (N=C), 1483 (C=C), 1392 (C=C), 1049 (B-F), 778 (C-S) cm^{-1}; UV/vis (MeOH): λ_{max} 265 (ε = 19,100 L mol^{-1} cm^{-1}), 408 (ε = 7,200 L mol^{-1} cm^{-1}) nm. ^1H NMR (DMSO-d_6, 400 MHz) δ ppm: 9.83 (s, 2H, N*H*), 9.44 (s, 2H, N=C*H*), 8.96 – 8.79 (m, 2H, Ar-*H*), 8.73 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 8.62 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 8.43 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 8.05 (t, *J* = 7.9 Hz, 2H, Ar-*H*), 7.71 – 7.53 (m, 6H, Ar-*H*), 7.42 (d, *J* = 8.3 Hz, 4H, Ar-*H*). Single crystals of $[Co(L_3)_2]BF_4{\cdot}3DMF$ were obtained as orange plates by slow diffusion of diethyl ether into a solution of the complex dissolved in dimethylformamide.

$[Co(L_4)_2]BF_4$: L_4H (54.4 mg, 0.155 mmol, 2 equiv.) and $Co(BF_4)_2{\cdot}6H_2O$ (29.7 mg, 0.087 mmol, 1 equiv.) in methanol (3 mL) gave $[Co(L_4)_2]BF_4$ (62.8 mg, 48%) as an orange solid. Mass Spec. (HR, ESI^+) m/z: 759.0740, ($[M]^{+\cdot}$ calc. for $C_{34}H_{24}CoN_{10}O_4S_2$ 759.0750); FTIR (ATR): ν (cm^{-1}): 3330 (N-H), 3089 (C-H), 1590 (N=C), 1490 (N=O), 1410 (C=C), 1327 (N=O), 1176 (B-F), 1051 (B-F), 748 (C-S)

cm^{-1}; UV/vis (MeOH): λ_{max} 391 (ε = 3,800 L mol^{-1} cm^{-1}) nm. ^{1}H NMR (DMSO-d_6, 400 MHz) δ ppm: 10.41 (s, 2H, N*H*), 9.58 (s, 2H, N=C*H*), 8.88 (s, 2H, Ar-*H*), 8.76 (s, 2H, Ar-*H*), 8.67 (s, 2H, Ar-*H*), 8.57 – 8.38 (m, 2H, Ar-*H*), 8.17 (s, 4H, Ar-*H*), 8.09 (s, 2H, Ar-*H*), 7.85 (s, 4H, Ar-*H*), 7.64 (s, 2H, Ar-*H*). Single crystals of $[Co(L_4)_2]BF_4 \cdot 3DMF \cdot 1⅓\ H_2O$ were obtained as orange needles by slow diffusion of diethyl ether into a solution of the complex dissolved in dimethylformamide.

$[Co(L_5)_2]BF_4$: L_5H (500 mg, 1.427 mmol, 2 equiv.) and $Co(BF_4)_2 \cdot 6H_2O$ (245 mg, 0.719 mmol, 1 equiv.) in methanol (20 mL) yielded $[Co(L_5)_2]BF_4$ (413 mg, 34%) as an orange solid. Mass Spec. (HR, ESI^+) m/z: 757.0851 ($[M]^{+\cdot}$ calc. for $C_{36}H_{26}CoN_8O_4S_2$ 757.0845); FTIR (ATR): ν (cm^{-1}): 3333 (N-H), 3047 (C-H), 1702 (C=O), 1591 (N=C), 1485 (C=C), 1053 (B-F), 768 (C-S) cm^{-1}; UV/vis (MeOH): λ_{max} 288 (ε = 23150 L mol^{-1} cm^{-1}), 398 (ε = 13,200 L mol^{-1} cm^{-1}) nm. ^{1}H NMR (DMSO-d_6, 400 MHz) δ ppm: 10.08 (s, 2H, N*H*), 9.54 (s, 2H, N=C*H*), 8.87 (d, J = 5.1 Hz, 2H, Ar-*H*), 8.74 (d, J = 7.8 Hz, 2H, Ar-*H*), 8.66 (d, J = 7.2 Hz, 2H, Ar-*H*), 8.45 (d, J = 8.0 Hz, 2H, Ar-*H*), 8.07 (t, J = 7.7 Hz, 2H, Ar-*H*), 7.86 (d, J = 8.5 Hz, 4H, Ar-*H*), 7.72 (d, J = 8.6 Hz, 4H, Ar-*H*), 7.63 (dd, J = 8.2, 5.4 Hz, 2H, Ar-*H*). Single crystals of $[Co(L_5)_2]BF_4 \cdot 4DMF \cdot Et_2O \cdot H_2O$ were obtained as orange needles by slow diffusion of diethyl ether into a solution of the complex dissolved in dimethylformamide.

$[Co(L_6)_2]BF_4$: L_6H (49.8 mg, 0.155 mmol, 2 equiv.) and $Co(BF_4)_2 \cdot 6H_2O$ (28.2 mg, 0.083 mmol) in methanol (3 mL) gave $[Co(L_6)_2]BF_4$ (54.2 mg, 44%) as an orange solid. Mass Spec. (HR, ESI^+) m/z: 699.1250 ($[M]^{+\cdot}$ calc. for $C_{34}H_{28}CoN_{10}S_2$ 699.1266); FTIR (ATR): ν (cm^{-1}): 3355 (N-H), 3032 (C-H), 1589 (N=C), 1497 (C=C), 1420 (C=C), 1061 (B-F), 1011 (B-F), 770 (C-S) cm^{-1}; UV/vis (MeOH): λ_{max} 246 (ε = 14,500 L mol^{-1} cm^{-1}), 322 (ε = 7,400 L mol^{-1} cm^{-1}) nm; ^{1}H NMR (DMSO-d_6, 400 MHz) δ ppm: 9.09 (s, 2H, N=C*H*), 8.75 – 8.68 (m, 4H, Ar-*H*), 8.58 (s, 2H, Ar-*H*), 8.49 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 8.42 (s, 2H, Ar-*H*), 8.36 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.98 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 7.67 (s, 2H, Ar-*H*), 7.55 (t, *J* = 6.4 Hz, 4H, Ar-*H*), 4.55 – 4.31 (m, 4H, CH_2). Single crystals of $[Co(L_6)_2]BF_4$ were obtained as orange needles by slow diffusion of diethyl ether into a solution of the complex dissolved in dimethylformamide.

$[Co(L_7)_2]BF_4$: L_7H (49.8 mg, 0.103 mmol, 2 equiv.) and $Co(BF_4)_2 \cdot 6H_2O$ (19.6 mg, 0.057 mmol, 1 equiv.) in methanol (3 mL) gave $[Co(L_7)_2]BF_4$ (44.4 mg, 39%) as an orange solid. Mass Spec. (HR, ESI^+) m/z: 1021.61 ($[M]^{+\cdot}$ calc. for $C_{58}H_{90}CoN_8S_2$ 1021.6056); FTIR (ATR): ν (cm^{-1}): 3205 (N-H), 2916 (C-H), 1586 (N=C), 1497 (C=C), 1467 (C=C), 1046 (B-F), 775 (C-S) cm^{-1}; UV/vis (MeOH): λ_{max} 245 (ε = 29,900 L mol^{-1} cm^{-1}), 402 (ε = 12,100 L mol^{-1} cm^{-1}) nm ^{1}H NMR (DMSO-d_6, 400 MHz) δ ppm: 9.09 (s, 4H, N*H* & N=C*H*), 8.76 – 8.62 (m, 4H, Ar-*H*), 8.48 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 8.32 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.97 (t, *J* = 7.9 Hz, 2H, *Ar*-H), 7.58 (t, *J* = 6.6 Hz, 2H, Ar-*H*), 3.10 (s, 4H, NHCH_2), 1.22 (s, 64H, CH_2), 0.84 (t, *J* = 6.4 Hz, 6H, CH_3).

$\{[Co(L_6)_2Ag](BF_4)_2\}_\infty$: $[Co(L_6)_2]BF_4$ (20 mg, 0.025 mmol) was dissolved with stirring at RT in MeCN (10 mL) giving a dark red solution. 1 equivalent of AgBF4 (4.8 mg, 0.025 mmol) dissolved in MeCN (2 mL) was added. Single crystals of $Ag[Co(L_6)_2](BF_4)_2$ were obtained as small dark orange blocks on evaporation of the acetonitrile solution

3. Results and Discussion

3.1 Synthesis and structural analysis of ligands L_1H – L_7H

Ligands **L_1H** – **L_7H** were prepared in moderate to good yields following the general procedure of refluxing a slight excess (1.1 equivalents) of the appropriate thiosemicarbazide with quinoline-8-carbaldehyde (1 equivalent) in methanol for 2 hours (Scheme 1). **L_1H** and **L_2H** have been reported in the literature, for use as ligand for Cu(II)[43, 44] but **L_3H** – **L_7H** are novel to this study. After cooling to room temperature, the ligands were all isolated as pale-yellow crystalline solids. All spectroscopic data (^{1}H-NMR, ^{13}C-NMR, IR, MS) were consistent with the successful formation of the desired ligands (ESI). Structural determination was carried out not only to confirm the successful formation of the thiosemicarbazone ligands, but also to provide an initial assessment of the influence

that the various structure directing substituents had on the packing of these systems in the solid state. In all cases, good quality yellow single crystals, of varying morphologies, were grown by either hot recrystallization from ethanol (**L_1H – L_5H** and **L_7H**) or slow evaporation of methanol (**L_6H**) and their low temperature (100 K) structures determined (**L_1H** has been reported previously).[43]

The molecular structures of **L_2H** – **L_7H** revealed the thiourea moiety adopted an anti-conformation and the imine bond adopted a *trans* arrangement. Regardless of the structure directing group, the ligand core containing the metal-binding pocket remained relatively planar with respect to the binding pocket (mean plane 2.73 – 12.01°), whereas the structure directing group was twisted relative to the metal binding pocket (mean plane 12.30 – 57.79°). As an example, Figure 2 shows the molecular structure of **L_6H·½MeOH** (see ESI for the remaining ligands). Pleasingly, the orientation of the structure directing group away from the metal-binding core leaves it free to participate in various supramolecular interactions (dependent on the functionality present) and dictate long range ordering within the material. It is this ordering that is important for many supramolecular materials-based applications, and indeed if these structure extending interactions are also observed in the metal complexes, we will have access to large families of metal-containing building blocks that can be assembled into larger, more complex architectures.

3.2 Synthesis and structural analysis of coordination complexes $[Co(L_1)_2]BF_4$ - $[Co(L_7)_2]BF_4$

Complexes **$[Co(L_1)_2]BF_4$** – **$[Co(L_7)_2]BF_4$** were synthesized by reaction of two equivalents of the desired ligand with $Co(BF_4)_2.6H_2O$ in methanol (Scheme 2). In each case the addition of the metal salt to the methanolic ligand solution resulted in dramatic color changes from pale yellow/orange to dark orange/brown. The resulting coordination complexes precipitated from solution over the course of the reaction (~1 hour) and were isolated as dark orange solids in moderate yields. The complexes were fully characterized using ^1H and ^{19}F (where appropriate) NMR, IR and UV/vis spectroscopy, mass spectrometry and where possible SC-XRD. All spectroscopic data was consistent with complexes adopting the general formula $[M(\mathbf{L_x})_2]BF_4$ with the cobalt in the 3+ oxidation state and the thiosemicarbazone ligands binding as monoanionic species *via* the thioenolate tautomer as opposed to the thioketo tautomer.

Characterisation data was fully consistent with successful formation of the complexes. High-resolution mass spectra showed the expected peaks and isotopic distributions for the $[M(\mathbf{L_x})_2]^+$ ions. Electronic spectra of all complexes were obtained in MeOH (*ca.* 1 x 10^{-5} mol L^{-1}) and showed the expected broad charge-transfer absorptions at ~400 nm. ^1H NMR spectra were collected of all Co(III) complexes in d_6-DMSO. All complexes showed shifted spectra when compared to the corresponding ligands and loss of one NH resonance (see Figures S1 – S14 in the ESI). The same NMR solutions were re-collected two weeks later and appeared unchanged indicating significant solution stability. Such solution stability is ideal for our goal of developing complex metallosupramolecular materials as solution processability can allow for immobilization via methods such as gel formation, Langmuir-Blodgett film formation and incorporation into polymer matrices.

Single crystals of all complexes except **$[Co(L_7)_2](BF_4)$** were grown by diffusion of diethyl ether into solutions of the complexes and structural characterisation carried out at low temperature (100 K, collection parameters and refinement data in ESI). All complexes comprise two ligands (at *ca.* 90° to each other) bound to the Co(III) centre through the quinoline nitrogen atom, the imine nitrogen atom and the sulfur atom. The tautomerised form of the ligands were further confirmed through analysis of the C-S bond length [range = 1.724(4) – 1.752(5) Å] relative to the shorter C=S bond length of the free ligand [range = 1.662(2) – 1.698(4) Å] (see table S3 in the supporting information). All complexes therefore adopt an N_4S_2 distorted octahedral coordination sphere which is confirmed through analysis of the Σ values [31.71 – 40.19°]. Bond lengths and angles (table 1) are all consistent with the expected LS

Co(III) state [Co-N_{quin} = 2.008(2) – 2.041(3) Å; Co-N_{imine} = 1.904(2) – 1.925(2) Å; Co-S = 2.195(2) – 2.236(5) Å].

The influence of the structure directing substituents was again analysed in order to ascertain how they alter packing and, more importantly, how they induce interaction between complex molecules throughout the solid state. In the majority of complexes the BF_4^- anion and interstitial solvent molecules form strong hydrogen bonding interactions to the thiourea NH groups, and the aromatic rings are typically involved in π-stacking interactions. With the focus of this manuscript being on structure extension *via* the ligand substituent, only interactions involving these substituents (structure directing groups) are discussed. [Co(**L₁**)₂]BF_4·2DMF crystallised in the monoclinic space-group *C*2/*c* and contained half of one complex molecule in the asymmetric unit with the other half generated by symmetry. The phenyl rings do not appear to contribute to the overall packing as there are no obvious structure directing interactions to or from the phenyl rings, this in essence acts as our "base-line" model complex from which to compare with the systems where deliberate structure directing moieties are included. [Co(**L₂**)₂]BF_4·2DMF·⅓H_2O crystallised in the triclinic space-group *P*-1 and contained one complex molecule in the asymmetric unit. The mono-fluorinated phenyl ring appears to facilitate very weak π-stacking interactions to quinoline groups of neighbouring complexes [centroid-centroid distances = 3.684 and 3.728 Å] (Figure 3).

[Co(**L₃**)₂]BF_4·3DMF crystallised in the triclinic space-group *P*-1 and contained one complex molecule in the asymmetric unit and has similar packing to that seen in [Co(**L₂**)₂]BF_4·2DMF·⅓H_2O where the *p*-iodophenyl substituent is involved in π-stacking to neighbouring quinoline, albeit significantly weaker [centroid-centroid distances = 3.862 Å and 3.921 Å].

[Co(**L₄**)₂]BF_4·3DMF·1⅓H_2O in which a *para*-nitro phenyl substituent is included, crystallised in the monoclinic space group *C*2/*c* and contained two half complexes in the asymmetric unit with the other halves generated by symmetry. The two crystallographically independent molecules differ in the arrangement of the ligands around the Co(III) centres. Interestingly, the structure shows very little in the way of structure extending interactions despite $NO_2\cdots NO_2$ interactions being involved in other crystal engineering studies.[45] Weak $CH\cdots NO_2$ [C(16)···O(22) = 3.412 Å and <(C(16)-H(16)···N(22)) = 169°] and $NO_2\cdots NO_2$ [O(1) ···N(25) = 3.568 Å] interactions appear to be present, however it appears that the weak structure directing ability of nitro groups sees the NO_2 groups interact with the DMF and H_2O interstitial solvent molecules rather than each other.

[Co(**L₅**)₂]BF_4·4DMF·H_2O·Et_2O crystallised in the monoclinic space group *Ia* and contained one complete complex molecule in the asymmetric unit. The carboxylic acid substituents are involved in typical COOH···HOOC dimer formation (Figure 5). The result of these dimeric interactions are zig-zag chains throughout the extended structure [O(1)···O(22) = 2.624(5) Å and <(O(1)- H(1A)···O(22))= 175.0(2)°], [O(21)···O(2) = 2.600(5) Å and <(O(21)-H(21)···O(2))= 175.1(2)°].

[Co(**L₆**)₂]BF_4 crystallised in the monoclinic space group $P2_1/c$ and contained one molecule in the asymmetric unit. The inclusion of the hydrogen bond donor picolyl group in [Co(**L₆**)₂]BF_4 significantly alters the long-range ordering relative to the aforementioned complexes. Rather than the thioamide NH groups interacting with the BF_4^- counter ion or interstitial solvent molecules as is the case in all other complexes, in [Co(**L₆**)₂]BF_4 the picolyl nitrogen atoms form strong hydrogen bonding interactions to the NH groups of neighbouring complex molecules resulting in the formation of a hydrogen-bonded extended network [N(4)···N(25)' = 2.916(2) Å and <(N(4)-H(4)···N(25)')= 166(2)°], [N(24)···N(5)' = 3.029(2) Å and <(N(24)-H(24)···N(5)')= 146(2)°] (Figure 6).
Whilst the 3-picolyl group can act as a hydrogen bond acceptor to form the aforementioned H-bonded network, it was originally incorporated into these ligand systems for its ability to act as a second metal coordination site. In order to test this we attempted to prepare a silver complex of [Co(**L₆**)₂]BF_4 as Ag(I) had previously been used to prepare mixed metal Ag(I)-Co(III) extended networks.

Complexation was carried out in a 1:1 ratio of $[Co(\mathbf{L_6})_2]BF_4$ to $Ag(BF_4)$ in DMF. Vapour diffusion of diethyl ether into the reaction solution gave a small number of dark red/grey block-like crystals.

The molecular structure shows coordination of the Ag(I) to to $[Co(\mathbf{L_6})_2]BF_4$ resulting in the formation of a 2D coordination polymer, where the silver ions coordinate to two picolyl nitrogen atoms from different molecules and bridge two sulfur atoms from the same molecule. The Co(III) retains its distorted octahedral geometry (Σ = 32.2°) with an N_4S_2 coordination sphere provided by the thiosemicarbazone-quinoline binding pocket. The Ag(I) centre adopts a 4-coordinate 'see-saw' geometry (τ_4 = 0.67)[46] with N_2S_2 coordination (Figure 7) where the Ag···N (2.245 and 2.296 Å) and Ag···S (2.731 and 2.733 Å) bond lengths are within the expected range for four-coordinate Ag(I) complexes.[47] There is also a weak interaction between the Ag(I) and one of the disordered BF_4^- counterions. The incorporation of Ag(I) into $[Co(\mathbf{L_6})_2]BF_4$ results in the linking of three $Co(\mathbf{L_6})_2^+$ cations where two sulfur donor atoms (S1 and S21) are provided by one complex, and two picolyl nitrogen donor-atoms (N5' and N25") are provided by two different neighbouring complexes. The overall result is formation of 2D sheets of $\{[Co(\mathbf{L_6})_2Ag](BF_4)_2\}$ that run perpendicular to the crystallographic a-axis (Figure 7). The layers of sheets are stacked along the a-axis where they interact *via* hydrogen bonding interactions to BF_4^- counterions (both NH···F and CH···F) and also π-stacking between neighbouring quinoline groups (centroid···centroid = 3.642 Å). The ability of these Co(III) systems to further self-assemble and form extended coordination networks is a key result from this study as it showcases the usefulness of these complexes for supramolecular materials formation.

3.3 Langmuir-Blodgett studies

The ability of $\mathbf{L_7H}$ and $[Co(\mathbf{L_7})_2]BF_4$ to self-assemble at an air−water interface and form Langmuir monolayers was investigated by spreading aliquots of $\mathbf{L_7H}$ or $[Co(\mathbf{L_7})_2]BF_4$ (30 μL) using DCM:Hexane (50:1) as the spreading solvent, onto the surface of a water subphase at room temperature. A typical surface pressure−area isotherm was obtained in each case (Figure 8) in which an exponential increase in surface pressure evidenced upon slow decrease of the area (10 mm min^{-1}). The films were observed to collapse at 28 mN m^{-1} for $\mathbf{L_7H}$ and 50 mN m^{-1} for $[Co(\mathbf{L_7})_2]BF_4$ with areas of 26 ± 5 $Å^2$ per molecule and 51 ± 5 $Å^2$ per molecule respectively. The areas observed for $\mathbf{L_7H}$ and $[Co(\mathbf{L_7})_2]BF_4$ are approximately those expected for one and two alkyl chains respectively and indicate that the complex remained intact at the air−water interface with supramolecular organization into monolayers. The Langmuir monolayer stability was also assessed by maintaining the monolayers at the liquid-condensed phase for an extended period of time (~ 50 min) and monitoring the surface pressure over that same time. The stability results are displayed in the inset in Figure 8 and show excellent stability properties for both the $\mathbf{L_7H}$ and $[Co(\mathbf{L_7})_2]BF_4$ films.

The complex $[Co(\mathbf{L_7})_2]BF_4$ was transferred onto a quartz slide, generating a Langmuir−Blodgett monolayer film with a transfer ratio of ∼1 on the *emersion* of the quartz slide (Figure S29 in ESI). Multi-layering studies were also carried out and it was found that $[Co(\mathbf{L_7})_2]BF_4$ was able to form a 2-layer Z-type (all head groups pointing towards the quartz substrate multi-layered film.[14] This was evidenced by transfer ratios of 0.8 - 1 on emersion, but 0 on immersion. After 2-layers were deposited the film appeared to delaminate on subsequent immersion as a transfer ratio of -1 was observed (see Figure S30 in ESI). The film was deposited again on emersion (transfer ratio of 1). UV-vis analysis of the mono- and multi-layered substrates indicated that the complex remained intact on deposition as it had the same spectral features as a solution of the complex (see Figure S31 in ESI). Specifically, the intense charge transfer band at ca. 450 nm observed in solution is present in the spectra of the mono- and multi-layers. This study again demonstrated the ability of thiosemicarbazone based complexes to successful form self-assembled monolayers, a critical aspect of this study – *i.e.* demonstrating the ability of these systems to form supramolecular materials.

4. Conclusions

We have reported on the synthesis and characterisation of seven new 8-Quinoline-4-**R**-3-thiosemicarbazone ligands and their Co(III) complexes. The complexes display significant stability in solution over extended periods of time. The nature of the ligand substituents dictated the solid-state packing of the resulting complexes and allowed for structure directing groups to be readily built into these switchable systems. In this study it ranged from simple aromatic substituents with minimal structure directing ability ($[\mathbf{Co(L_1)_2}]\mathbf{BF_4}$ through to $[\mathbf{Co(L_4)_2}]\mathbf{BF_4}$) through to those with H-bonding abilities (e.g. the *p*-benzoic acid substituent in $[\mathbf{Co(L_5)_2}]\mathbf{BF_4}$ showed the expected H-bond dimerization into chain like networks while the H-bond picolyl acceptor in $[\mathbf{Co(L_6)_2}]\mathbf{BF_4}$ showed 3D H-bond network formation). The ability to target specific materials applications was demonstrated in $[\mathbf{Co(L_6)_2}]\mathbf{BF_4}$ where the metal binding picolyl group was used for multi-metal coordination polymer formation (by reaction of $[\mathbf{Co(L_6)_2}]\mathbf{BF_4}$ with Ag^+ to give $\{[Co(\mathbf{L_6})_2Ag](BF_4)_2\}_\infty$. Perhaps the best example of targeted supramolecular materials development was seen in $[\mathbf{Co(L_7)_2}]\mathbf{BF_4}$ where the long alkyl carbon chain was included for the express purpose of ultra-thin-film formation using Langmuir-Blodgett deposition. Overall, the facile and modular synthesis of these systems, the stable and predictable coordination to transition metals, and the ability to introduce many different peripheral structure directing groups renders these complexes as excellent candidates for multi-functional supramolecular materials.

5. References

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Tables

Table 1: **Selected bond lengths (Å), angles (°) and structural parameters for Co(III) complexes**

	$[Co(L_1)_2]BF_4 \cdot 2DMF$	$[Co(L_2)_2]BF_4 \cdot 2DMF \cdot \frac{1}{3}H_2O$	$[Co(L_3)_2]BF_4 \cdot 3DMF$	$[Co(L_4)_2]BF_4 \cdot 3DMF \cdot 1H_2O$	$[Co(L_5)_2]BF_4 \cdot 4DMF \cdot Et_2O \cdot H_2O$	$[Co(L_6)_2]BF_4$
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
$Co–N_{quinoline}$	2.008(2)	2.041(3)	2.012(5)	2.021(2)	2.015(4)	2.013(2)
		2.017(4)	2.020(4)		2.030(4)	2.016(2)
$Co–N_{imine}$	1.915(2)	1.904(3)	1.914(4)	1.925(2)	1.918(5)	1.909(2)
		1.912(3)	1.906(4)		1.920(5)	1.913(2)
Co–S	2.2173(7)	2.227(2)	2.203(2)	2.2105(6)	2.226(2)	2.2220(5)
		2.196(2)	2.228(2)		2.220(2)	2.2360(5)
Cis angle range	85.59(6) – 94.13(8)	85.0(2) - 94.5(2)	85.3(2) - 94.7(2)	85.97(5) - 95.01(7)	85.6(2) - 95.6(2)	85.17(5) - 94.68(6)
Σ	37.67	31.71	36.71	37.93	40.19	36.44

Figure Captions

Figure 1: Properties of quinoline thiosemicarbazone transition metal complexes which render them excellent candidates for functional supramolecular materials

Scheme 1: Synthesis of ligands L_1H – L_7H

Figure 2: Molecular structure and atom labelling scheme for $L_6H·½MeOH$ (partial occupancy MeOH removed for clarity; thermal ellipsoids 50%).

Scheme 2. Synthesis of complexes $[Co(L_1)_2]BF_4$ - $[Co(L_7)_2]BF_4$

Figure 3. Weak π-stacking interactions between fluorinated phenyl rings and quinoline rings of adjacent molecules of $[Co(L_2)_2]BF_4·2DMF·⅓H_2O$ (H-atoms, anions and solvent emitted for clarity). Colour code: grey = carbon; blue = nitrogen; yellow = sulfur, green = fluorine and purple = cobalt, Symmetry *-x, +y, 0.5-z*.

Figure 4. Molecular structures showing selected atom numbering scheme of a) $[Co(L_1)_2]BF_4·2DMF$ [*-x, +y, 0.5-z*] b) $[Co(L_2)_2]BF_4·2DMF·⅓H_2O$, c) $[Co(L_3)_2]BF_4·3DMF$ d) $[Co(L_4)_2]BF_4·3DMF·1⅓H_2O$ [*-x, +y, 0.5-z*], e) $[Co(L_5)_2]BF_4·4DMF·Et_2O·H_2O$, f) $[Co(L_6)_2]BF_4$. Hydrogen atoms, anions and solvent molecules have been excluded for clarity (thermal ellipsoids 50%).

Figure 5: Chains of $[Co(L_5)_2]^+$ formed by hydrogen bonding interactions between carboxylate groups on adjacent molecules. Colour code: grey = carbon; blue = nitrogen; yellow = sulfur, red = oxygen and purple = cobalt.

Figure 6: Extended hydrogen bonding network formed between molecules of $[Co(L_6)_2]^+$. Colour code: Grey = carbon; blue = nitrogen; yellow = sulfur and purple = cobalt.

Figure 7: Extended Ag^+ coordination network formed between molecules of $[Co(L_6)_2]^+$ giving rise to the coordination polymer $\{[Co(L_6)_2Ag](BF_4)_2\}_\infty$. Colour code: Grey = carbon; blue = nitrogen; yellow = sulfur, purple = cobalt and pink = silver.

Figure 8: Surface pressure-area isotherm for L_7H and $[Co(L_7)_2]BF_4$, and the stability of the monolayers over time (inset).