

Synthesis, chemical characterization and cancer cell growth-inhibitory activities of Cu(II) and Ru(III) aliphatic and aromatic dithiocarbamate complexes.

L. Brustolin,^{†a,b} C. Nardon,^{†a} N. Pettenuzzo,^a N. Z. Fantoni,^a S. Quarta,^c F. Chiara,^d A. Gambalunga,^d A. Trevisan,^d L. Marchiò,^e P. Pontisso,^c D. Fregona^{*a}

^a Department of Chemical Sciences, University of Padova, Via F. Marzolo 1, 35131 Padova (Italy)

^b Department of Surgical, Oncologic and Gastroenterological Sciences, University of Padova, Via Giustiniani 2, 35128, Padova (Italy)

^c Department of Medicine, University of Padova, Via Giustiniani 2, 35128, Padova (Italy)

^d Department of Cardiac, Thoracic, and Vascular Sciences, University of Padova, Via Giustiniani 2, 35128, Padova (Italy)

^e Department of Chemical, Life and Sustainability Sciences, Parco Area delle Scienze 11/a, 43124, Parma (Italy)

[†] These authors contributed equally.

*Author to whom correspondence may be addressed: dolores.fregona@unipd.it

Experimental Section

Instruments

Analytical TLC was carried out on Kiesegel F254; UV light ($\lambda = 254$ nm). Gravity column chromatography was performed on Silica gel 60 (0.063-0.200 mm, 70-230 mesh) (Merck); the elution of each loaded compound was obtained by using a proper eluent mixture.

Elemental analyses were carried out at the Microanalysis Laboratory of the Department of Chemical Sciences, University of Padova by using a microanalyzer Fisons EA-1108 CHNS-O and a microanalyzer Carlo Erba 1108 CHNS-O.

ESI-MS spectra were recorded by a Mariner Perspective Biosystem instrument, in the positive mode setting a 5-kV ionization potential and a 20 $\mu\text{L}/\text{min}$ flow rate. A mixture of coumarin and 6-methyl-triptophan was used as a standard. Samples were dissolved in methanol, water or acetonitrile, whereas methanol with 1% formic acid was used as an eluent. ESI-MS spectra have been processed by the software Data Explorer.

Near-FTIR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded at room temperature (32 scans, resolution 2 cm^{-1}) by Nicolet Nexus 55XC spectrophotometer. KBr pellets of samples were prepared according to

standard procedures. Far-FTIR spectra ($600\text{--}50\text{ cm}^{-1}$) were acquired at room temperature with a Nicolet Nexus 870 spectrophotometer. For the analysis, films of sample dispersed in nujol were loaded into polyethylene discs (250 scans, resolution 4 cm^{-1}). Spectra were processed with OMNIC 5.2 (Nicolet Instrument Corporation).

^1H -NMR spectra of metal-DTC complexes were recorded at 298 K with a Bruker Avance DRX300 spectrometer equipped with a BBI [^1H , X] probe-head, Bruker. Typical acquisition parameters for 1D ^1H -NMR spectra (^1H : 300.13 MHz): normal pulse sequence, 64 transients, spectral width 15 ppm (80 ppm in the case of $[\text{Ru}(\text{DTC})_3]$ compounds), using a delay time of 1.0 - 4.0 seconds. The data sets were processed with the standard Bruker processing software package Topspin 1.3. Chemical shifts were referenced to solvent signal. Peak assignment and integral calculations were carried out by means of MestReNova (version 6.2.0, Mestrelab Research S.L.).

Absorption spectra of freshly-prepared solutions of the samples were acquired at 25 °C and 37 °C in the range 200-800 nm with an Agilent Cary 100 UV-Vis double beam spectrophotometer, taking into account the solvent cutoff. Samples were dissolved in the proper solvents and the resulting solutions were placed in QS quartz cuvettes (path length 1 cm).

For *n*-octanol/water partition coefficient ($\text{Log}P$) measurements, a weighted amount of a selected metal-DTC complex (*ca.* 1 mg) was dissolved in *n*-octanol (20 mL), previously pre-saturated with deionized water for 24 hours. The obtained solution was shaken for 2 hours in the presence of 20 mL of deionized water at 25 °C and, subsequently, the mixture was left to equilibrate for 30 minutes. The concentration of every metal-DTC derivative in the *n*-octanol phase before (C_0) and after partitioning (C_1) was measured by UV-Vis spectrophotometry, followed by the evaluation of the corresponding $\text{Log}P = \log (C_1)/(C_0 - C_1)^{31}$.

For the X-ray analysis, a summary of data collection and structure refinement for the derivatives $[\text{Cu}(\text{ProOMeDTC})_2]$, and $[\text{Cu}(\text{ProOtBuDTC})_2]$ is reported in **Table SI 1**. Single crystal data were collected with a Bruker Smart Breeze and a Bruker D8 venture PhotonII, Mo K_α : $\lambda = 0.71073\text{ \AA}$. The intensity data were integrated from several series of exposures frames (0.3° width) covering the sphere of reciprocal space (SMART (control) and SAINT (integration) software for CCD systems; Bruker (2012) - Bruker AXS Inc., Madison, Wisconsin, USA). Absorption correction was applied using the program SADABS.¹ The structures were solved by the dual space algorithm implemented in the SHELXT code² or by direct methods using SIR2004.³ Fourier analysis and refinement were performed by the full-matrix least-squares methods based on F^2 implemented in SHELXL-2014.⁴ Graphical

material was prepared with the Mercury 3.9 program.⁵ CCDC 1845778 and 1845779 contain the supplementary crystallographic data for this paper.

	[Cu(ProOMeDTC) ₂]	[Cu(ProOtBuDTC) ₂]
Empirical formula	C ₁₄ H ₂₀ CuN ₂ O ₄ S ₄	C ₂₀ H ₃₂ CuN ₂ O ₄ S ₄
Formula weight	472.10	556.25
Temperature/K	293(2)	250(2)
Crystal system	orthorhombic	monoclinic
Space group	P2 ₁ 2 ₁ 2	C2
a/Å	14.80(1)	27.516(2)
b/Å	6.623(5)	6.701(5)
c/Å	10.02(1)	17.479(1)
α/°	90	90
β/°	90	119.506(3)
γ/°	90	90
Volume/Å ³	982.2(14)	2805.0(4)
Z	2	4
ρ _{calc} /cm ³	1.596	1.317
μ/mm ⁻¹	1.558	1.102
F(000)	486.0	1164.0
Crystal size/mm ³	0.41 × 0.12 × 0.10	0.23 × 0.04 × 0.04
2θ range (°)	4.064 to 49.55	5.960 to 51.396
Reflections collected/unique	10449/1693	36929/5315
Data/restraints/ parameters	1693/0/115	5315/1/286
Goodness-of-fit on F ²	1.008	1.068
R ₁ [I > 2σ (I)]	0.0367	0.0352
wR ₂ [I > 2σ (I)]	0.0771	0.0952
Flack parameter	0.015(19)	0.031(6)

Table SI 1. Summary of X-ray crystallographic data for [Cu(ProOMeDTC)₂] and [Cu(ProOtBuDTC)₂].

$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Synthesis of the selected cyclic N,N-disubstituted dithiocarbamate ligands **a-i**

Sodium pyrrolidine dithiocarbamate (NaPDT, **a**) is commercially available and was purchased, as well as all the necessary reagents for chemical syntheses, from Sigma-Aldrich.

*Synthesis of the aliphatic dithiocarbamate ligands derived from piperidine **b** and morpholine **c***

An equimolar amount (10 mmol) of the parent amine (piperidine or morpholine) and potassium hydroxide were dissolved in 100 mL ethanol and the solution was set at 0 °C. Then, an excess of

carbon disulfide (CS₂) was added, yielding a light yellow mixture which was kept under vigorous stirring for 1 hour. Afterwards, the solvent volume was reduced and the product precipitated by adding cold diethyl ether, filtered, and dried *in vacuum* in the presence of P₂O₅.

Both the dithiocarbamate ligands result soluble in water, methanol, ethanol, DMSO, DMF, and acetonitrile. Slightly soluble in chloroform and dichloromethane.

Piperidine dithiocarbamate potassium salt (K PipeDTC), **b**

Aspect: white solid. Yield: 95%. Mp.: 215 °C (dec.). ¹H-NMR (DMSO-d₆, 300.13 MHz): δ (ppm) = 1.39 (m, 4H, H₍₃₎ + H₍₅₎), 1.54 (m, 2H, H₍₄₎), 4.27 (t, 4H, H₍₂₎ + H₍₆₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2923.75, 2851.10 (ν_a, C-H); 1417.12 (ν_a, N-CSS); 965.00 (ν_a, CSS); 516.25 (ν_s, CSS). ESI-MS *m/z*, [DTC⁻] found (calc.): 160.03 (160.02). Anal. Calc. for C₆H₁₀KNS₂ (MW = 199.38 g·mol⁻¹): C 36.14; H 5.06; N 7.03; S 32.16. Found: C 35.84; H 5.02; N 7.05; S 32.22.

Morpholine dithiocarbamate potassium salt (K MorphDTC), **c**

Aspect: white solid. Yield: 85%. Mp.: 323 °C (dec.). ¹H-NMR (DMSO-d₆, 300.13 MHz): δ (ppm) = 3.47 (m, 4H, H₍₂₎ + H₍₆₎), 4.30 (t, 4H, H₍₃₎ + H₍₅₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2982.44, 2921.73, 2867.68 (ν_a, C-H); 1410.44 (ν_a, N-CSS); 1109.77 (ν_a, C-O); 989.60 (ν_a, CSS); 546.56 (ν_s, CSS). ESI-MS *m/z*, [DTC⁻] found (calc.): 162.01 (162.00). Anal. Calc. for C₅H₈KNOS₂ (MW = 200.97 g·mol⁻¹): C 29.83; H 4.00; N 6.96; S 31.85. Found: C 29.88; H 4.03; N 6.91; S 31.91.

*Synthesis of the aliphatic dithiocarbamate ligand derived from indoline **d***

An excess of potassium hydroxide (KOH) was suspended in 100 mL of tetrahydrofuran (THF); then 5.5 mmol of indoline were added and the solution mixture was set at 0 °C. Afterwards, 10 mmol of carbon disulfide were added, resulting in a bright yellow mixture which was kept under vigorous stirring for 1 hour. Then, the residual KOH was filtered and the solution evaporated, leading to a solid product, which was dried *in vacuum* over P₂O₅.

The ligand results soluble in water, methanol, ethanol, DMSO, DMF, and THF. Slightly soluble in chloroform and dichloromethane.

Indoline dithiocarbamate potassium salt (K IndolineDTC), **d**

Aspect: bright yellow solid. Yield: 88%. Mp.: 335 °C (dec.). ¹H-NMR (DMSO-d₆, 300.13 MHz): δ (ppm) = 2.87 (t, 2H, H₍₃₎), 4.45 (t, 2H, H₍₂₎), 6.80 (t, 1H, H₍₅₎), 7.00 (t, 1H, H₍₆₎), 7.10-7.12 (d, 1H, H₍₄₎), 9.52-9.55 (d, 1H, H₍₇₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2931.52 (ν_a, C-H); 1452.26 (ν, C=C ring); 1371.36 (ν_a, N-CSS); 931.11 (ν_a, CSS); 743.21 (δ, C-H); 507.81 (ν_s, CSS). ESI-MS *m/z*, [DTC⁻] found (calc.): 194.02

(194.01). Anal. Calc. for $C_9H_8KNS_2$ (MW = 233.39 g·mol⁻¹): C 46.31; H 3.45; N 6.00; S 27.48. Found: C 46.19; H 3.44; N 6.09; S 27.40.

Synthesis of dithiocarbamate ligands of L-proline derivatives e, f

The sodium salts of L-proline methyl ester dithiocarbamate (Na ProOMeDTC, **e**) and L-proline *tert*-butyl ester dithiocarbamate (Na ProOtBuDTC, **f**) were synthesized in a Schlenk-line apparatus under a N₂ atmosphere. 10 mmol of sodium *tert*-butoxide were dissolved in 20 mL of anhydrous methanol. Afterwards, 5 mmol of the chosen amine hydrochloride, previously dissolved in 10 mL of anhydrous methanol, were added and the solution mixture was set at 0 °C. Then, 10 mmol of carbon disulfide were added, leading to a light yellow mixture which was kept under vigorous stirring for 1 hour. Then, the solvent was evaporated under reduced pressure and the product was taken up in dichloromethane in order to remove NaCl as a byproduct. Finally, the solvent was removed, yielding a hygroscopic solid, which was dried in pump over P₂O₅. Being highly hygroscopic, both products are stored under inert atmosphere.

Both the proline-dithiocarbamate ligands result soluble in water, methanol, ethanol, DMSO, DMF, ethyl acetate, and acetone. Slightly soluble in chloroform and dichloromethane.

L-proline methyl ester dithiocarbamate sodium salt (Na ProOMeDTC), **e**

Aspect: white hygroscopic solid. Yield: 78%. Mp.: n.d. ¹H-NMR (CD₃OD, 300.13 MHz): δ (ppm) = 2.03-2.33 (m, 4H, H₍₃₎ + H₍₄₎), 3.69 (s, 3H, O-CH₃), 3.95 (m, 2H, H₍₅₎), 5.07-5.11 (dd, 1H, H₍₂₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2953.03 (ν_a , C-H); 1733.20 (ν , C=O); 1392.38 (ν_a , N-CSS); 1177.76 (ν_a , C-OMe); 944.78 (ν_a , CSS); 504.45 (ν_s , CSS). ESI-MS *m/z*, [DTC⁻] found (calc.): 204.03 (204.02). Anal. Calc. for C₇H₁₀NNaO₂S₂ (MW = 227.28 g·mol⁻¹): C 36.99; H 4.43; N 6.16; S 28.22. Found: C 36.82; H 4.51; N 6.10; S 28.28.

L-proline *tert*-butyl ester dithiocarbamate sodium salt (Na ProOtBuDTC), **f**

Aspect: beige hygroscopic solid. Yield: 77%. Mp.: n.d. ¹H-NMR (CD₃OD, 300.13 MHz): δ (ppm) = 1.47 (s, 9H, O-C(CH₃)₃), 2.01-2.30 (m, 4H, H₍₃₎ + H₍₄₎), 3.94 (m, 2H, H₍₅₎), 4.97-4.99 (dd, 1H, H₍₂₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2974.63 (ν_a , C-H); 1722.65 (ν , C=O); 1388.27 (ν_a , N-CSS); 1151.18 (ν_a , C-OtBu); 932.89 (ν_a , CSS); 502.02 (ν_s , CSS). ESI-MS *m/z*, [DTC⁻] found (calc.): 246.07 (246.06). Anal. Calc. for C₁₀H₁₆NNaO₂S₂ (MW = 269.36 g·mol⁻¹): C 44.59; H 5.99; N 5.20; S 23.81. Found: C 44.41; H 6.02; N 5.19; S 23.76.

Synthesis of dithiocarbamate ligand of aromatic N-heterocycles g-i

The sodium salts of carbazole dithiocarbamate (Na CDT), indole dithiocarbamate (Na IndDTC), and pyrrole dithiocarbamate (Na PyrrDTC) were synthesized in a Schlenk-line apparatus in a N₂ atmosphere with a modification of literature procedure.⁶ Pyrrole was purified by distillation immediately before use.

To 1.44 mmol of aromatic amine previously dissolved in anhydrous THF, 2.88 mmol of NaH 60% suspension were added at 0 °C. The mixture was kept under vigorous stirring for 10 minutes, followed by filtration under inert atmosphere of nitrogen to remove NaH residues. Subsequently, 2.88 mmol of carbon disulfide were added to the resulting solution under stirring at 0 °C. After 2 h, the solvent was removed under reduced pressure and the solid was taken up in a minimum amount of anhydrous THF and precipitated with hexane. The resulting solid was filtered and dried under vacuum in the presence of P₂O₅. All products were stored under inert atmosphere, as they resulted highly hygroscopic and air sensitive. Analyses are in agreement with literature data.⁶

These aromatic dithiocarbamate ligands result soluble in water, methanol, ethanol, DMSO, DMF, and THF. Slightly soluble in chloroform, dichloromethane and benzene.

Carbazole dithiocarbamate sodium salt (Na CDT), **g**

Aspect: orange hygroscopic solid. Yield: 88%. Mp.: n.d. ¹H-NMR (DMSO-d₆, 300.13 MHz): δ (ppm) = 7.17 (t, 2H, H₍₃₎ + H₍₆₎), 7.33 (t, 2H, H₍₂₎ + H₍₇₎), 8.05-8.08 (d, 2H, H₍₄₎ + H₍₅₎), 8.45-8.47 (d, 2H, H₍₁₎ + H₍₈₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 1435.84 (ν, C=C ring); 1281.47 (ν_a, N-CSS); 1040.03 (ν_a, CSS); 832.62 (ω, C-H); 742.53 (δ, C-H); 569.77 (ν_s, CSS). ESI-MS *m/z*, [DTC⁻] found (calc.): 242.01 (242.01). Anal. Calc. for C₁₃H₈NNaS₂ (MW = 265.33 g·mol⁻¹): C 58.85; H 3.04; N 5.28; S 24.17. Found: C 58.69; H 3.15; N 5.31; S 24.11.

Indole dithiocarbamate sodium salt (Na IndDTC), **h**

Aspect: yellow-orange hygroscopic solid. Yield: 71%. Mp.: n.d. ¹H-NMR (DMSO-d₆, 300.13 MHz): δ (ppm) = 6.36-6.37 (d, 1H, H₍₃₎), 7.03-7.11 (m, 2H, H₍₅₎ + H₍₆₎), 7.45-7.48 (d, 1H, H₍₄₎), 8.66-8.68 (d, 1H, H₍₂₎), 9.31-9.34 (d, 1H, H₍₇₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2923.17 (ν_a, C-H); 1439.44 (ν, C=C ring); 1289.94 (ν_a, N-CSS); 997.91 (ν_a, CSS); 824.65 (ω, C-H); 752.33 (δ, C-H); 550.32 (ν_s, CSS). ESI-MS *m/z*, [DTC⁻] found (calc.): 192.00 (191.99). Anal. Calc. for C₉H₆NNaS₂ (MW = 215.27 g·mol⁻¹): C 50.21; H 2.81; N 6.51; S 29.79. Found: C 50.11; H 2.99; N 6.40; S 29.89.

Pyrrole dithiocarbamate sodium salt (Na PyrrDTC), **i**

Aspect: dark yellow hygroscopic solid. Yield: 66%. Mp.: n.d. ¹H-NMR (DMSO-d₆, 300.13 MHz): δ (ppm) = 5.99 (s, 2H, H₍₃₎ + H₍₄₎), 8.03 (s, 2H, H₍₂₎ + H₍₅₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2923.10 (ν_a, C-

H); 1457.21 (ν , C=C ring); 1259.12 (ν_a , N-CSS); 1012.45 (ν_a , CSS); 815.10 (ω , C-H); 746.04 (δ , C-H); 548.16 (ν_s , CSS). ESI-MS m/z , [DTC⁻] found (calc.): 141.98 (141.98). Anal. Calc. for C₅H₄NNaS₂ (MW = 165.21 g·mol⁻¹): C 36.35; H 2.44; N 8.48; S 38.22. Found: C 36.22; H 2.57; N 8.69; S 38.31.

Synthesis of the Cu(II) derivatives of the a-i ligands, [Cu^{II}(DTC)₂]

Synthesis of Cu(II) dithiocarbamate complexes of the aliphatic ligands a-d

1.7 mmol (2 eq) of the selected dithiocarbamate salt (**a-d**) dissolved in methanol (5 mL) have been added to a methanol solution of CuCl₂·2H₂O (0.85 mmol), according to literature procedure^{6,7}. The green cupric solution rapidly turned into brown with a precipitate immediately formed. The reaction mixture was let to stir at room temperature for 30 minutes, then the precipitate was centrifuged, washed with water (2x 5mL), cold methanol (2x3 mL) and cold diethyl ether (2x3 mL). Finally, the obtained dark brown solid was dried *in vacuum* in the presence of P₂O₅. Analyses for [Cu(PDT)₂] [Cu(IndolineDTC)₂] are in agreement with literature data.^{6,7}

Bis(pyrrolidine dithiocarbamate)copper(II), [Cu(PDT)₂]

Aspect: brown solid. Yield: 83%. Mp.: 250 °C (dec.). ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 4.47 (s br, 8H, H₍₃₎ + H₍₄₎), 8.76 (s br, 4H, H₍₂₎ + H₍₅₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2965.40, 2871.44 (ν_a , C-H); 1497.92 (ν_a , N-CSS); 947.33 (ν_a , CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 559.05 (ν_s , CSS); 338.54 (ν_a , Cu-S); 291.40 (ν_s , Cu-S). ESI-MS m/z , [M⁺] found (calc.): 354.95 (354.95). Anal. Calc. for C₁₀H₁₈CuN₂S₄ (MW = 356.05 g·mol⁻¹): C 33.73; H 4.53; N 7.87; S 36.02. Found: C 33.83; H 4.22; N 7.33; S 35.94. Solubility: chloroform, dichloromethane, DMSO, acetonitrile.

Bis(piperidine dithiocarbamate)copper(II), [Cu(PipeDTC)₂]

Aspect: dark brown solid. Yield: 90%. Mp.: 254 °C. ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 0.33 (s, 4H, H₍₄₎), 1.17 (s, 4H, H₍₃₎ + H₍₅₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2941.17, 2850.28 (ν_a , C-H); 1501.54 (ν_a , N-CSS); 947.25 (ν_a , CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 563.41 (ν_s , CSS); 353.57 (ν_a , Cu-S); 291.76 (ν_s , Cu-S). ESI-MS m/z , [M⁺] found (calc.): 382.98 (382.98). Anal. Calc. for C₁₂H₂₀CuN₂S₄ (MW = 384.11 g·mol⁻¹): C 37.52; H 5.25; N 7.29; S 33.39. Found: C 37.54; H 4.77; N 7.10; S 33.18. Solubility: chloroform, dichloromethane, DMSO, acetonitrile.

Bis(morpholine dithiocarbamate)copper(II), [Cu(MorphDTC)₂]

Aspect: brown solid. Yield: 94%. Mp.: 296 °C (dec.). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2968.97, 2853.40 (ν_a , C-H); 1485.33 (ν_a , N-CSS); 1110.23 (ν_a , C-O); 1010.40 (ν_a , CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 558.69 (ν_s , CSS); 338.25 (ν_a , Cu-S); 291.38 (ν_s , Cu-S). ESI-MS m/z , [M⁺] found (calc.): 386.94 (386.94). Anal. Calc. for C₁₀H₁₆CuN₂O₂S₄ (MW = 388.07 g·mol⁻¹): C 30.95; H 4.16; N 7.22; S 33.05. Found: C 31.08; H 4.18; N 7.09; S 32.94. Solubility: slightly soluble in DMSO.

Bis(indoline dithiocarbamate)copper(II), [Cu(IndolineDTC)₂]

Aspect: dark brown solid. Yield: 94%. Mp.: 263 °C. Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2923.89 (ν_a , C-H); 1481.41 (ν , C=C ring); 1422.33 (ν_a , N-CSS); 1038.58 (ν_a , CSS); 739.18 (δ , C-H). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 556.43 (ν_s , CSS); 343.83 (ν_a , Cu-S); 271.35 (ν_s , Cu-S). ESI-MS m/z , [M⁺] found (calc.): 450.96 (450.95). Anal. Calc. for C₁₈H₁₆CuN₂S₄ (MW = 452.14 g·mol⁻¹): C 47.82; H 3.57; N 6.20; S 28.37. Found: C 47.33; H 3.37; N 5.99; S 28.27. Solubility: soluble in a mixture pyridine/chloroform 1:1 (axial coordination of pyridine).

Synthesis of Cu(II) dithiocarbamate complexes of L-proline ester derivatives e, f

The copper(II) derivatives of L-proline ester dithiocarbamates were obtained by adding dropwise 1.4 mmol (2 eq) of the dithiocarbamate salt dissolved in ethanol (5 mL) to an ethanol solution containing 0.70 mmol of CuCl₂·2H₂O. The cupric green solution turned rapidly into green/brown, and the mixture was let to stir at room temperature for 30 minutes. Then, the solvent volume was reduced by half and the solution was placed at -20 °C for 12 hours, allowing the formation of a green/brown precipitate (sometimes as crystals), which was centrifuged, and washed with water (2x 5mL) and *n*-pentane (3x3 mL). Finally, the obtained solid was dried under vacuum in the presence of P₂O₅.

Bis(L-proline methyl ester dithiocarbamate)copper(II), [Cu(ProOMeDTC)₂]

Aspect: dark green solid. Yield: 80%. Mp.: 215 °C. ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 2.11-2.93 (m, 8H, H₍₃₎ + H₍₄₎), 3.94 (m, 6H, O-CH₃). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2951.87 (ν_a , C-H); 1750.79 (ν , C=O); 1471.56 (ν_a , N-CSS); 1153.76 (ν_a , C-OMe); 939.75 (ν_a , CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 565.71 (ν_s , CSS); 342.87 (ν_a , Cu-S); 279.96 (ν_s , Cu-S). ESI-MS m/z , [M⁺] found (calc.): 470.97 (470.96). Anal. Calc. for C₁₄H₂₀CuN₂O₄S₄ (MW = 472.13 g·mol⁻¹): C 35.62; H 4.27; N 5.93; S 27.17. Found: C 35.83; H 4.13; N 5.81; S 27.47. Solubility: methanol, ethanol, ethyl acetate, chloroform, dichloromethane, DMSO, acetonitrile.

Bis(L-proline tert-butyl ester dithiocarbamate)copper(II), [Cu(ProOtBuDTC)₂]

Aspect: brown solid. Yield: 74%. Mp.: 207 °C. ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 1.57 (s, 18H, O-C(CH₃)₃), 1.99-2.83 (m, 8H, H₍₃₎ + H₍₄₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2974.81 (ν_a , C-H); 1733.37 (ν , C=O); 1469.68 (ν_a , N-CSS); 1148.53 (ν_a , C-OtBu); 930.08 (ν_a , CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 568.57 (ν_s , CSS); 340.11 (ν_a , Cu-S); 276.11 (ν_s , Cu-S). ESI-MS m/z , [M⁺] found (calc.): 555.06 (555.05). Anal. Calc. for C₂₀H₃₂CuN₂O₄S₄ (MW = 556.29 g·mol⁻¹): C 43.18; H 5.80; N 5.04; S 23.06. Found: C 43.42; H 5.92; N 4.90; S 23.21. Solubility: methanol, ethanol, ethyl acetate, chloroform, dichloromethane, DMSO, acetonitrile.

Synthesis of Cu(II) dithiocarbamate complexes of aromatic N-heterocycles g-i

The copper(II) complexes involving the aromatic ligands **g-i** were obtained according to literature procedure⁶ by dropwise addition of 1.5 mmol (2 eq) of the dithiocarbamate salt (dissolved in 5 mL of tetrahydrofuran) to a solution containing 0.75 mmol of CuCl₂·2H₂O dissolved in THF. The cupric green solution quickly turned into black and a dark solid immediately precipitated. The reaction mixture was let to stir at room temperature for 30 minutes, then the precipitate was centrifuged, and washed with water (5x 5mL), diethyl ether (3x3 mL) and *n*-hexane (3x3 mL). Finally, the obtained dark brown solid was dried in vacuum pump in the presence of P₂O₅. Analyses are in agreement with literature data.⁶

Bis(carbazole dithiocarbamate)copper(II), [Cu(CDT)₂]

Aspect: dark brown solid. Yield: 89%. Mp.: 241 °C. Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 3011.02 (ν_a , C-H); 1485.75, 1446.99, 1435.70 (ν , C=C ring); 1333.30 (ν_a , N-CSS); 1038.66 (ν_a , CSS); 843.59 (ω , C-H); 743.78, 707.83 (δ , C-H). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 595.47 (ν_s , CSS); 412.14 (ν_a , Cu-S); 346.20 (ν_s , Cu-S). ESI-MS m/z , [M⁺] found (calc.): 546.98 (546.95). Anal. Calc. for C₂₆H₁₆CuN₂S₄ (MW = 548.22 g·mol⁻¹): C 56.96; H 2.94; N 5.11; S 23.40. Found: C 56.40; H 2.45; N 4.94; S 23.20. Solubility: soluble in a mixture pyridine/chloroform 1:1 (axial coordination of pyridine).

Bis(indole dithiocarbamate)copper(II), [Cu(IndDTC)₂]

Aspect: dark brown solid. Yield: 87%. Mp.: 245 °C. Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 3046.82 (ν_a , C-H); 1445.35, 1388.04 (ν , C=C ring); 1333.98 (ν_a , N-CSS); 1017.17 (ν_a , CSS); 847.19 (ω , C-H); 749.97, 730.36 (δ , C-H). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 591.13 (ν_s , CSS); 413.37 (ν_a , Cu-S); 340.40 (ν_s , Cu-S). ESI-MS m/z , [M⁺] found (calc.): 446.94 (446.92). Anal. Calc. for C₁₈H₁₂CuN₂S₄ (MW = 448.11 g·mol⁻¹): C 48.25; H 2.70; N 6.25; S 28.62. Found: C 48.07; H 2.31; N 6.14; S 28.85. Solubility: soluble in a mixture pyridine/chloroform 1:1 (axial coordination of pyridine).

Bis(pyrrole dithiocarbamate)copper(II), [Cu(PyrroleDTC)₂]

Aspect: dark brown solid. Yield: 88%. Mp.: 219 °C (dec.). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 3131.02 (ν_a , C-H); 1472.85, 1409.66 (ν , C=C ring); 1333.66 (ν_a , N-CSS); 1012.56 (ν_a , CSS); 836.97 (ω , C-H); 729.40 (δ , C-H). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 591.99 (ν_s , CSS); 411.07 (ν_a , Cu-S); 338.87 (ν_s , Cu-S). ESI-MS m/z , [M⁺] found (calc.): 346.90 (346.89). Anal. Calc. for C₁₀H₈CuN₂S₄ (MW = 347.99 g·mol⁻¹): C 34.51; H 2.32; N 8.05; S 36.86. Found: C 34.61; H 2.29; N 8.08; S 36.68. Solubility: soluble in a mixture pyridine/chloroform 1:1 (axial coordination of pyridine).

Synthesis of the Ru(III) complexes of the α -i ligands, the neutral $[\text{Ru}^{\text{III}}(\text{DTC})_3]$, and the ionic dinuclear β - $[\text{Ru}^{\text{III}}_2(\text{DTC})_5]\text{Cl}$

Synthesis of Ru(III) dithiocarbamate complexes of the aliphatic ligands α -i

According to a literature procedure,⁸ a solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (1.5 mmol) in water (4 mL), 10 mL of an aqueous solution of the dithiocarbamate salt (4.5 mmol) were added dropwise. A dark brown solid started to precipitate in few minutes. The mixture was stirred for 1 h at room temperature, afterwards the solid was filtrated and washed with water (3 x 3.0 mL) and diethyl ether (2 x 2.5 mL). The isolated product was dried and re-dissolved in CH_2Cl_2 to be purified by silica gel chromatography. A gradient from pure CH_2Cl_2 to $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 90:10 was used to elute first the mononuclear complex and then the dinuclear derivative (as mixture of α + β isomers). Afterwards, the mixture of α,β - $[\text{Ru}_2(\text{PDT})_5]\text{Cl}$ was isomerized to the thermodynamically stable β - $[\text{Ru}_2(\text{PDT})_5]\text{Cl}$ by reflux in methanol for 8 hours. All the compounds were re-precipitated from CH_2Cl_2 - diethyl ether, washed with *n*-pentane, and dried in vacuum pump in the presence of P_2O_5 . Analyses for Ru(III)-PDT derivatives are in agreement with literature data.⁸

Tris(pyrrolidine dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{PDT})_3]$

Aspect: dark green solid. Yield: 31%. R.f. (on silica gel, CH_2Cl_2): 0.85. Mp.: 256 °C. $^1\text{H-NMR}$ (CDCl_3 , 300.13 MHz): δ (ppm) = 0.39 (s, 12H, $\text{H}_{(3)} + \text{H}_{(4)}$), 35.83 (s br, 6H, $\text{H}_{(2)} + \text{H}_{(5)}$), 44.29 (s br, 6H, $\text{H}_{(2)} + \text{H}_{(5)}$). Medium FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2945.32, 2865.58 (ν_a , C-H); 1487.12, 1469.76, 1444.15 (ν_a , N-CSS); 942.18 (ν_a , CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm^{-1}) = 565.37 (ν_s , CSS); 447.75 (ν_a , Ru-S); 318.90 (ν_s , Ru-S). ESI-MS m/z , $[\text{M}^+]$ found (calc.): 539.96 (539.93). Anal. Calc. for $\text{C}_{15}\text{H}_{24}\text{N}_3\text{RuS}_6$ (MW = 539.83 g·mol⁻¹): C 33.37; H 4.48; N 7.78; S 35.64. Found: C 33.50; H 4.49; N 7.72; S 35.51. Solubility: methanol, ethanol, chloroform, dichloromethane, acetonitrile, DMSO.

β -pentakis(pyrrolidine dithiocarbamate)diruthenium(III) chloride, β - $[\text{Ru}_2(\text{PDT})_5]\text{Cl}$

Aspect: dark red solid. Yield: 32%. R.f. (on silica gel, $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 92:8): 0.23. Mp.: 236 °C. $^1\text{H-NMR}$ (CDCl_3 , 300.13 MHz): δ (ppm) = 1.81-2.19 (m, 20H, $\text{H}_{(3)} + \text{H}_{(4)}$), 3.46-3.94 (m, 20H, $\text{H}_{(2)} + \text{H}_{(5)}$). Medium FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2947.10, 2667.69 (ν_a , C-H); 1505.71, 1473.13, 1447.94 (ν_a , N-CSS); 946.59 (ν_a , CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm^{-1}) = 563.86 (ν_s , CSS); 445.81 (ν_a , Ru-S); 347.83 (ν_s , Ru-S). ESI-MS m/z , $[\text{M-Cl}^+]$ found (calc.): 932.87 (932.86). Anal. Calc. for $\text{C}_{25}\text{H}_{40}\text{ClN}_5\text{Ru}_2\text{S}_{10}$ (MW = 968.86 g·mol⁻¹): C 30.99; H 4.16; N 7.23; S 33.10. Found: C 31.12; H 4.26; N 7.39; S 33.30. Solubility: methanol, ethanol, chloroform, dichloromethane, acetonitrile, DMSO.

Tris(piperidine dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{PipeDTC})_3]$

Aspect: dark green solid. Yield: 34%. R.f. (on silica gel, CH₂Cl₂): 0.80. Mp.: 277 °C. ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 0.87 (s, 12H, H₍₃₎ + H₍₅₎), 3.54 (s, 6H, H₍₄₎), 24.03 (s br, 12H, H₍₂₎ + H₍₆₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2936.08, 2850.82 (ν_a, C-H); 1487.83, 1455.07, 1439.06 (ν_a, N-CSS); 1001.97 (ν_a, CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 538.14 (ν_s, CSS); 405.74 (ν_a, Ru-S); 330.99 (ν_s, Ru-S). ESI-MS *m/z*, [M⁺] found (calc.): 581.98 (581.98). Anal. Calc. for C₁₈H₃₀N₃RuS₆ (MW = 581.91 g·mol⁻¹): C 37.15; H 5.20; N 7.22; S 33.06. Found: C 37.21; H 5.29; N 7.25; S 33.22. Solubility: methanol, ethanol, chloroform, dichloromethane, acetonitrile, DMSO.

β-pentakis(piperidine dithiocarbamate)diruthenium(III) chloride, β-[Ru₂(PipeDTC)₅]Cl

Aspect: brown solid. Yield: 29%. R.f. (on silica gel, CH₂Cl₂/MeOH 9:1): 0.39. Mp.: 243 °C. ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 1.50 (m, 10H, H₍₄₎), 1.83 (m, 20H, H₍₃₎ + H₍₅₎), 3.03-4.65 (m, 20H, H₍₂₎ + H₍₆₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2933.43 (ν_a, C-H); 1503.23, 1441.03 (ν_a, N-CSS); 1001.63 (ν_a, CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 544.23 (ν_s, CSS); 406.62 (ν_a, Ru-S); 321.88 (ν_s, Ru-S). ESI-MS *m/z*, [M-Cl⁺] found (calc.): 1003.93 (1003.94). Anal. Calc. for C₃₀H₅₀ClN₅Ru₂S₁₀ (MW = 1039.00 g·mol⁻¹): C 34.68; H 4.85; N 6.74; S 30.86. Found: C 34.58; H 4.80; N 6.81; S 30.88. Solubility: methanol, ethanol, chloroform, dichloromethane, acetone, acetonitrile, DMSO.

Tris(morpholine dithiocarbamate)ruthenium(III), [Ru(MorphDTC)₃]

Aspect: dark green solid. Yield: 33%. R.f. (on silica gel, CH₂Cl₂/MeOH 98:2): 0.83. Mp.: 240 °C (dec.). ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 3.15 (s, 12H, H₍₂₎ + H₍₆₎), 24.90 (s br, 12H, H₍₃₎ + H₍₅₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2859.46 (ν_a, C-H); 1486.03, 1430.57 (ν_a, N-CSS); 1111.74 (ν_a, C-O); 994.13 (ν_a, CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 541.55 (ν_s, CSS); 412.70 (ν_a, Ru-S); 324.59 (ν_s, Ru-S). ESI-MS *m/z*, [M⁺] found (calc.): 587.92 (587.92). Anal. Calc. for C₁₅H₂₄N₃O₃RuS₆ (MW = 587.83 g·mol⁻¹): C 30.65; H 4.12; N 7.15; S 32.73. Found: C 30.62; H 4.15; N 7.19; S 32.56. Solubility: methanol, ethanol, chloroform, dichloromethane, acetone, acetonitrile, DMSO.

β-pentakis(morpholine dithiocarbamate)diruthenium(III) chloride, β-[Ru₂(MorphDTC)₅]Cl

Aspect: brick red solid. Yield: 32%. R.f. (on silica gel, CH₂Cl₂/MeOH 9:1): 0.30. Mp.: 200 °C (dec.). ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 3.25-4.65 (m, 40H, H₍₂₎ + H₍₃₎ + H₍₅₎ + H₍₆₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2846.95 (ν_a, C-H); 1503.25, 1435.18 (ν_a, N-CSS); 1106.81 (ν_a, C-O); 993.99 (ν_a, CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 546.95 (ν_s, CSS); 413.98 (ν_a, Ru-S); 310.23 (ν_s, Ru-S). ESI-MS *m/z*, [M-Cl⁺] found (calc.): 1013.86 (1013.83). Anal. Calc. for C₃₀H₅₀ClN₅O₅Ru₂S₁₀ (MW = 1048.86 g·mol⁻¹): C 28.63; H 3.84; N 6.68; S 30.57. Found: C 28.49; H 3.90; N 6.72; S 30.63. Solubility: methanol, ethanol, chloroform, dichloromethane, acetone, acetonitrile, DMSO.

Tris(indoline dithiocarbamate)ruthenium(III), [Ru(IndolineDTC)₃]

Aspect: dark green solid. Yield: 27%. R.f. (on silica gel, CH₂Cl₂): 0.92. Mp.: 244 °C (dec.). ¹H-NMR (CD₂Cl₂, 300.13 MHz): δ (ppm) = 0.16 (m, 6H, H₍₃₎), 7.27 (m, 3H, H₍₅₎), 8.67 (s, 3H, H₍₄₎), 8.95 (s, 3H, H₍₆₎), 35.92 (s br, 3H, H₍₂₎), 45.63 (s br, 3H, H₍₂₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2842.06 (ν_a, C-H); 1475.67 (ν, C=C ring); 1387.37, 1347.88, 1322.11 (ν_a, N-CSS); 947.54 (ν_a, CSS); 750.41 (δ, C-H). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 546.68 (ν_s, CSS); 424.20 (ν_a, Ru-S); 333.12 (ν_s, Ru-S). ESI-MS *m/z*, [M⁺] found (calc.): 683.95 (683.93). Anal. Calc. for C₂₇H₂₄N₃RuS₆ (MW = 683.96 g·mol⁻¹): C 47.41; H 3.54; N 6.14; S 28.13. Found: C 47.58; H 3.56; N 6.15; S 28.24. Solubility: methanol, ethanol, chloroform, dichloromethane, acetonitrile, DMSO.

β-pentakis(indoline dithiocarbamate)diruthenium(III) chloride, β-[Ru₂(IndolineDTC)₅]Cl

Aspect: brown solid. Yield: 25%. R.f. (on silica gel, CH₂Cl₂/MeOH 95:5): 0.40. Mp.: 200 °C (dec.). ¹H-NMR (CD₂Cl₂, 300.13 MHz): δ (ppm) = 3.22-4.88 (m, 20H, H₍₂₎ + H₍₃₎), 7.35-8.87 (m, 20H, H₍₄₎ + H₍₅₎ + H₍₆₎ + H₍₇₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2850.49 (ν_a, C-H); 1484.25 (ν, C=C ring); 1431.19, 1323.61 (ν_a, N-CSS); 952.20 (ν_a, CSS); 750.98 (δ, C-H). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 558.76 (ν_s, CSS); 421.19 (ν_a, Ru-S); 323.76 (ν_s, Ru-S). ESI-MS *m/z*, [M-Cl⁺] found (calc.): 1173.88 (1173.86). Anal. Calc. for C₃₀H₅₀ClN₅Ru₂S₁₀ (MW = 1209.08 g·mol⁻¹): C 44.70; H 3.33; N 5.79; S 26.52. Found: C 44.74; H 3.38; N 6.01; S 26.47. Solubility: methanol, ethanol, chloroform, dichloromethane, acetonitrile, DMSO.

Synthesis of Ru(III) dithiocarbamate complexes of L-proline ester derivatives e, f

To a solution of RuCl₃·3H₂O (1.5 mmol) in water (4 mL), 10 mL of an aqueous solution of the sodium salt of L-proline ester dithiocarbamate (4.5 mmol) were added dropwise. A dark brown solid quickly precipitated but the mixture was stirred for 1 h at room temperature. Then, the solid was filtrated and washed with water (3 x 3 mL) and *n*-hexane (3 x 5 mL). The isolated product was dried and re-dissolved in CH₂Cl₂ to be purified by silica gel chromatography (gradient from pure CH₂Cl₂ to CH₂Cl₂/MeOH 90:10, to first elute the mononuclear complex, followed by the dinuclear derivative). The dinuclear derivative is obtained as a mixture of α+β isomers, then put at reflux in methanol for 8 hours to isolate the thermodynamically stable β-[Ru₂(PDT)₅]Cl. All the compounds were re-precipitated from ethyl acetate-hexane, washed with *n*-pentane, and dried *in vacuum* over P₂O₅.

Tris(L-proline methyl ester dithiocarbamate)ruthenium(III), [Ru(ProOMeDTC)₃]

Aspect: dark green solid. Yield: 34%. R.f. (on silica gel, CH₂Cl₂): 0.50. Mp.: 138 °C. ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 0.47-2.27 (m, 12H, H₍₃₎ + H₍₄₎), 3.07 (m, 9H, O-CH₃), 23.55-28.34 (4s br, 3H, H₍₅₎), 31.41-34.64 (3s br, 3H, H₍₅₎), 38.65-46.27 (4s br, 3H, H₍₂₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2949.05 (ν_a, C-H); 1742.31 (ν, C=O); 1439.74 (ν_a, N-CSS); 1169.25 (ν_a, C-OMe); 942.14 (ν_a, CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 546.88 (ν_s, CSS); 453.06 (ν_a, Ru-S); 323.86 (ν_s, Ru-S). ESI-MS *m/z*, [M⁺] found

(calc.): 713.97 (713.95). Anal. Calc. for $C_{21}H_{30}N_3O_3RuS_6$ (MW = 713.94 g·mol⁻¹): C 35.33; H 4.24; N 5.89; S 26.95. Found: C 35.31; H 4.28; N 5.95; S 26.83. Solubility: methanol, ethanol, chloroform, dichloromethane, ethyl acetate, acetone, acetonitrile, DMSO.

β -pentakis(L-proline methyl ester dithiocarbamate)diruthenium(III) chloride, β -[Ru₂(ProOMeDTC)₅]Cl

Aspect: dark red solid. Yield: 37%. R.f. (on silica gel, CH₂Cl₂/MeOH 94:6): 0.40. Mp.: 200 °C (dec.). ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 2.20 (m, 20H, H₍₃₎ + H₍₄₎), 3.28-3.98 (m, 25H, H₍₅₎ + O-CH₃), 5.02-5.38 (m, 5H, H₍₂₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2950.23 (ν_a , C-H); 1741.36 (ν , C=O); 1480.37, 1447.83 (ν_a , N-CSS); 1170.04 (ν_a , C-OMe); 944.45 (ν_a , CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 546.95 (ν_s , CSS); 461.98 (ν_a , Ru-S); 335.16 (ν_s , Ru-S). ESI-MS m/z , [M-Cl⁺] found (calc.): 1223.92 (1223.89). Anal. Calc. for $C_{30}H_{50}ClN_5Ru_2S_{10}$ (MW = 1259.04 g·mol⁻¹): C 33.39; H 4.00; N 5.56; S 25.47. Found: C 33.46; H 4.04; N 5.59; S 25.40. Solubility: methanol, ethanol, chloroform, dichloromethane, ethyl acetate, acetone, acetonitrile, DMSO.

Tris(L-proline tert-butyl ester dithiocarbamate)ruthenium(III), [Ru(ProOtBuDTC)₃]

Aspect: dark green solid. Yield: 29%. R.f. (on silica gel, CH₂Cl₂): 0.70. Mp.: 200 °C (dec.). ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 0.50-2.27 (m, 39H, H₍₃₎ + H₍₄₎ + O-C(CH₃)₃), 23.65-26.70 (4s, 3H, H₍₅₎), 30.00-33.38 (4s, 3H, H₍₅₎), 40.07-44.47 (4s, 3H, H₍₂₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2975.22, 2872.34 (ν_a , C-H); 1736.11 (ν , C=O); 1440.10 (ν_a , N-CSS); 1148.66 (ν_a , C-OtBu); 933.50 (ν_a , CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 547.60 (ν_s , CSS); 470.56 (ν_a , Ru-S); 320.98 (ν_s , Ru-S). ESI-MS m/z , [M⁺] found (calc.): 840.12 (840.09). Anal. Calc. for $C_{30}H_{48}N_3O_3RuS_6$ (MW = 840.18 g·mol⁻¹): C 42.89; H 5.76; N 5.00; S 22.90. Found: C 42.83; H 5.72; N 5.17; S 22.99. Solubility: methanol, ethanol, chloroform, dichloromethane, ethyl acetate, acetone, acetonitrile, DMSO.

β -pentakis(L-proline tert-butyl ester dithiocarbamate)diruthenium(III) chloride, β -[Ru₂(ProOtBuDTC)₅]Cl

Aspect: dark red solid. Yield: 32%. R.f. (on silica gel, CH₂Cl₂/MeOH 94:6): 0.52. Mp.: 200 °C (dec.). ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 1.41-2.26 (m, 65H, H₍₃₎ + H₍₄₎ + O-C(CH₃)₃), 3.21-4.02 (m, 10H, H₍₅₎), 4.36-5.30 (m, 5H, H₍₂₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2975.16 (ν_a , C-H); 1735.39 (ν , C=O); 1481.10, 1450.06 (ν_a , N-CSS); 1148.87 (ν_a , C-OtBu); 935.12 (ν_a , CSS). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 551.30 (ν_s , CSS); 471.19 (ν_a , Ru-S); 325.69 (ν_s , Ru-S). ESI-MS m/z , [M-Cl⁺] found (calc.): 1434.16 (1434.12). Anal. Calc. for $C_{50}H_{80}ClN_5O_{10}Ru_2S_{10}$ (MW = 1469.64 g·mol⁻¹): C 40.87; H 5.49; N 4.77; S

21.82. Found: C 40.80; H 5.39; N 4.60; S 21.88. Solubility: methanol, ethanol, chloroform, dichloromethane, ethyl acetate, acetone, acetonitrile, DMSO.

Synthesis of Ru(II) dithiocarbamate complex of the aromatic N-heterocycles g

The synthesis was carried out in a Schlenk-line apparatus under N₂ atmosphere according to literature procedure.⁸ Briefly, 2.7 mmol of synthesized carbazole dithiocarbamate Na(CDT) and 0.9 mmol of RuCl₃·3H₂O were dissolved in 18 mL of anhydrous tetrahydrofuran (THF). The mixture was left under stirring for 15 h at room temperature. The solvent was subsequently removed under reduced pressure giving a black solid that was washed with cold pentane (5 x 5.0 mL). The dinuclear complex [Ru₂(CDT)₅]Cl (as a mixture of α+β isomers) was isolated by several precipitation cycles in THF/pentane mixture (room temperature), and then refluxed in CH₂Cl₂ for 8 hours to obtain the isomer β-[Ru₂(CDT)₅]Cl. On the other hand, the THF/pentane solution was concentrated up to obtain a dark green solid that was dried under vacuum and purified by silica gel chromatography using CH₂Cl₂/*n*-hexane 40:60 to elute the mononuclear complex. All the complexes have been re-precipitated in CH₂Cl₂- *n*-hexane, washed with *n*-pentane and dried *in vacuum* over P₂O₅. Analyses are in agreement with literature data.⁸

Tris(carbazole dithiocarbamate)ruthenium(III), [Ru(CDT)₃]

Aspect: dark green solid. Yield: 20%. R.f. (on silica gel, CH₂Cl₂/hexane 1:1): 0.88. Mp.: 218 °C. ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 7.71-7.73 (d, 6H, H₍₄₎ + H₍₅₎), 8.90 (t, 6H, H₍₃₎ + H₍₆₎), 9.01-9.03 (d, 6H, H₍₂₎ + H₍₇₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 2953.17 (ν_a, C-H); 1484.71, 1435.79 (ν, C=C ring); 1363.04, 1324.09, 1294.58 (ν_a, N-CSS); 1035.97 (ν_a, CSS); 847.98 (ω, C-H); 745.87 (δ, C-H). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 586.98 (ν_s, CSS); 459.76 (ν_a, Ru-S); 413.25 (ν_s, Ru-S). ESI-MS *m/z*, [M⁺] found (calc.): 827.97 (827.94). Anal. Calc. for C₃₉H₂₄N₃RuS₆ (MW = 828.09 g·mol⁻¹): C 56.57; H 2.92; N 5.07; S 23.23. Found: C 56.59; H 2.96; N 5.21; S 23.20. Solubility: chloroform, dichloromethane, THF.

β-pentakis(carbazole dithiocarbamate)diruthenium(III) chloride, β-[Ru₂(CDT)₅]Cl

Aspect: brown solid. Yield: 22%. R.f. (on silica gel, CH₂Cl₂/hexane 1:1): 0.60. Mp.: 230 °C. ¹H-NMR (CDCl₃, 300.13 MHz): δ (ppm) = 7.46-7.53 (m, 20H, H₍₂₎ + H₍₃₎ + H₍₆₎ + H₍₇₎), 7.98-8.00 (d, 10H, H₍₄₎ + H₍₅₎), 9.17-9.19 (d, 10H, H₍₁₎ + H₍₈₎). Medium FT-IR (KBr): $\tilde{\nu}$ (cm⁻¹) = 3056.37 (ν_a, C-H); 1485.29, 1436.67 (ν, C=C ring); 1364.09, 1325.58, 1299.44 (ν_a, N-CSS); 1038.43 (ν_a, CSS); 851.92 (ω, C-H); 744.39 (δ, C-H). Far FT-IR (nujol): $\tilde{\nu}$ (cm⁻¹) = 586.98 (ν_s, CSS); 466.20 (ν_a, Ru-S); 415.14 (ν_s, Ru-S). ESI-MS *m/z*, [M-Cl⁺] found (calc.): 1490.89 (1490.87). Anal. Calc. for C₆₅H₄₀ClN₅Ru₂S₁₀ (MW = 1449.29 g·mol⁻¹): C 53.87; H 2.78; N 4.83; S 22.12. Found: C 53.94; H 2.91; N 4.92; S 22.18. Solubility: chloroform, dichloromethane, THF.

In vitro biological studies

Stability studies

All the metal-DTC derivatives have been tested for their stability in DMSO (used as a solubilizing agent), in cell culture medium (D-MEM, diluted to 10% v/v with phosphate buffered saline), and human serum (from a volunteer 28-year old Caucasian male with A positive blood group, diluted to 5% v/v with phosphate buffered saline). Briefly, the complexes were dissolved in DMSO at a concentration of 2÷5 mM (based on the extinction coefficient of the tested compound), and 100-fold diluted in a solution of pure DMSO, D-MEM 10% in PBS, or human serum 5% in PBS. Subsequently, samples were placed in a QS quartz cuvette (path length 1 cm), and their UV-Vis spectra were recorded over 72 hours at 37 °C (temperature stabilized *via* a Peltier system) .

In vitro antiproliferative studies with HeLa cell line

HeLa cells (American Type Culture Collection, ATCC) were cultured in 75 cm² cell culture flasks in Dulbeccos's Modified Eagle Medium (D-MEM), with addition of Fetal Bovine Serum (FBS) (10%), L-glutamine (5 mM), streptomycin (100 µg/mL), and penicillin (100 units/mL), and incubated at 37 °C in a 5% carbon dioxide controlled atmosphere. For the cytotoxicity assay, the medium was removed from the flask, and the cells washed with 6 mL of PBS, and then shaken in presence of 1 mL of trypsin, followed by 3-min incubation. D-MEM was hence added, and the obtained cellular suspension seeded in 96-well microplates (5·10³ cells/well; V_{well}=200 µL) and incubated at 37 °C in a 5% CO₂ atmosphere for 24 h to allow cell adhesion, prior to drug testing. HeLa culture was exposed to different concentrations of the metal-DTC complexes (*i.e.*, 10 µM, 5 µM, 2 µM, 1 µM, 0.5 µM and in some cases lower) for 72 hours, and cell viability was evaluated *via* resazurine assay, according to standard procedures.

In vitro antiproliferative studies on HepG2 cell line

In vitro tests involving the HepG2 cell line (Provitro, Berlin, Germany) have been conducted with cells stably transfected with the plasmid vector pCDNA3.1 carrying the SERPINB3 gene (HepG2/SB3 cells), and in parallel with cells stably transfected with the empty vector alone (HepG2/CTR cells, where CTR stands for "control"). The transfection has been performed according to a literature procedure.⁹

Afterwards, HepG2/CTR and HepG2/SB3 cells were separately cultured in 75 cm² cell culture flasks in Minimum Essential Medium (MEM), with addition of FBS (10%), L-glutamine (2 mM), 1X MEM non-essential amino acid, streptomycin (100 µg/mL), and penicillin (100 units/mL), and incubated at 37 °C in a 5% carbon dioxide controlled atmosphere. For the cytotoxicity assay, the cells were

washed with PBS and trypsinized with 1X trypsin-EDTA. The cellular suspension was seeded in 96-well microplates ($2 \cdot 10^4$ cells/well), and incubated at 37 °C in a 5% CO₂ atmosphere. The day after seeding, cells were treated with vehicle (control; namely DMSO or saline solution) or each compound (dissolved in the vehicle) in fresh culture medium at the defined concentrations (*i.e.*, 10 μ M, 5 μ M, 2 μ M, 1 μ M, 0.5 μ M and in some cases lower) for 72 hours. Cell viability was evaluated *via* MTT assay, according to standard procedures.

IR resuming tables

	$\nu(\text{C=O})$	$\nu(\text{C=C})$	$\nu(\text{N-CSS})$	$\nu_{\alpha}(\text{C-O})$	$\nu_{\alpha}(\text{CSS})$	$\omega(\text{C-H})$	$\delta(\text{C-H})$	$\nu_s(\text{CSS})$
Na PDT	-	-	1422 cm^{-1}	-	942 cm^{-1}	-	-	542 cm^{-1}
K PipeDTC	-	-	1417 cm^{-1}	-	965 cm^{-1}	-	-	516 cm^{-1}
K MorphDTC	-	-	1410 cm^{-1}	1109 cm^{-1}	990 cm^{-1}	-	-	547 cm^{-1}
K IndolineDTC	-	1452 cm^{-1}	1371 cm^{-1}	-	931 cm^{-1}		743 cm^{-1}	508 cm^{-1}
Na ProOMeDTC	1733 cm^{-1}	-	1392 cm^{-1}	1178 cm^{-1}	945 cm^{-1}	-	-	504 cm^{-1}
Na ProOtBuDTC	1723 cm^{-1}	-	1388 cm^{-1}	1151 cm^{-1}	933 cm^{-1}	-	-	502 cm^{-1}
Na CDT	-	1436 cm^{-1}	1281 cm^{-1}	-	1040 cm^{-1}	832 cm^{-1}	742 cm^{-1}	570 cm^{-1}
Na IndDTC	-	1439 cm^{-1}	1290 cm^{-1}	-	998 cm^{-1}	825 cm^{-1}	752 cm^{-1}	550 cm^{-1}
Na PyrrDTC	-	1457 cm^{-1}	1259 cm^{-1}	-	1012 cm^{-1}	815 cm^{-1}	746 cm^{-1}	548 cm^{-1}

Table SI 2. Collection of diagnostic IR-vibrations (4000-500 cm^{-1}) of the synthesized dithiocarbamate salts.

	$\nu(\text{C=O})$	$\nu(\text{C=C})$	$\nu(\text{N-CSS})$	$\nu_{\alpha}(\text{C-O})$	$\nu_{\alpha}(\text{CSS})$	$\omega(\text{C-H})$	$\delta(\text{C-H})$	$\nu_s(\text{CSS})$	$\nu_{\alpha}(\text{Cu-S})$	$\nu_s(\text{Cu-S})$
[Cu(PDT) ₂]	-	-	1498 cm^{-1}	-	947 cm^{-1}	-	-	559 cm^{-1}	339 cm^{-1}	291 cm^{-1}
[Cu(PipeDTC) ₂]	-	-	1502 cm^{-1}	-	947 cm^{-1}	-	-	563 cm^{-1}	354 cm^{-1}	292 cm^{-1}
[Cu(MorphDTC) ₂]	-	-	1485 cm^{-1}	1110 cm^{-1}	1010 cm^{-1}	-	-	559 cm^{-1}	338 cm^{-1}	291 cm^{-1}
[Cu(IndolineDTC) ₂]	-	1481 cm^{-1}	1422 cm^{-1}	-	1039 cm^{-1}	-	739 cm^{-1}	556 cm^{-1}	344 cm^{-1}	271 cm^{-1}
[Cu(ProOMeDTC) ₂]	1751 cm^{-1}	-	1472 cm^{-1}	1154 cm^{-1}	940 cm^{-1}	-	-	566 cm^{-1}	343 cm^{-1}	280 cm^{-1}
[Cu(ProOtBuDTC) ₂]	1733 cm^{-1}	-	1470 cm^{-1}	1149 cm^{-1}	930 cm^{-1}	-	-	569 cm^{-1}	340 cm^{-1}	276 cm^{-1}
[Cu(CDT) ₂]	-	1486, 1447, 1436 cm^{-1}	1333 cm^{-1}	-	1039 cm^{-1}	844 cm^{-1}	744, 708 cm^{-1}	595 cm^{-1}	412 cm^{-1}	346 cm^{-1}
[Cu(IndDTC) ₂]	-	1445, 1388 cm^{-1}	1334 cm^{-1}	-	1017 cm^{-1}	847 cm^{-1}	750, 730 cm^{-1}	591 cm^{-1}	413 cm^{-1}	340 cm^{-1}
[Cu(PyrrDTC) ₂]	-	1473,	1334	-	1013	837	729	592	411	339

	1410 cm ⁻¹	cm ⁻¹		cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹
--	--------------------------	------------------	--	------------------	------------------	------------------	------------------	------------------	------------------

Table SI 3. Collection of the fundamental IR-vibrations (4000-200 cm⁻¹) of the analyzed Cu(II)-DTC complexes.

	$\nu(\text{C=O})$	$\nu(\text{C=C})$	$\nu(\text{N-CSS})$	$\nu_{\alpha}(\text{C-O})$	$\nu_{\alpha}(\text{CSS})$	$\omega(\text{C-H})$	$\delta(\text{C-H})$	$\nu_{\beta}(\text{CSS})$	$\nu_{\alpha}(\text{Ru-S})$	$\nu_{\beta}(\text{Ru-S})$
[Ru(PDT)₃]	-	-	1487, 1470, 1444 cm ⁻¹	-	942 cm ⁻¹	-	-	565 cm ⁻¹	448 cm ⁻¹	319 cm ⁻¹
β[Ru₂(PDT)₅]Cl	-	-	1506, 1473, 1448 cm ⁻¹	-	947 cm ⁻¹	-	-	564 cm ⁻¹	446 cm ⁻¹	348 cm ⁻¹
[Ru(PipeDTC)₃]	-	-	1488, 1455, 1439 cm ⁻¹	-	1002 cm ⁻¹	-	-	538 cm ⁻¹	405 cm ⁻¹	330 cm ⁻¹
β[Ru₂(PipeDTC)₅]Cl	-	-	1503, 1441 cm ⁻¹	-	1002 cm ⁻¹	-	-	544 cm ⁻¹	407 cm ⁻¹	322 cm ⁻¹
[Ru(MorphDTC)₃]	-	-	1486, 1431 cm ⁻¹	1112 cm ⁻¹	994 cm ⁻¹	-	-	542 cm ⁻¹	413 cm ⁻¹	325 cm ⁻¹
β[Ru₂(MorphDTC)₅]Cl	-	-	1503, 1435 cm ⁻¹	1107 cm ⁻¹	994 cm ⁻¹	-	-	547 cm ⁻¹	414 cm ⁻¹	310 cm ⁻¹
[Ru(IndolineDTC)₃]	-	1476 cm ⁻¹	1387, 1348, 1322 cm ⁻¹	-	948 cm ⁻¹	-	750 cm ⁻¹	547 cm ⁻¹	424 cm ⁻¹	333 cm ⁻¹
β[Ru₂(IndolineDTC)₅]Cl	-	1484 cm ⁻¹	1431, 1324 cm ⁻¹	-	952 cm ⁻¹	-	751 cm ⁻¹	559 cm ⁻¹	421 cm ⁻¹	324 cm ⁻¹
[Ru(ProOMeDTC)₃]	1742 cm ⁻¹	-	1440 cm ⁻¹	1169 cm ⁻¹	942 cm ⁻¹	-	-	547 cm ⁻¹	453 cm ⁻¹	324 cm ⁻¹
β[Ru₂(ProOMeDTC)₅]Cl	1741 cm ⁻¹	-	1480, 1448 cm ⁻¹	1170 cm ⁻¹	944 cm ⁻¹	-	-	547 cm ⁻¹	462 cm ⁻¹	335 cm ⁻¹
[Ru(ProOtBuDTC)₃]	1736 cm ⁻¹	-	1440 cm ⁻¹	1149 cm ⁻¹	934 cm ⁻¹	-	-	548 cm ⁻¹	471 cm ⁻¹	321 cm ⁻¹
β[Ru₂(ProOtBuDTC)₅]Cl	1735 cm ⁻¹	-	1481, 1450 cm ⁻¹	1149 cm ⁻¹	935 cm ⁻¹	-	-	551 cm ⁻¹	471 cm ⁻¹	326 cm ⁻¹
[Ru(CDT)₃]	-	1485, 1436 cm ⁻¹	1363, 1324, 1295 cm ⁻¹	-	1036 cm ⁻¹	848 cm ⁻¹	746 cm ⁻¹	587 cm ⁻¹	460 cm ⁻¹	413 cm ⁻¹
β[Ru₂(CDT)₅]Cl	-	1485, 1437 cm ⁻¹	1364, 1326, 1299 cm ⁻¹	-	1038 cm ⁻¹	852 cm ⁻¹	744 cm ⁻¹	587 cm ⁻¹	466 cm ⁻¹	415 cm ⁻¹

Table SI 4. Collection of the main IR-vibrations (4000-200 cm⁻¹) of the analyzed Ru(III)-DTC complexes.**¹H-NMR resuming tables**

	<i>H</i> ₍₁₎	<i>H</i> ₍₂₎	<i>H</i> ₍₃₎	<i>H</i> ₍₄₎	<i>H</i> ₍₅₎	<i>H</i> ₍₆₎	<i>H</i> ₍₇₎	<i>H</i> ₍₈₎	<i>H</i> ₍₉₎	<i>OMe</i>	<i>OtBu</i>
Na PDT	<i>n.d.</i>	3.67	1.84	1.84	3.67	-	-	-	-	-	-
	(2.24)	(2.67)	(1.55)	(1.55)	(2.67)						
K PipeDTC	<i>n.d.</i>	4.27	1.39	1.54	1.39	4.27	-	-	-	-	-
	(2.21)	(2.68)	(1.40)	(1.40)	(1.40)	(2.68)					
K MorphDTC	-	3.47	4.30	<i>n.d.</i>	4.30	3.47	-	-	-	-	-
		(3.53)	(2.77)	(2.42)	(2.77)	(3.53)					
K IndolineDTC	<i>n.d.</i>	4.45	2.87	7.11	6.80	7.00	9.53	-	-	-	-
	(3.51)	(3.40)	(2.91)	(7.08)	(6.69)	(6.97)	(7.12)				
Na ProOMeDTC	<i>n.d.</i>	5.09	2.03-	2.03-	3.95	-	-	-	-	3.69	-
	(3.57)	(4.72)	2.33	2.33	(2.84-					(3.67)	
			(1.80-	(1.80-	3.06)						
			2.10)	2.10)							
Na ProOtBuDTC	<i>n.d.</i>	4.98	2.01-	2.01-	3.94	-	-	-	-	-	1.47
	(3.59)	(4.71)	2.30	2.30	(2.85-						(1.50)
			(1.79-	(1.79-	3.05)						
			2.11)	2.11)							
Na CDT	8.46	7.33	7.17	8.07	8.07	7.17	7.33	8.46	<i>n.d.</i>	-	-
	(7.42)	(7.42)	(7.24)	(8.09)	(8.09)	(7.24)	(7.42)	(7.42)	(11.22)		
Na IndDTC	<i>n.d.</i>	8.67	6.36	7.46	7.07	7.07	9.33	-	-	-	-
	(11.04)	(7.05)	(6.42)	(7.57)	(7.33)	(7.33)	(7.29)				
Na PyrrDTC	<i>n.d.</i>	8.03	5.99	5.99	8.03	-	-	-	-	-	-
	(10.75)	(6.73)	(6.01)	(6.01)	(6.73)						

Table SI 5. Comparison between proton chemical shifts (ppm) of the dithiocarbamate salts and the parent amine (reported in brackets). The *H*-signals proximal to the dithiocarbamic moiety are highlighted by bold fonts; *n.d.* stands for “not detected”. Attribution was made following *IUPAC* nomenclature for *N*-heterocyclic compounds. All the spectra were recorded in DMSO-*d*₆ except for those of L-proline esters, obtained in CD₃OD, with a 300.13 MHz NMR spectrometer.

	<i>H</i> ₍₁₎	<i>H</i> ₍₂₎	<i>H</i> ₍₃₎	<i>H</i> ₍₄₎	<i>H</i> ₍₅₎	<i>H</i> ₍₆₎	<i>OMe</i>	<i>OtBu</i>
[Cu(PDT) ₂]	<i>n.d.</i>	8.76	4.47	4.47	8.76	-	-	-
[Cu(PipeDTC) ₂]	<i>n.d.</i>	<i>n.d.</i>	1.17	0.33	1.17	<i>n.d.</i>	-	-
[Cu(ProOMeDTC) ₂]	<i>n.d.</i>	<i>n.d.</i>	2.11-	2.11-	<i>n.d.</i>	-	3.94	-
			2.93	2.93				
[Cu(ProOtBuDTC) ₂]	<i>n.d.</i>	<i>n.d.</i>	1.99-	1.99-	<i>n.d.</i>	-	-	1.57

Table SI 6. List of the proton chemical shifts (ppm) of the Cu(II) derivatives of PDT, PipeDTC and L-proline ester DTCs. The *H*-signals proximal to the dithiocarbamic moiety are labeled with bold font; *n.d.* stands for “not detected”. Attribution was carried out according to the *IUPAC* nomenclature for *N*-heterocyclic compounds. All the spectra were recorded in CDCl₃ with a 300.13 MHz spectrometer at 298 K.

	<i>H</i> ₍₁₎	<i>H</i> ₍₂₎	<i>H</i> ₍₃₎	<i>H</i> ₍₄₎	<i>H</i> ₍₅₎	<i>H</i> ₍₆₎	<i>H</i> ₍₇₎	<i>H</i> ₍₈₎	<i>H</i> ₍₉₎	<i>OMe</i>	<i>OtBu</i>
[Ru(PDT) ₃]	<i>n.d.</i>	35.83, 44.29	0.39	0.39	35.83, 44.29	-	-	-	-	-	-
β[Ru ₂ (PDT) ₅]Cl	<i>n.d.</i>	3.46- 3.94	1.81- 2.19	1.81- 2.19	3.46- 3.94	-	-	-	-	-	-
[Ru(PipeDTC) ₃]	<i>n.d.</i>	24.03	0.87	3.54	0.87	24.03	-	-	-	-	-
β[Ru ₂ (PipeDTC) ₅]Cl	<i>n.d.</i>	3.03- 4.65	1.83	1.50	1.83	3.03- 4.65	-	-	-	-	-
[Ru(MorphDTC) ₃]	-	3.15	24.90	<i>n.d.</i>	24.90	3.15	-	-	-	-	-
β[Ru ₂ (MorphDTC) ₅]Cl	-	3.25- 4.65	3.25- 4.65	<i>n.d.</i>	3.25- 4.65	3.25- 4.65	-	-	-	-	-
[Ru(IndolineDTC) ₃]	<i>n.d.</i>	35.92, 45.63	0.16	8.67	7.27	8.95	<i>n.d.</i>	-	-	-	-
β[Ru ₂ (IndolineDTC) ₅]Cl	<i>n.d.</i>	3.22- 4.88	3.22- 4.88	7.35- 8.87	7.35- 8.87	7.35- 8.87	7.35- 8.87	-	-	-	-
[Ru(ProOMeDTC) ₃]	<i>n.d.</i>	38.65- 46.27	0.47- 2.27	0.47- 2.27	23.55- 28.34, 31.41- 34.64	-	-	-	-	3.07	-
β[Ru ₂ (ProOMeDTC) ₅]Cl	<i>n.d.</i>	5.02- 5.38	2.20	2.20	3.28- 3.98	-	-	-	-	3.28- 3.98	-
[Ru(ProOtBuDTC) ₃]	<i>n.d.</i>	40.07- 44.47	0.50- 2.27	0.50- 2.27	23.65- 26.70, 30.00- 33.38	-	-	-	-	-	0.50- 2.27
β[Ru ₂ (ProOtBuDTC) ₅]Cl	<i>n.d.</i>	4.36- 5.30	1.41- 2.26	1.41- 2.26	3.21- 4.02	-	-	-	-	-	1.41- 2.26
[Ru(CDT) ₃]	<i>n.d.</i>	9.01- 9.03	8.90	7.71- 7.73	7.71- 7.73	8.90	9.01- 9.03	<i>n.d.</i>	<i>n.d.</i>	-	-
β[Ru ₂ (CDT) ₅]Cl	9.17- 9.19	7.46- 7.53	7.46- 7.53	7.98- 8.00	7.98- 8.00	7.46- 7.53	7.46- 7.53	9.17- 9.19	<i>n.d.</i>	-	-

Table SI 7: List of the proton chemical shifts (ppm) of Ru(III)-DTC derivatives, both mono- and dinuclear, synthesized in this work. The signals of protons close to the dithiocarbamic moiety are highlighted by bold font; *n.d.* stands for “not detected”. Attribution was made based on the *IUPAC* nomenclature for *N*-heterocyclic compounds. All the spectra were recorded with a 300.13 MHz spectrometer at 298 K in CDCl₃, except for those of the Ru(III)-IndolineDTC derivatives, obtained in CD₂Cl₂.

UV-Visible resuming tables

	λ (ϵ , $M^{-1} cm^{-1}$)				
	<i>band I</i>	<i>band II</i>	<i>band III</i>	<i>band IV</i>	<i>band V</i>
[Cu(PDT)₂]	269 nm (27004)	287 nm (14432)	453 nm (10760)	512 nm (2199) ^{sh}	614 nm (771)
[Cu(PipeDTC)₂]	272 nm (29246)	285 nm (17565)	436 nm (11314)	495 nm (3760) ^{sh}	604 nm (872)
[Cu(ProOMeDTC)₂]	270 nm (25646)	292 nm (13990)	435 nm (9788)	506 nm (1996) ^{sh}	617 nm (620)
[Cu(ProOtBuDTC)₂]	270 nm (27232)	291 nm (14805)	435 nm (10361)	509 nm (2060) ^{sh}	627 nm (646)

Table SI 8. UV-visible spectral data (800-240 nm) of soluble Cu(II) dithiocarbamate complexes in CH₂Cl₂ at 25 °C; sh= shoulder.

	λ (ϵ , $M^{-1} cm^{-1}$)					
	<i>band I</i>	<i>band II</i>	<i>band III</i>	<i>band IV</i>	<i>band V</i>	<i>band VI</i>
[Ru(PDT)₃]	241 nm (42450)	255 ^{sh} nm (39130)	280 ^{sh} nm (25761)	362 nm (10190)	467 nm (2542)	565 nm (1415)
β[Ru₂(PDT)₅]Cl	247 nm (42097)	268 nm (44151)	288 nm (43678)	333 ^{sh} nm (21886)	468 ^{sh} nm (2633)	-
[Ru(PipeDTC)₃]	242 nm (43002)	259 nm (41288)	290 nm (26690)	367 nm (11716)	472 nm (2980)	557 nm (1823)
β[Ru₂(PipeDTC)₅]Cl	246 nm (42333)	267 nm (42667)	287 nm (42351)	332 nm (18040)	464 nm (2033)	-
[Ru(MorphDTC)₃]	241 nm (41989)	258 nm (38726)	286 nm (26096)	368 nm (10078)	470 nm (2236)	566 nm (1020)
β[Ru₂(MorphDTC)₅]Cl	244 nm (39666)	268 nm (41001)	284 nm (39618)	327 nm (19050)	445 nm (3167)	-
[Ru(IndolineDTC)₃]	- ^a	- ^a	280 nm (33333)	345 nm (29740)	449 nm (16206)	612 nm (2073)
β[Ru₂(IndolineDTC)₅]Cl	- ^a	- ^a	286 nm (54229)	330 nm (50490)	410 nm (31116)	-
[Ru(ProOMeDTC)₃]	240 nm (40920)	259 nm (34654)	284 nm (20950)	359 nm (9181)	460 nm (1693)	575 nm (956)
β[Ru₂(ProOMeDTC)₅]Cl	248 nm (39500)	262 nm (39371)	288 nm (32752)	323 nm (14706)	453 nm (2533)	-
[Ru(ProOtBuDTC)₃]	241 nm (41996)	260 nm (35400)	283 nm (23840)	362 nm (9297)	463 nm (2076)	577 nm (1626)
β[Ru₂(ProOtBuDTC)₅]Cl	249 nm	264 nm	287 nm	322 nm	449 nm	-

	(40433)	(41860)	(37448)	(15880)	(2666)	
[Ru(CDT)₃]	- ^a	- ^a	279 nm (39870)	341 nm (31920)	445 nm (18440)	626 nm (2760)
β[Ru₂(CDT)₅]Cl	- ^a	- ^a	278 nm (60794)	361 nm (56490)	421 nm (35672)	-

Table SI 9. UV-Visible spectral data (800-240 nm) of the synthesized Ru(III) dithiocarbamate complexes in CH₂Cl₂ at 25 °C; sh= shoulder; ^a= the band is not reported since it is placed below the solvent cut-off (240 nm).

IR spectra

FT-IR spectra of the synthesized dithiocarbamate ligands

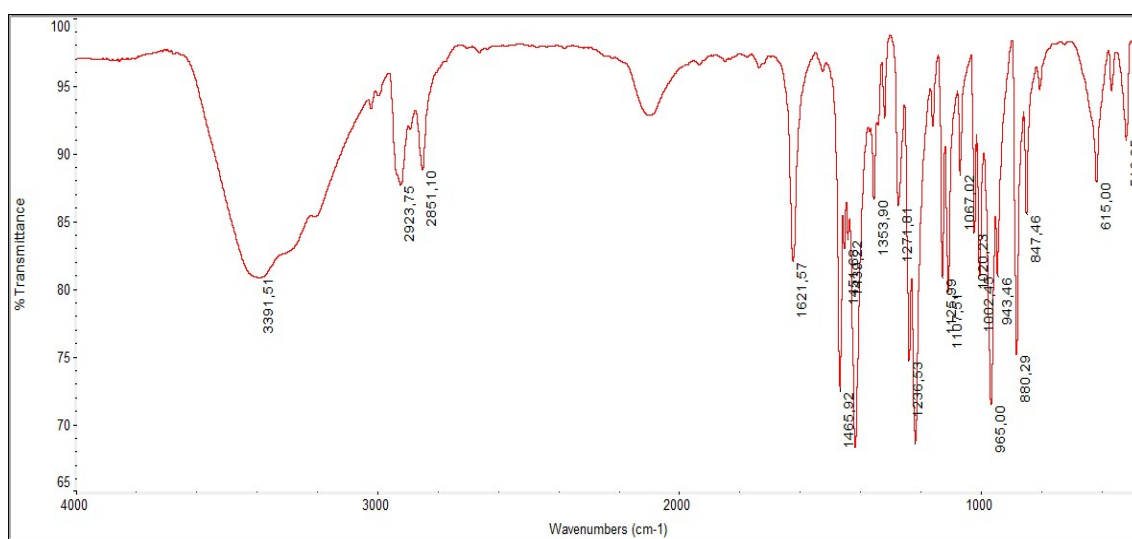


Figure SI 1. Medium FT-IR (4000-500 cm⁻¹, KBr) spectrum of piperidine dithiocarbamate potassium salt (Na PipeDTC).

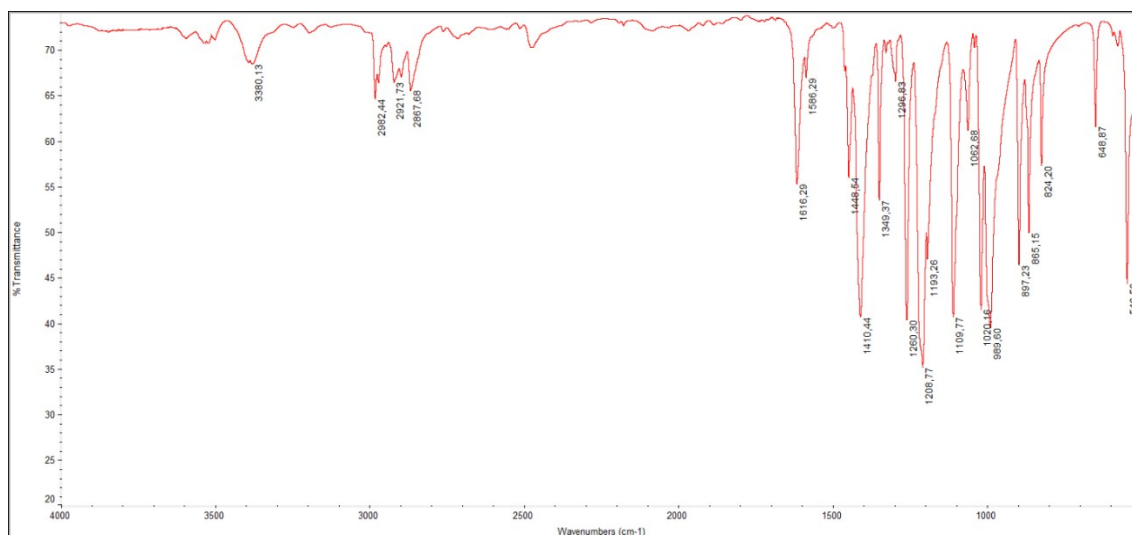


Figure SI 2. Medium FT-IR (4000-500 cm⁻¹, KBr) spectrum of morpholine dithiocarbamate potassium salt (Na MorphDTC).

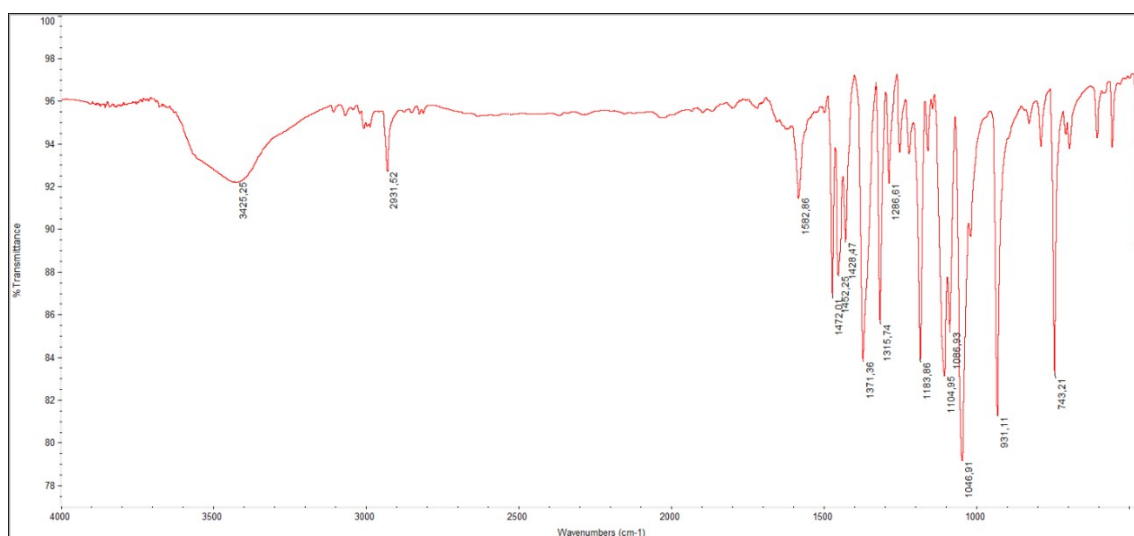


Figure SI 3. Medium FT-IR (4000-500 cm^{-1} , KBr) spectrum of indoline dithiocarbamate potassium salt (K IndolineDTC).

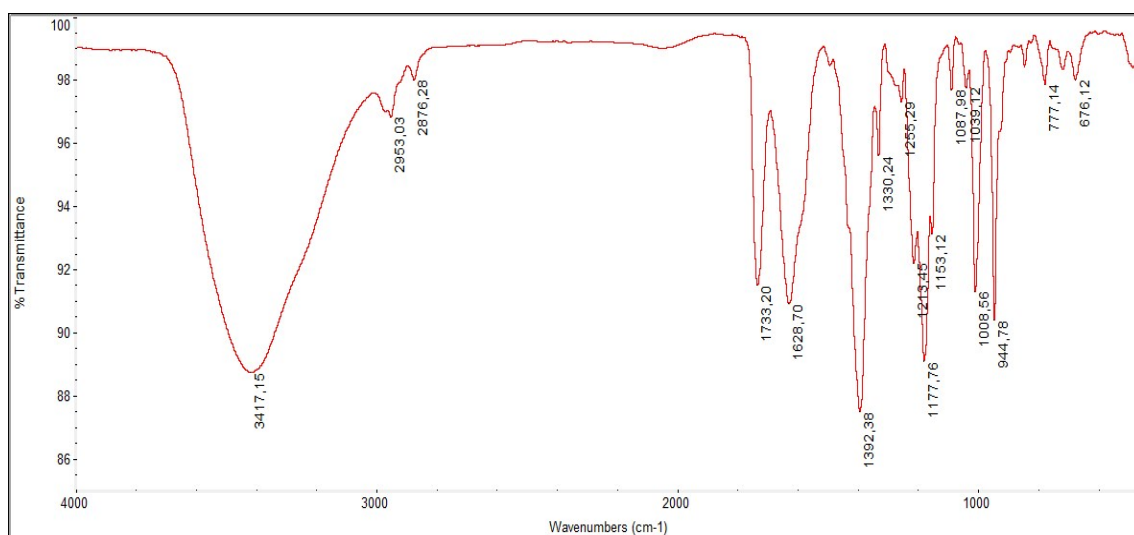


Figure SI 4. Medium FT-IR (4000-500 cm^{-1} , KBr) spectrum of L-proline methyl ester dithiocarbamate sodium salt (Na ProOMeDTC).

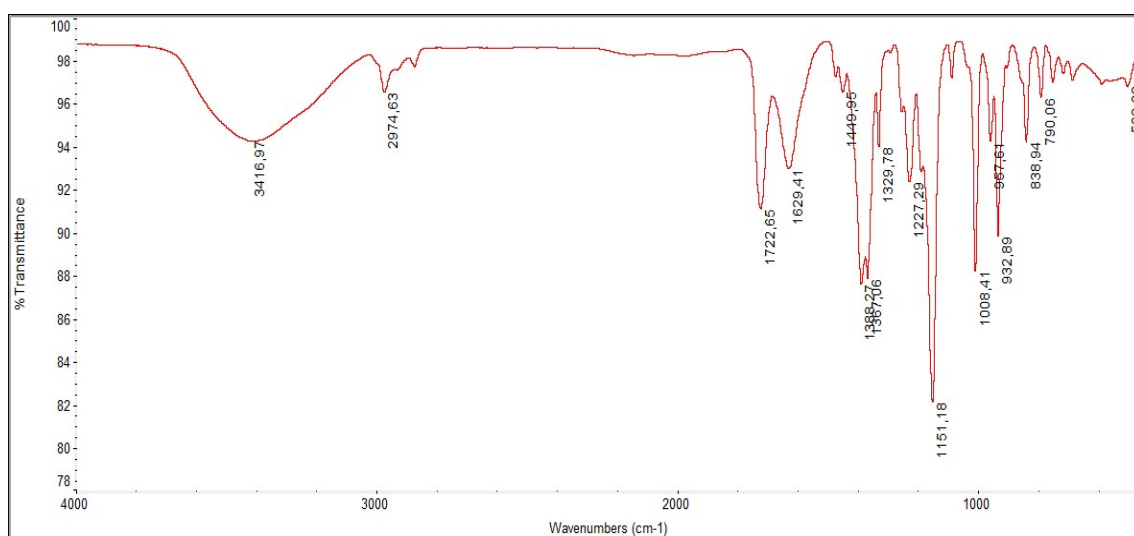


Figure SI 5. Medium FT-IR (4000-500 cm^{-1} , KBr) spectrum of L-proline *tert*-butyl ester dithiocarbamate sodium salt (Na ProOtBuDTC).

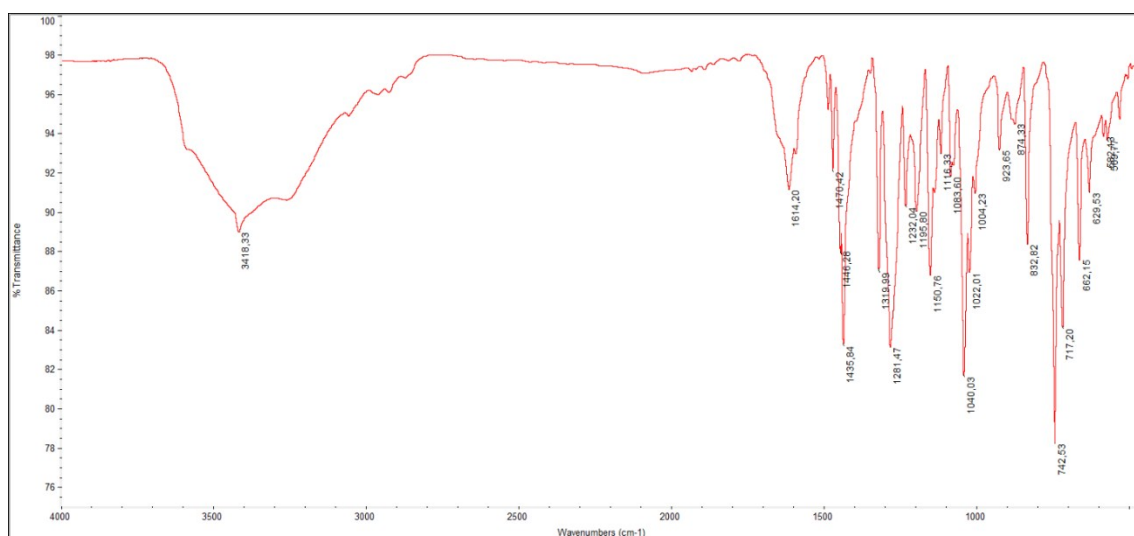


Figure SI 6. Medium FT-IR (4000-500 cm^{-1} , KBr) spectrum of carbazole dithiocarbamate sodium salt (Na CDT).

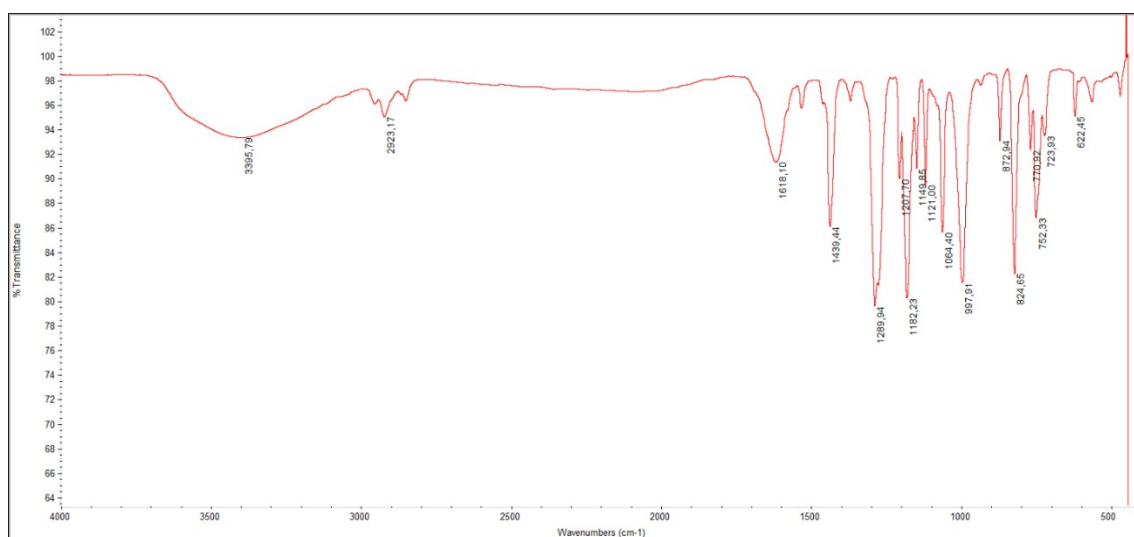


Figure SI 7. Medium FT-IR (4000-500 cm^{-1} , KBr) spectrum of indole dithiocarbamate sodium salt (Na IndDTC).

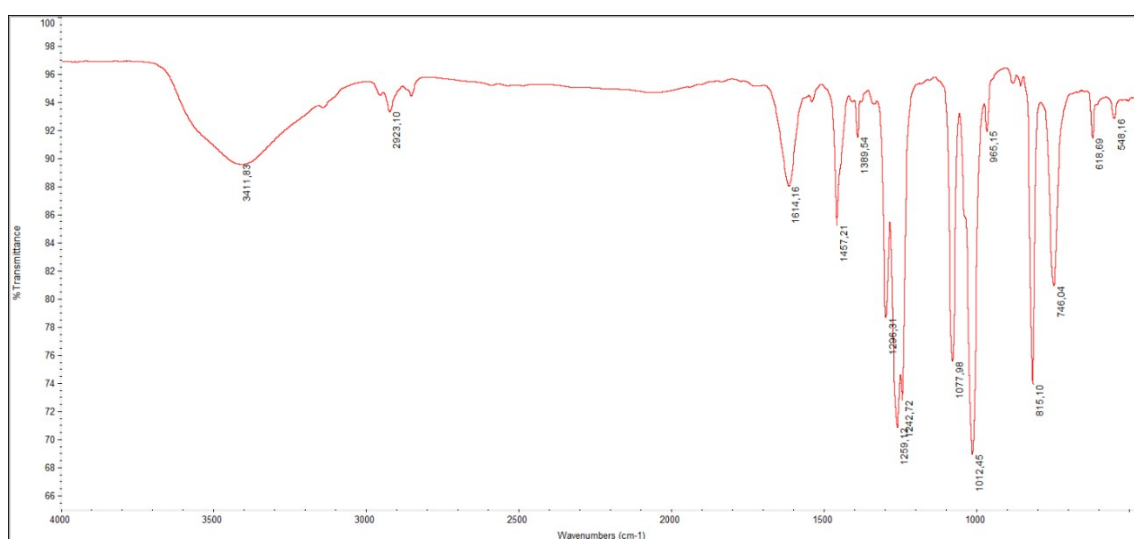


Figure SI 8. Medium FT-IR (4000-500 cm^{-1} , KBr) spectrum of pyrrole dithiocarbamate.

FT-IR spectra of the synthesized Ru(III) dithiocarbamate complexes

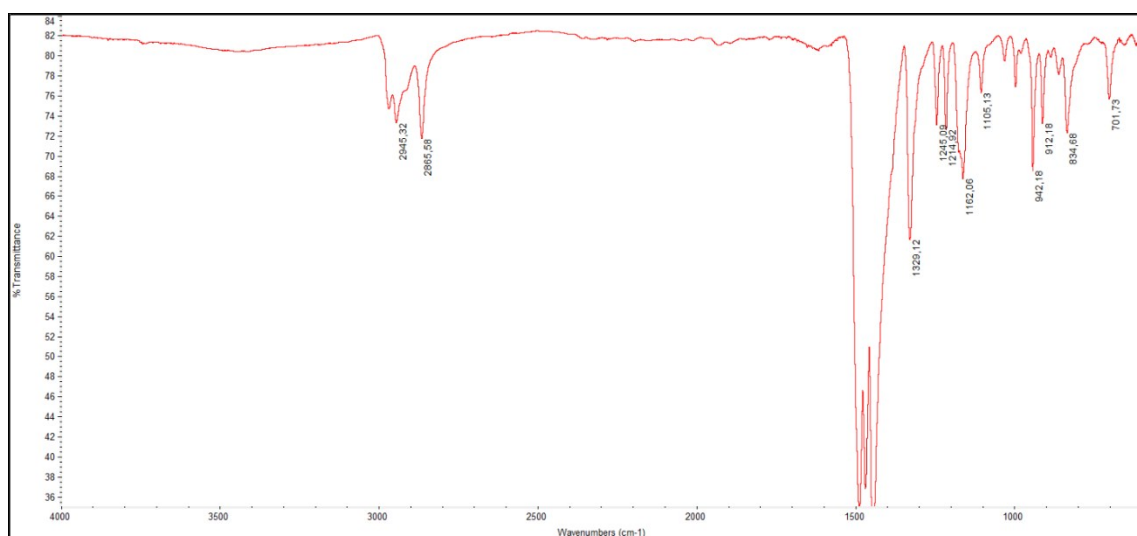


Figure SI 9. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of tris(pyrrolidine dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{PDT})_3]$.

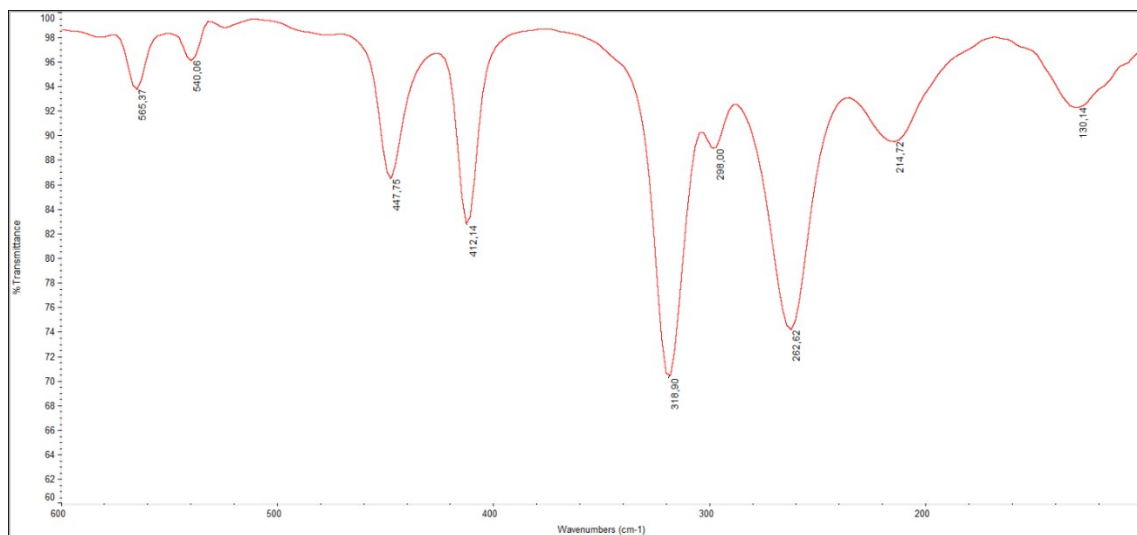


Figure SI 10. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of tris(pyrrolidine dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{PDT})_3]$.

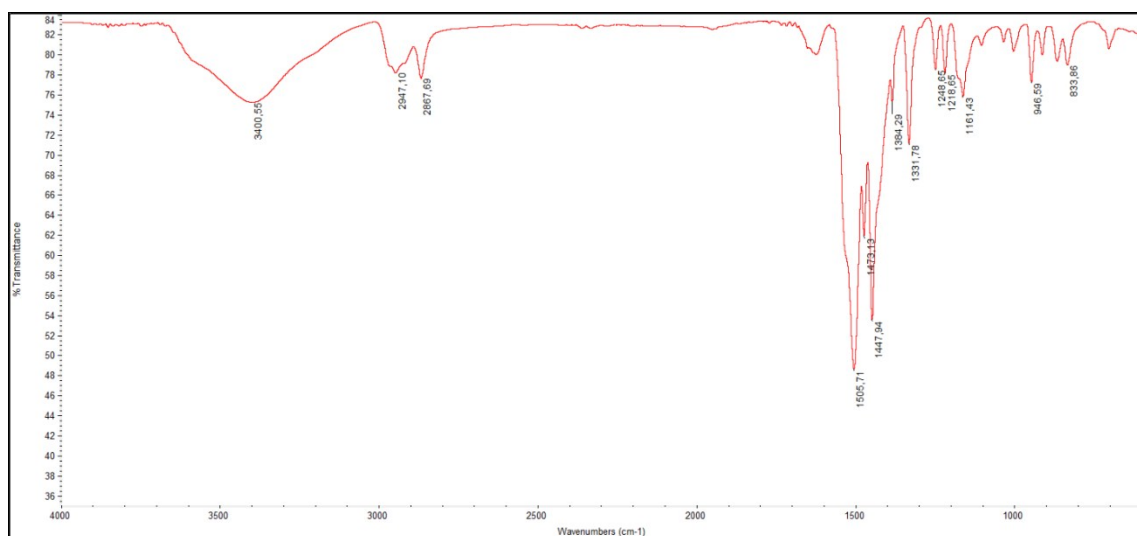


Figure SI 11. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of β -pentakis(pyrrolidine dithiocarbamate)diruthenium(III) chloride, β - $[\text{Ru}_2(\text{PDT})_5]\text{Cl}$.

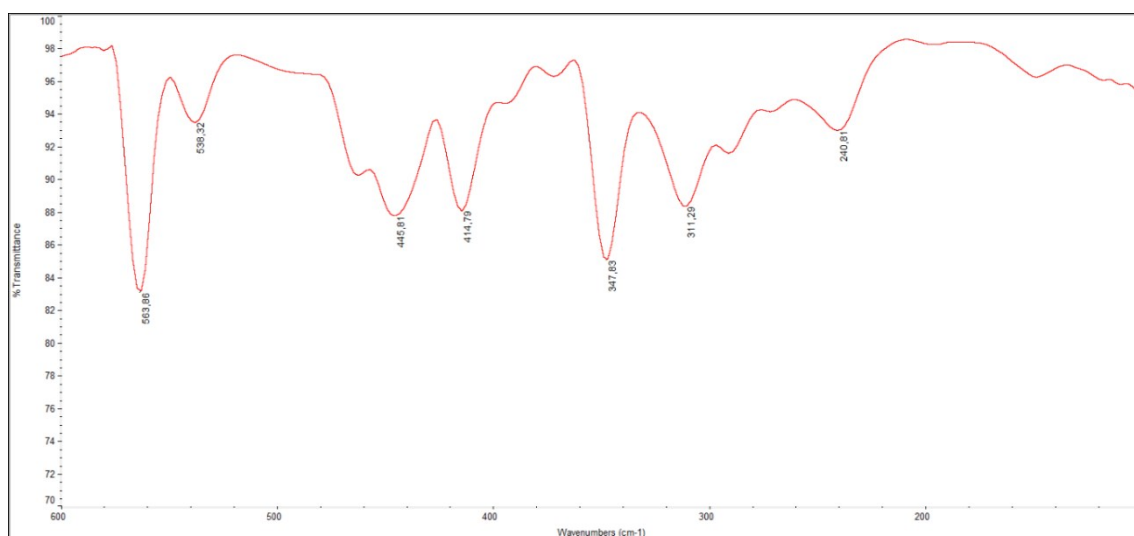


Figure SI 12. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of β -pentakis(pyrrolidine dithiocarbamate)diruthenium(III) chloride, $\beta\text{-[Ru}_2\text{(PDT)}_5\text{]Cl}$.

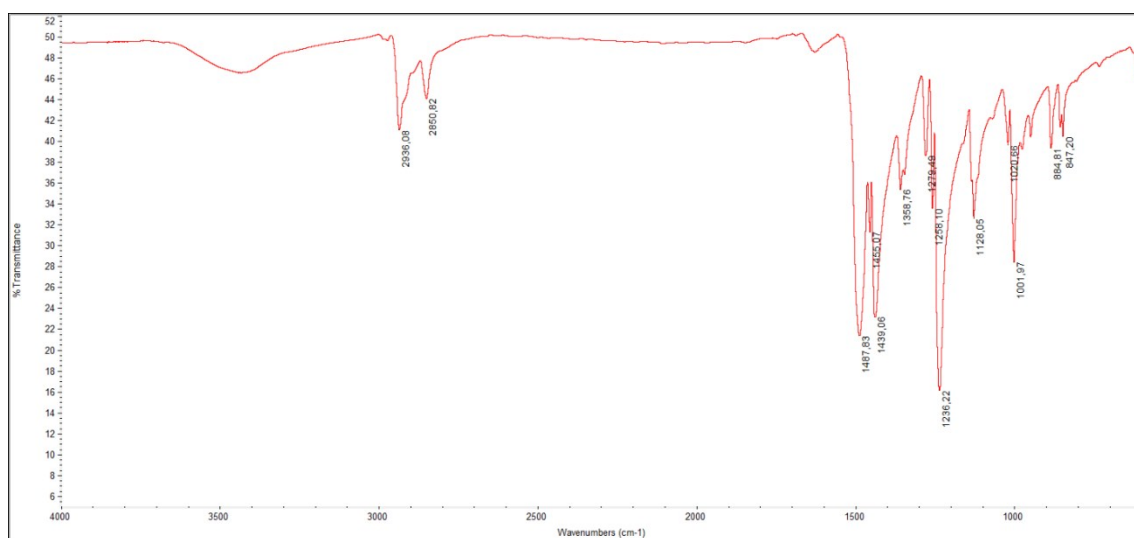


Figure SI 13. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of tris(piperidine dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{PipeDTC})_3]$.

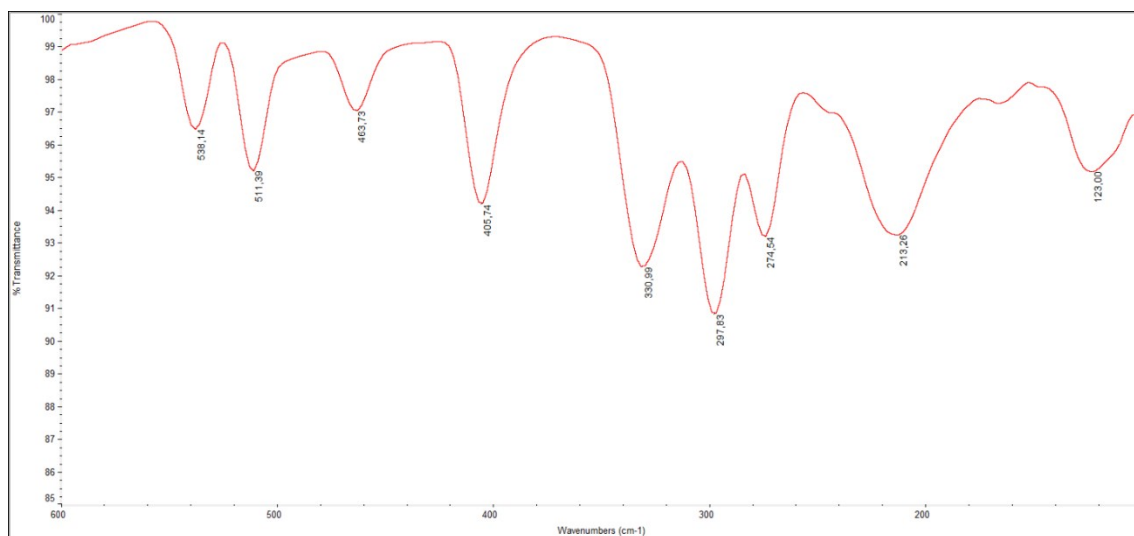


Figure SI 14. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of tris(piperidine dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{PipeDTC})_3]$.

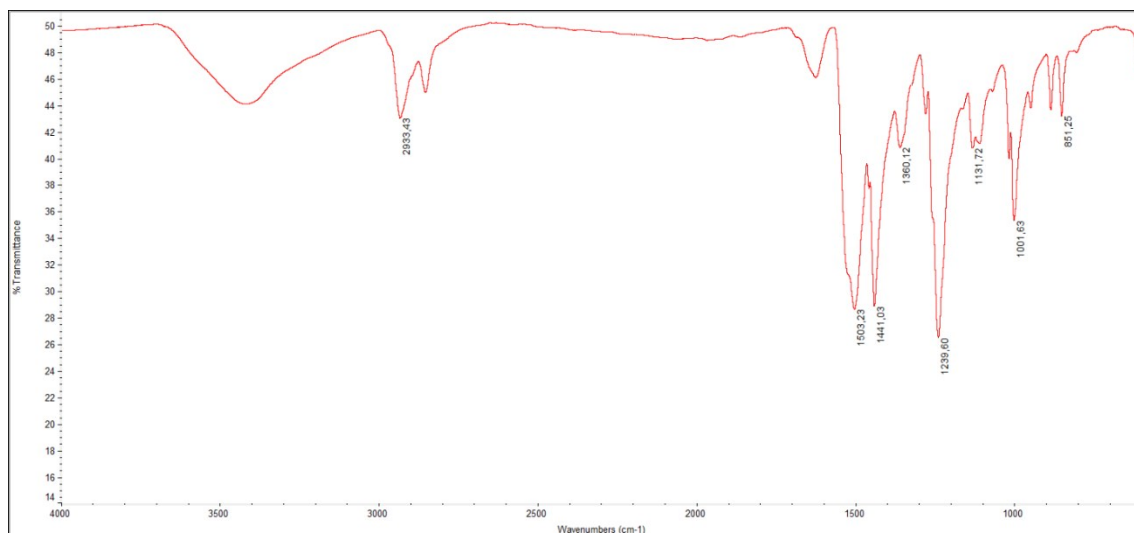


Figure SI 15. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of β -pentakis(piperidine dithiocarbamate)diruthenium(III) chloride, β - $[\text{Ru}_2(\text{PipeDTC})_5]\text{Cl}$.

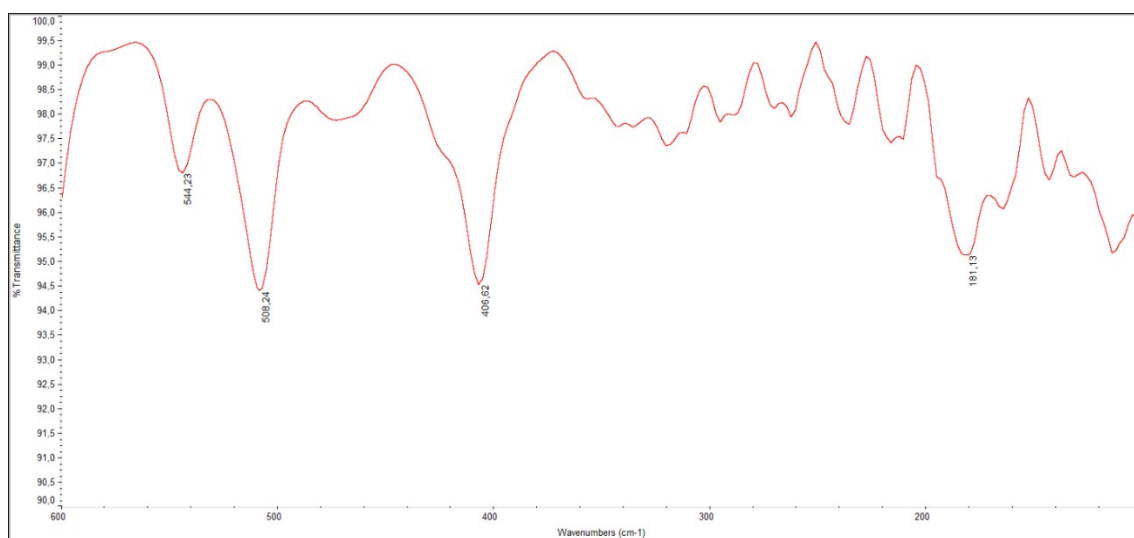


Figure SI 16. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of β -pentakis(piperidine dithiocarbamate)diruthenium(III) chloride, β - $[\text{Ru}_2(\text{PipeDTC})_5]\text{Cl}$.

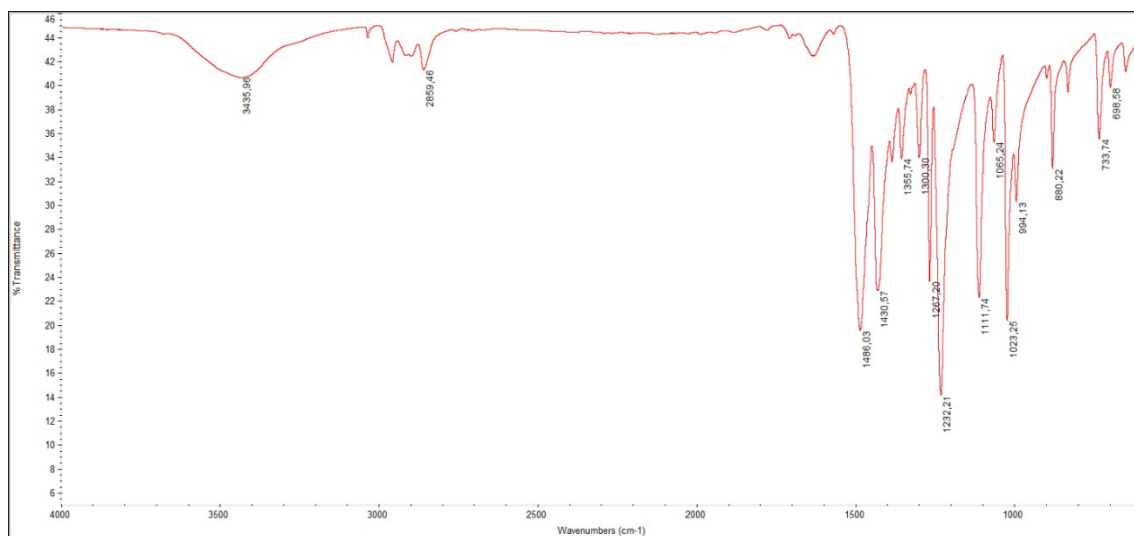


Figure SI 17. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of tris(morpholine dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{MorphDTC})_3]$.

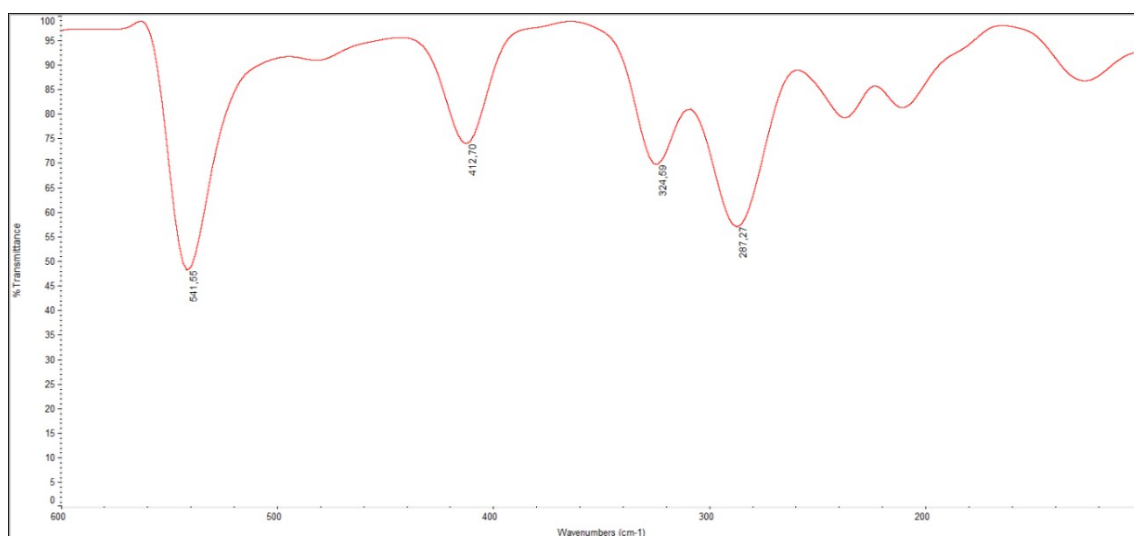


Figure SI 18. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of tris(morpholine dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{MorphDTC})_3]$.

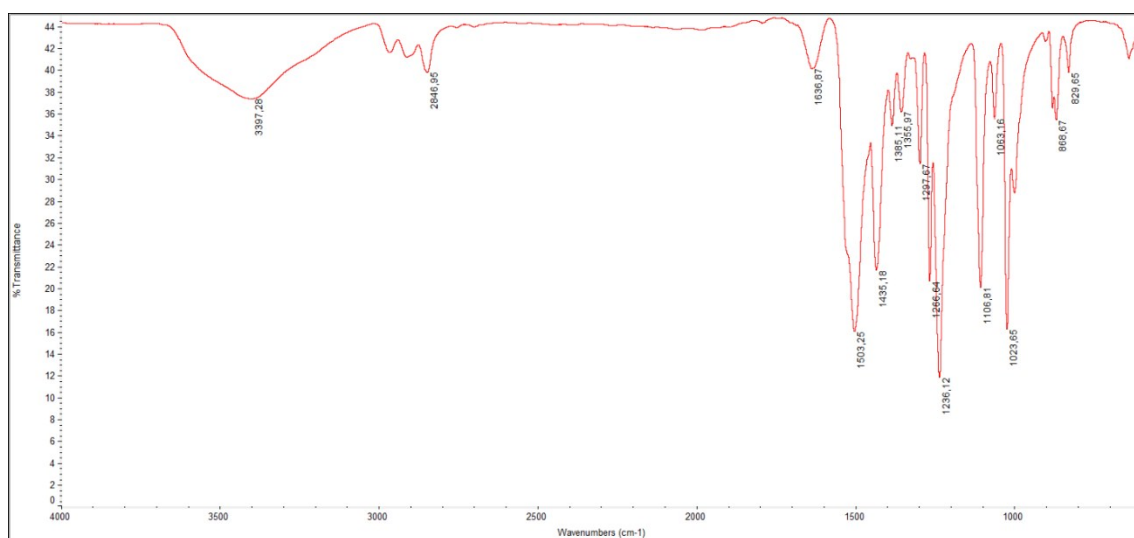


Figure SI 19. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of β -pentakis(morpholine dithiocarbamate)diruthenium(III) chloride, β - $[\text{Ru}_2(\text{MorphDTC})_5]\text{Cl}$.

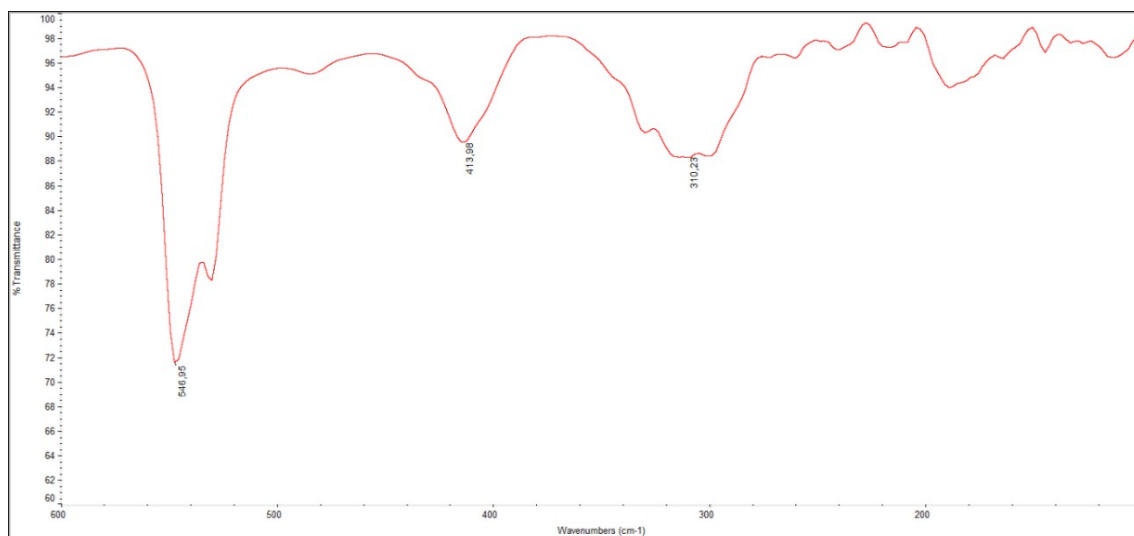


Figure SI 20. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of β -pentakis(morpholine dithiocarbamate)diruthenium(III) chloride, β - $[\text{Ru}_2(\text{MorphDTC})_5]\text{Cl}$.

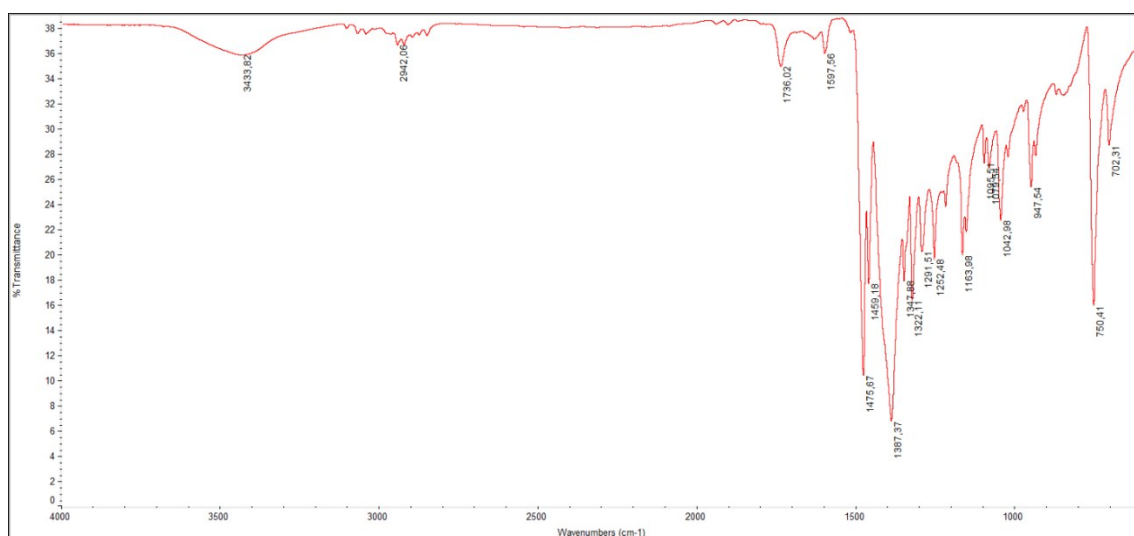


Figure SI 21. Medium FT-IR (4000-600 cm⁻¹, KBr) spectrum of tris(indoline dithiocarbamate)ruthenium(III), [Ru(IndolineDTC)₃].

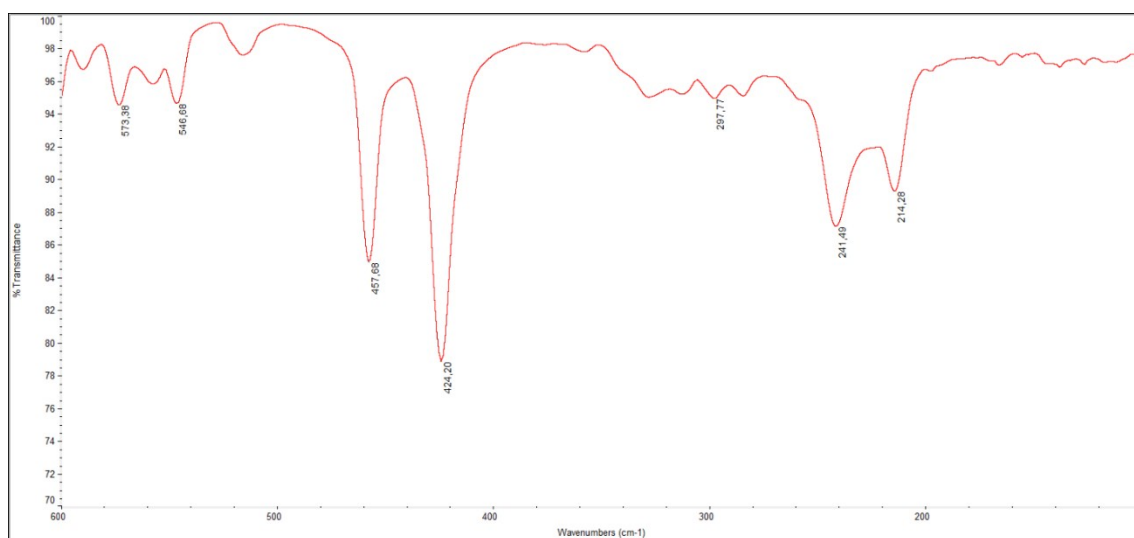


Figure SI 22. Far FT-IR (600-100 cm⁻¹, nujol) spectrum of tris(indoline dithiocarbamate)ruthenium(III), [Ru(IndolineDTC)₃].

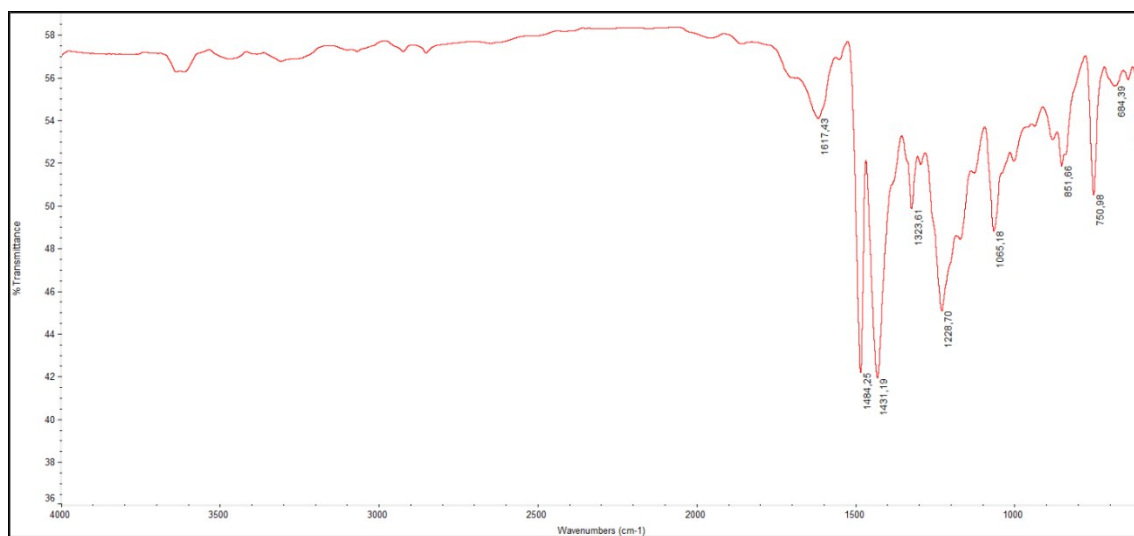


Figure SI 23. Medium FT-IR (4000-600 cm⁻¹, KBr) spectrum of β -pentakis(indoline dithiocarbamate)diruthenium(III) chloride, β -[Ru₂(IndolineDTC)₅]Cl.

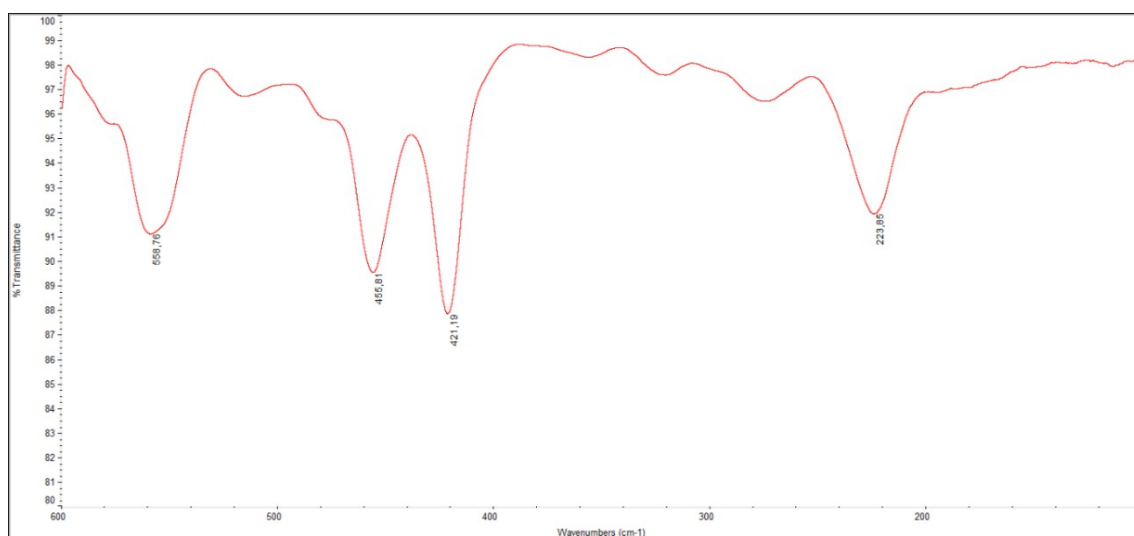


Figure SI 24. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of β -pentakis(indoline dithiocarbamate)diruthenium(III) chloride, β - $[\text{Ru}_2(\text{IndolinedTC})_5]\text{Cl}$.

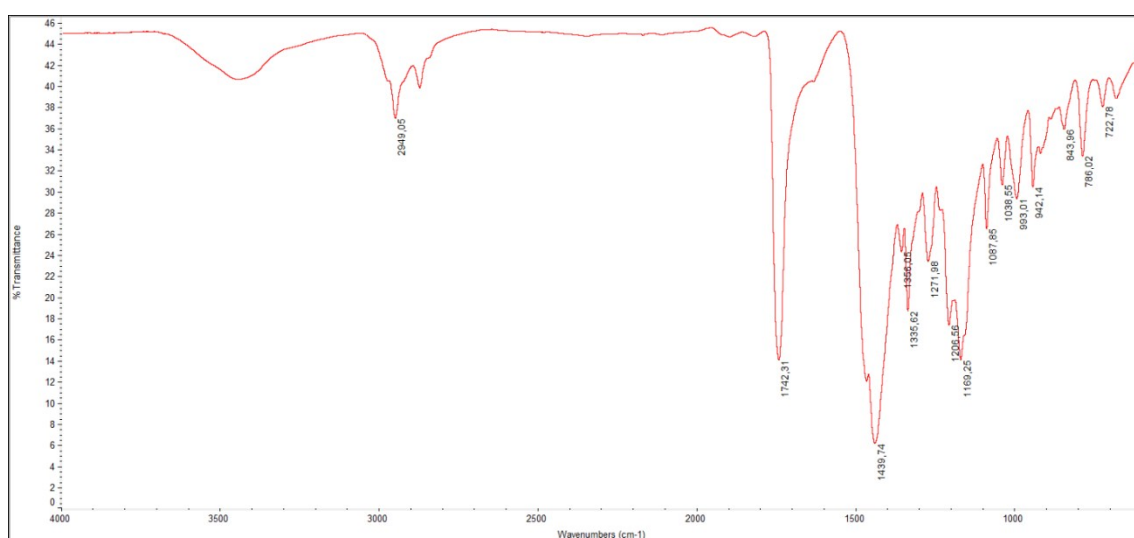


Figure SI 25. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of tris(L-proline methyl ester dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{ProOMeDTC})_3]$.

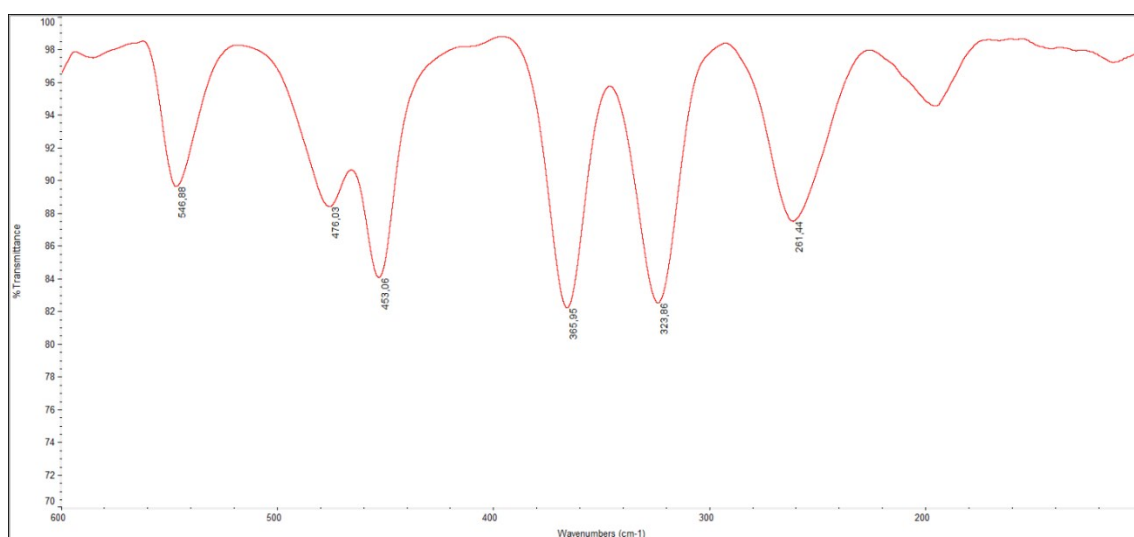


Figure SI 26. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of tris(L-proline methyl ester dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{ProOMeDTC})_3]$.

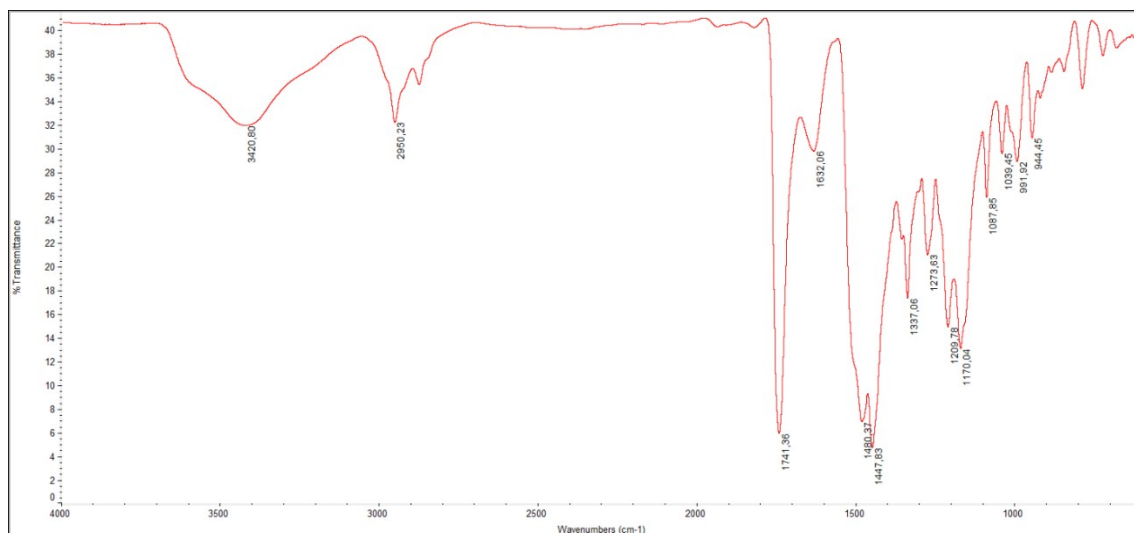


Figure SI 27. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of β -pentakis(L-proline methyl ester dithiocarbamate)diruthenium(III) chloride, $\beta\text{-[Ru}_2(\text{ProOMeDTC})_5\text{]Cl}$.

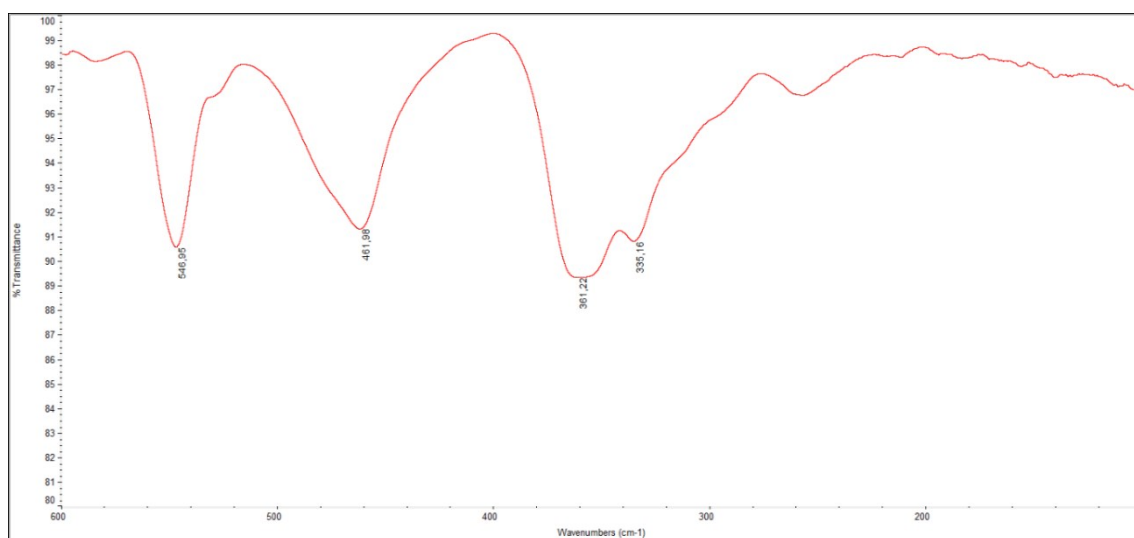


Figure SI 28. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of β -pentakis(L-proline methyl ester dithiocarbamate)diruthenium(III) chloride, $\beta\text{-[Ru}_2(\text{ProOMeDTC})_5\text{]Cl}$.

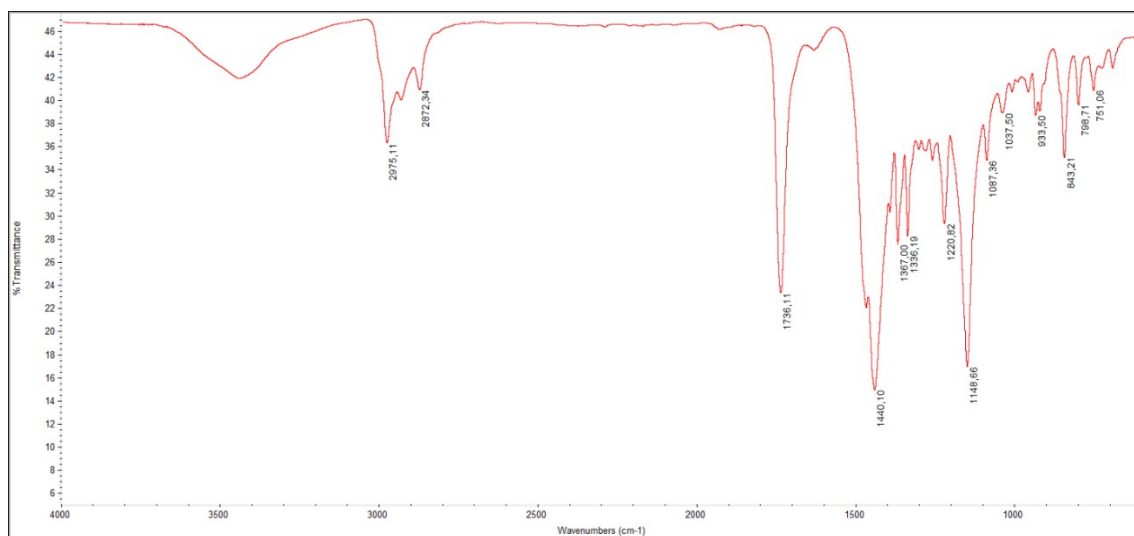


Figure SI 29. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of tris(L-proline *tert*-butyl ester dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{ProOtBuDTC})_3]$.

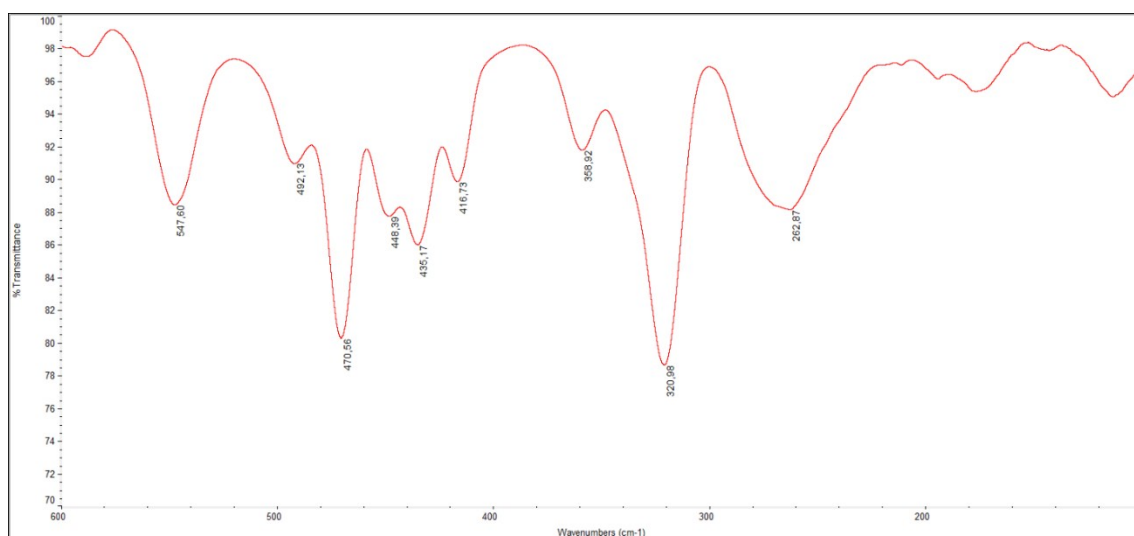


Figure SI 30. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of tris(L-proline *tert*-butyl ester dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{ProOtBuDTC})_3]$.

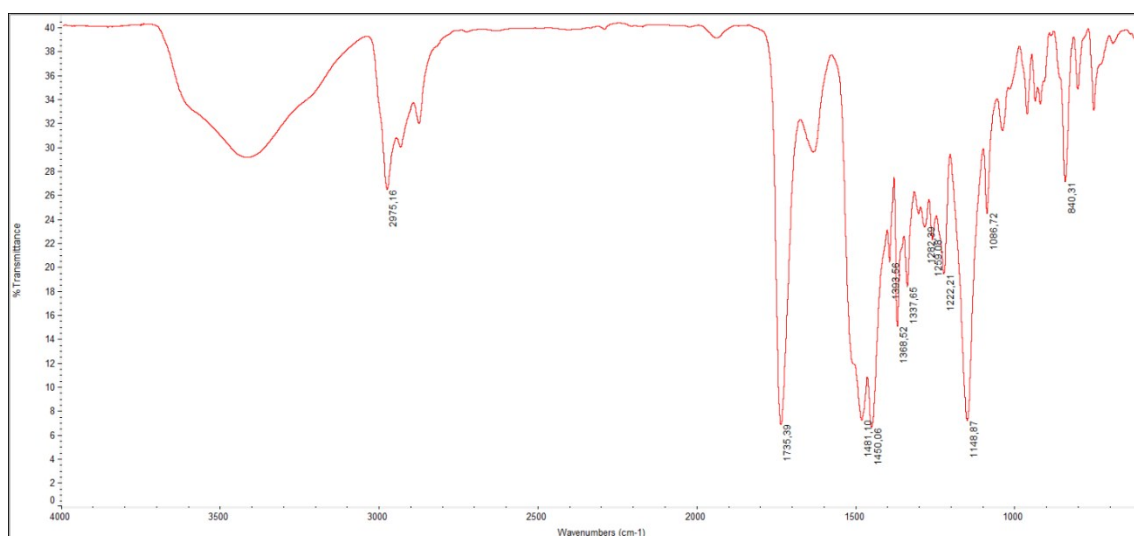


Figure SI 31. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of β -pentakis(L-proline *tert*-butyl ester dithiocarbamate)diruthenium(III) chloride, $\beta\text{-}[\text{Ru}_2(\text{ProOtBuDTC})_5]\text{Cl}$.

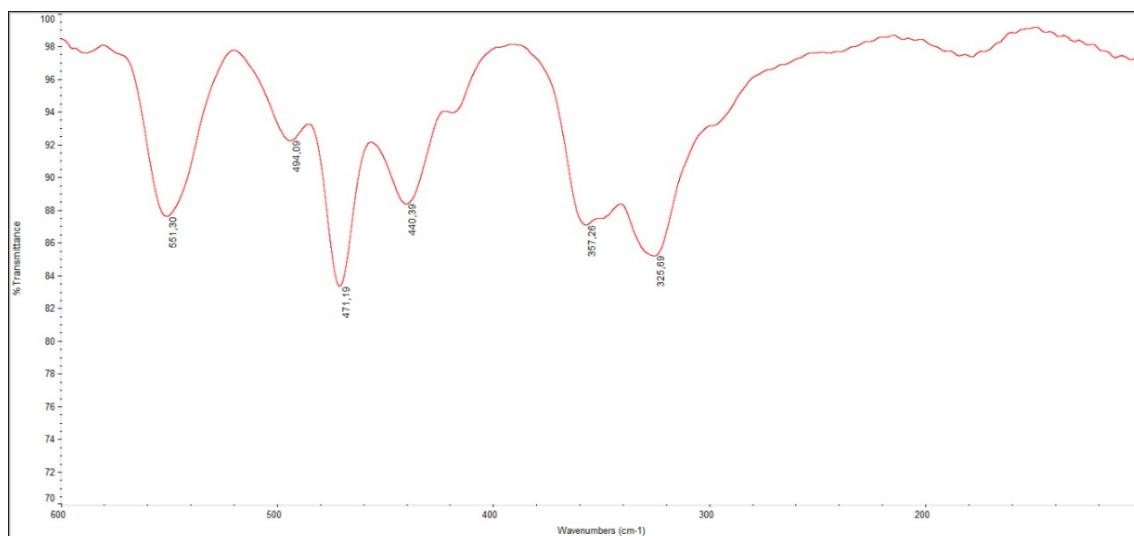


Figure SI 32. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of β -pentakis(L-proline *tert*-butyl ester dithiocarbamate)diruthenium(III) chloride, $\beta\text{-}[\text{Ru}_2(\text{ProOtBuDTC})_5]\text{Cl}$.

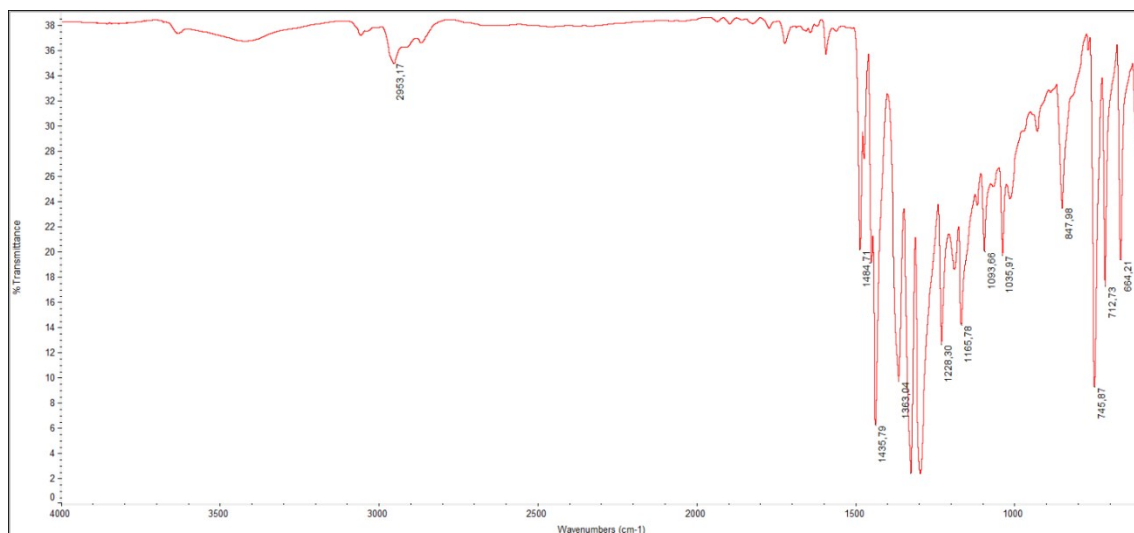


Figure SI 33. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of tris(carbazole dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{CDT})_3]$.

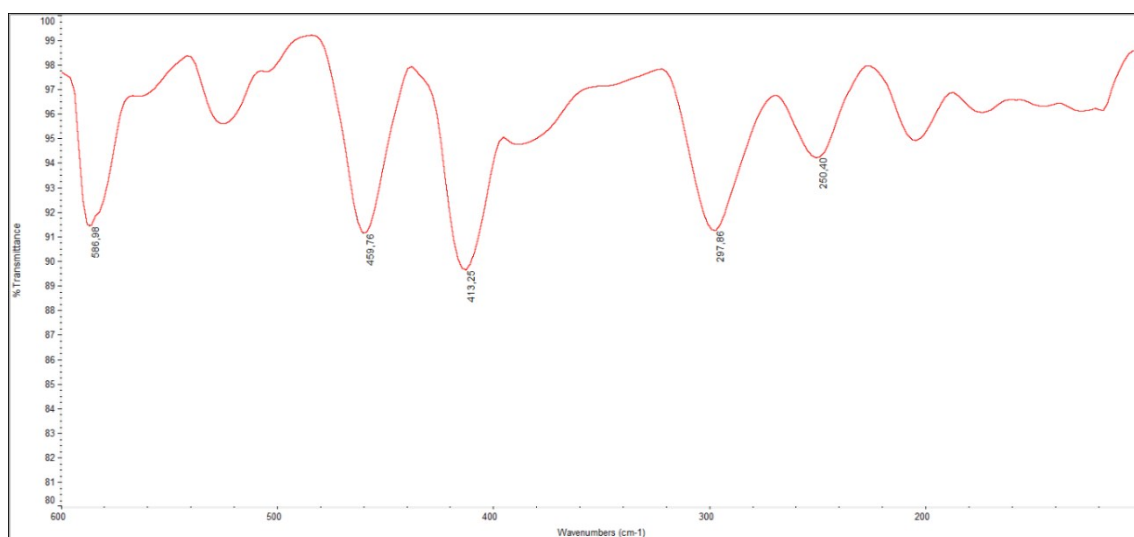


Figure SI 34. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of tris(carbazole dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{CDT})_3]$.

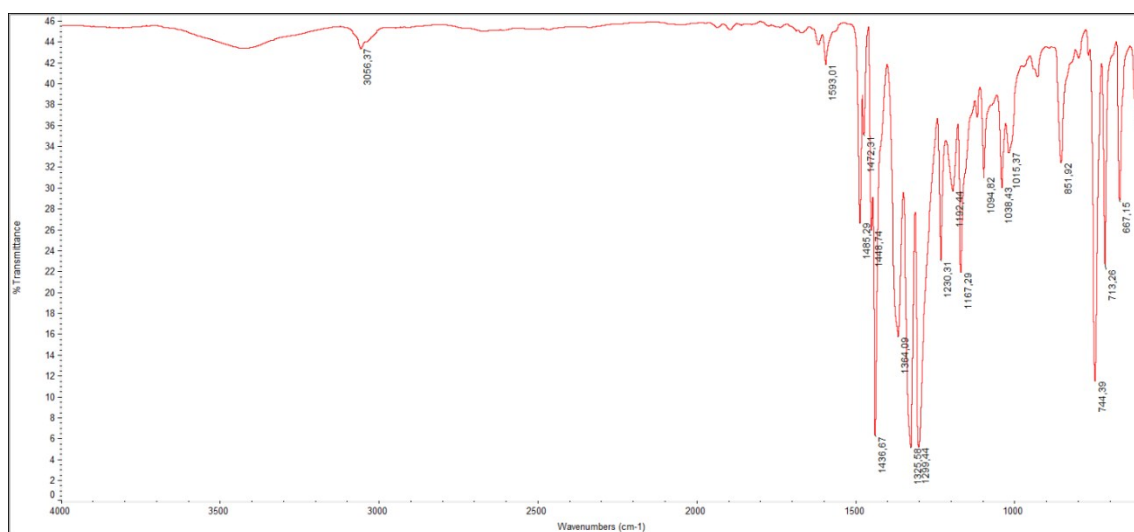


Figure SI 35. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of β -pentakis(carbazole dithiocarbamate)diruthenium(III) chloride, β - $[\text{Ru}_2(\text{CDT})_5]\text{Cl}$.

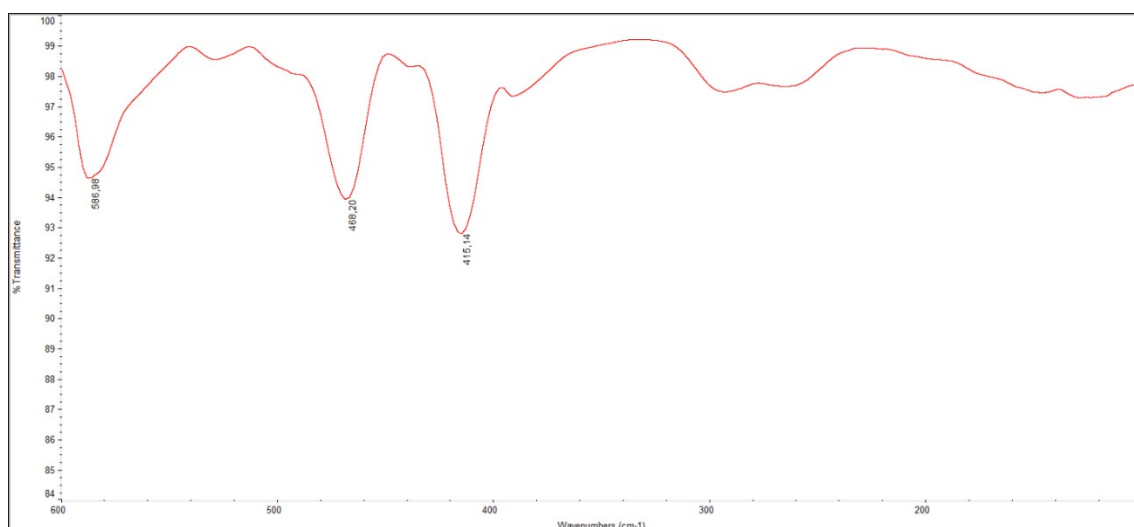


Figure SI 36. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of β -pentakis(carbazole dithiocarbamate)diruthenium(III) chloride, $\beta\text{-}[\text{Ru}_2(\text{CDT})_5]\text{Cl}$.

FT-IR spectra of the synthesized Cu(II) dithiocarbamate complexes

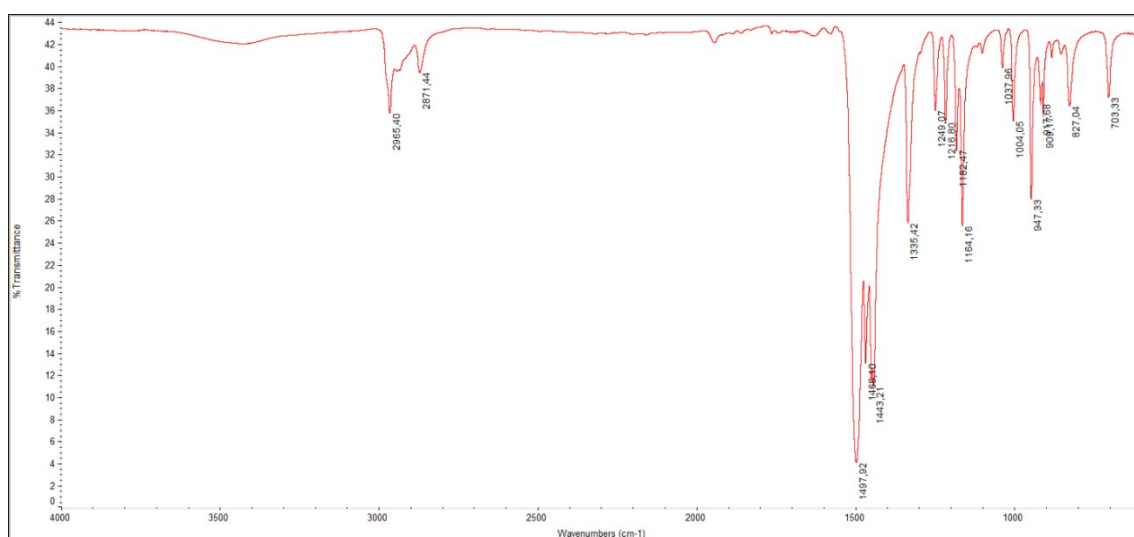


Figure SI 37. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of bis(pyrrolidine dithiocarbamate)copper(II), $[\text{Cu}(\text{PDT})_2]$.

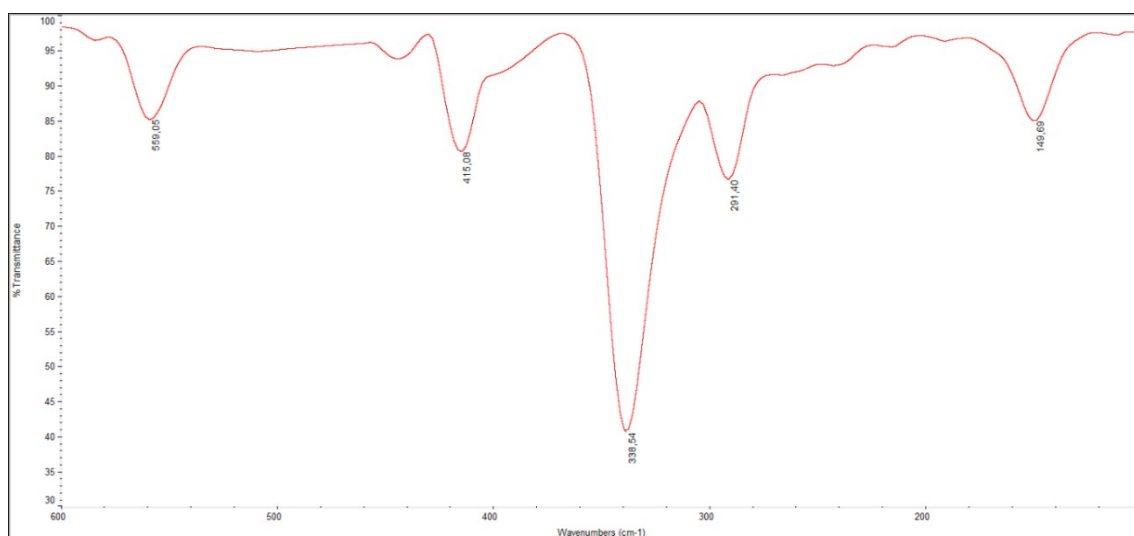


Figure SI 38. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of bis(pyrrolidine dithiocarbamate)copper(II), $[\text{Cu}(\text{PDT})_2]$.

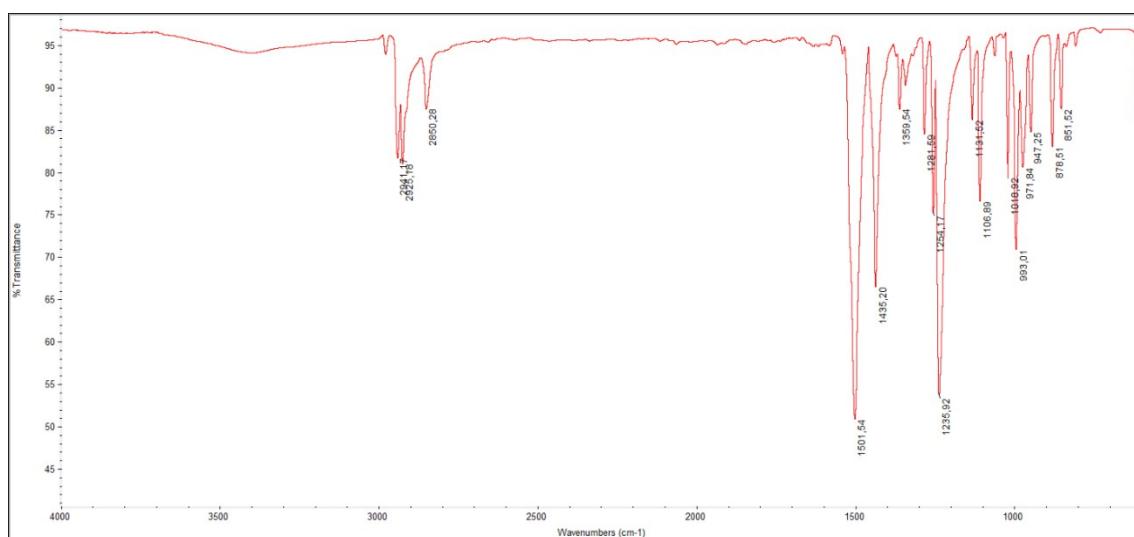


Figure SI 39. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of bis(piperidine dithiocarbamate)copper(II), $[\text{Cu}(\text{PipeDTC})_2]$.

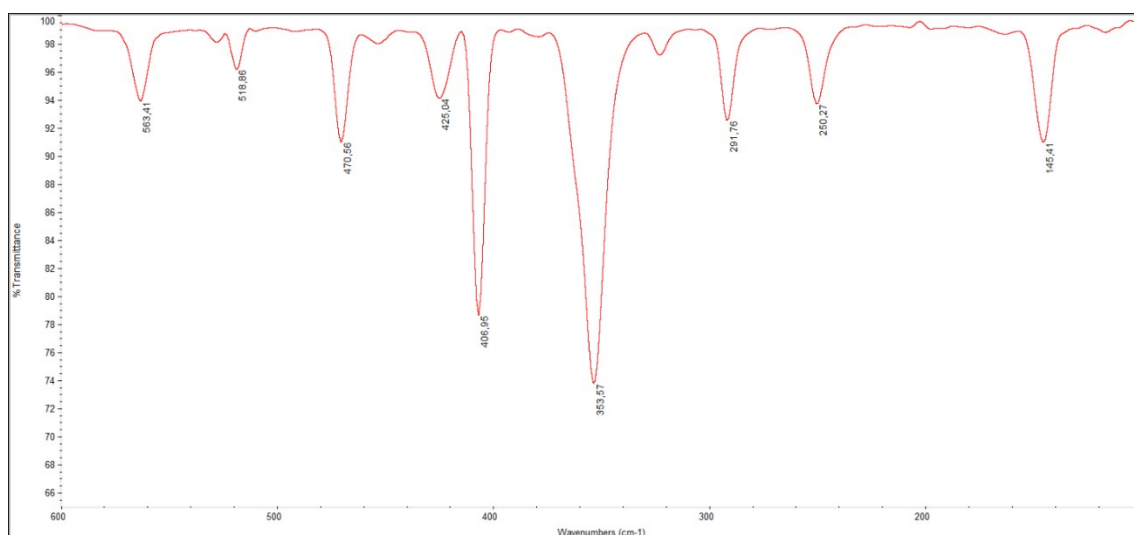


Figure SI 40. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of bis(piperidine dithiocarbamate)copper(II), $[\text{Cu}(\text{PipeDTC})_2]$.

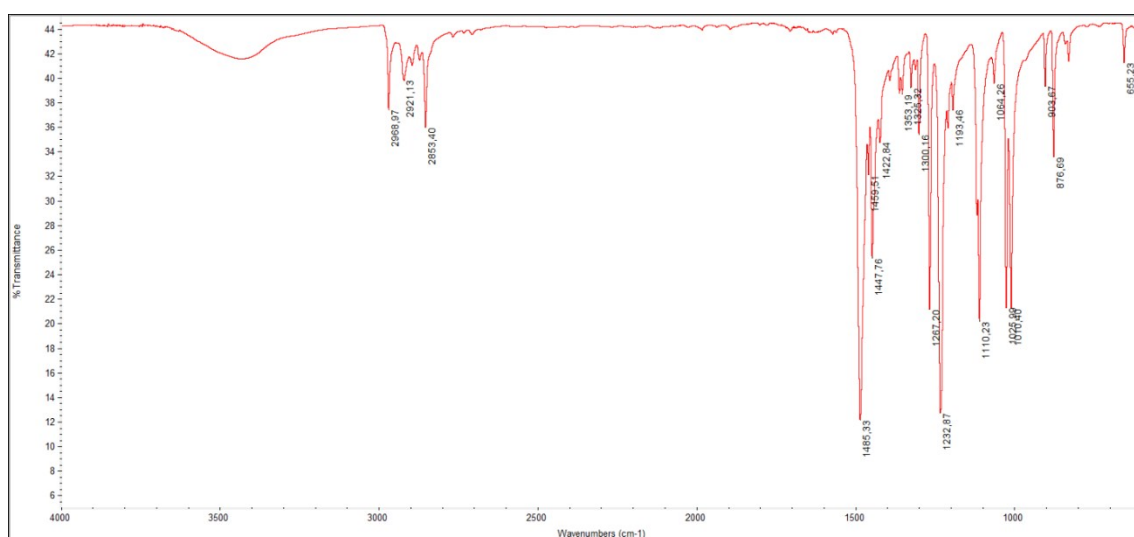


Figure SI 41. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of bis(morpholine dithiocarbamate)copper(II), $[\text{Cu}(\text{MorphDTC})_2]$.

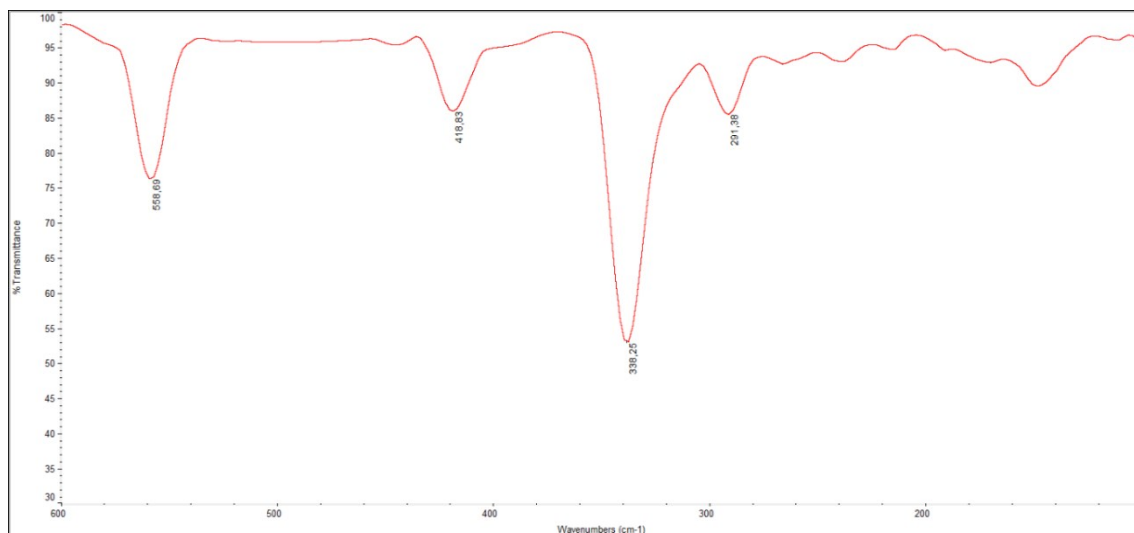


Figure SI 42. Far FT-IR (600-100 cm⁻¹, nujol) spectrum of bis(morpholine dithiocarbamate)copper(II), [Cu(MorphDTC)₂].

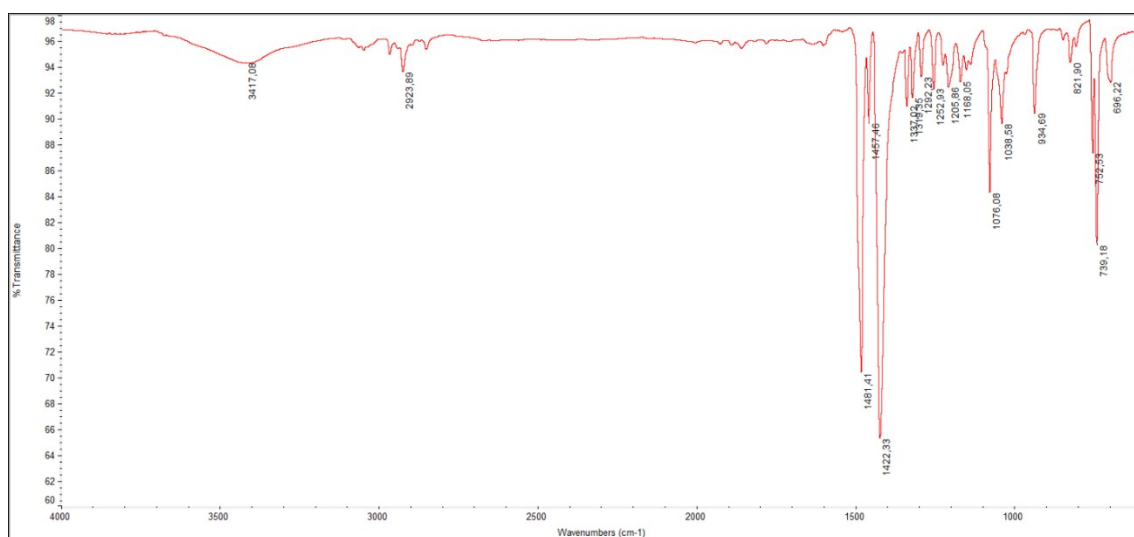


Figure SI 43. Medium FT-IR (4000-600 cm⁻¹, KBr) spectrum of bis(indoline dithiocarbamate)copper(II), [Cu(IndolineDTC)₂].

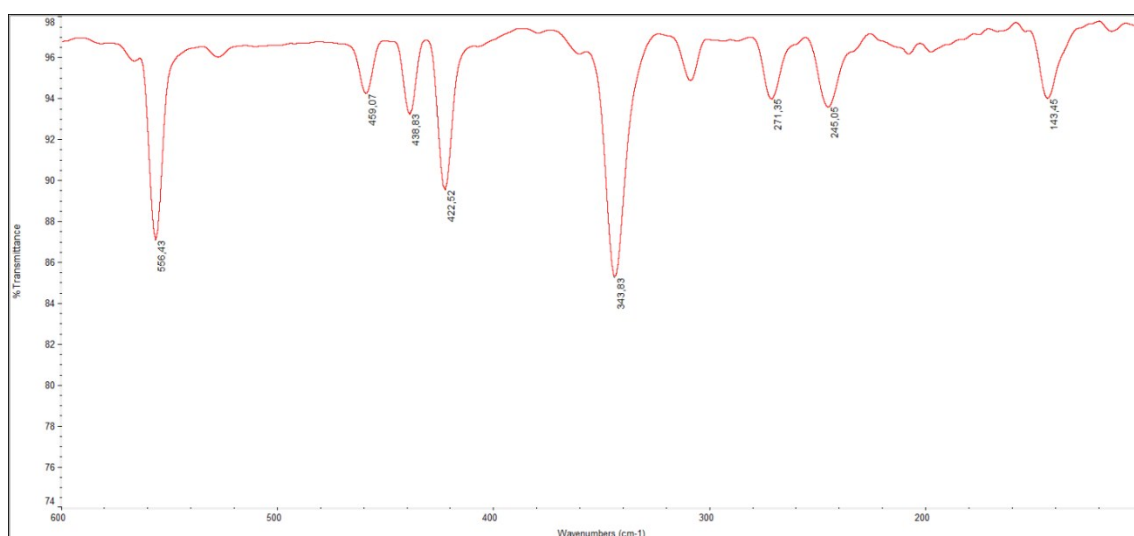


Figure SI 44. Far FT-IR (600-100 cm⁻¹, nujol) spectrum of bis(indoline dithiocarbamate)copper(II), [Cu(IndolineDTC)₂].

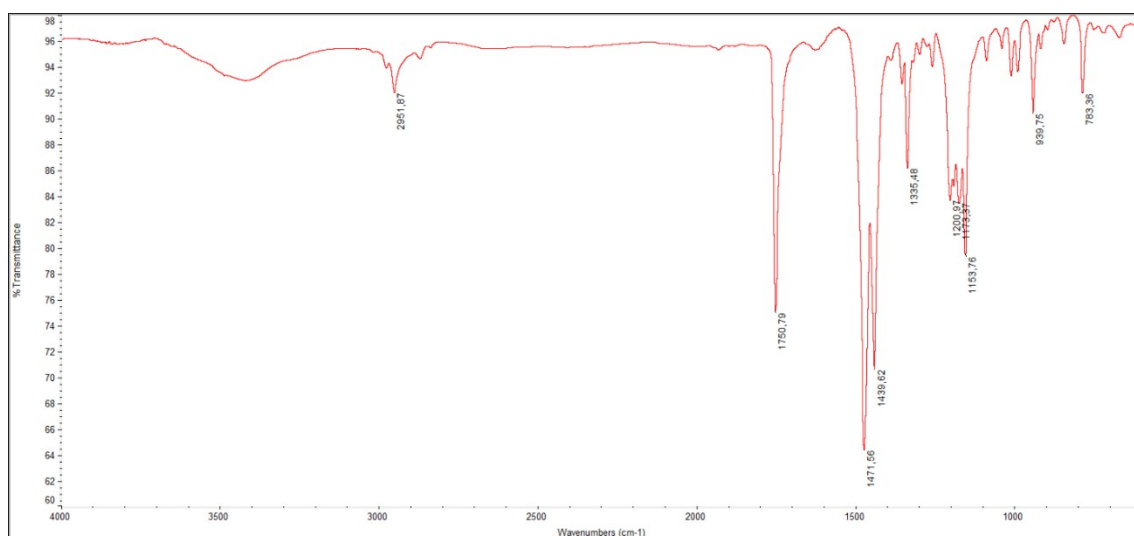


Figure SI 45. Medium FT-IR (4000-600 cm⁻¹, KBr) spectrum of bis(L-proline methyl ester dithiocarbamate)copper(II), [Cu(ProOMeDTC)₂].

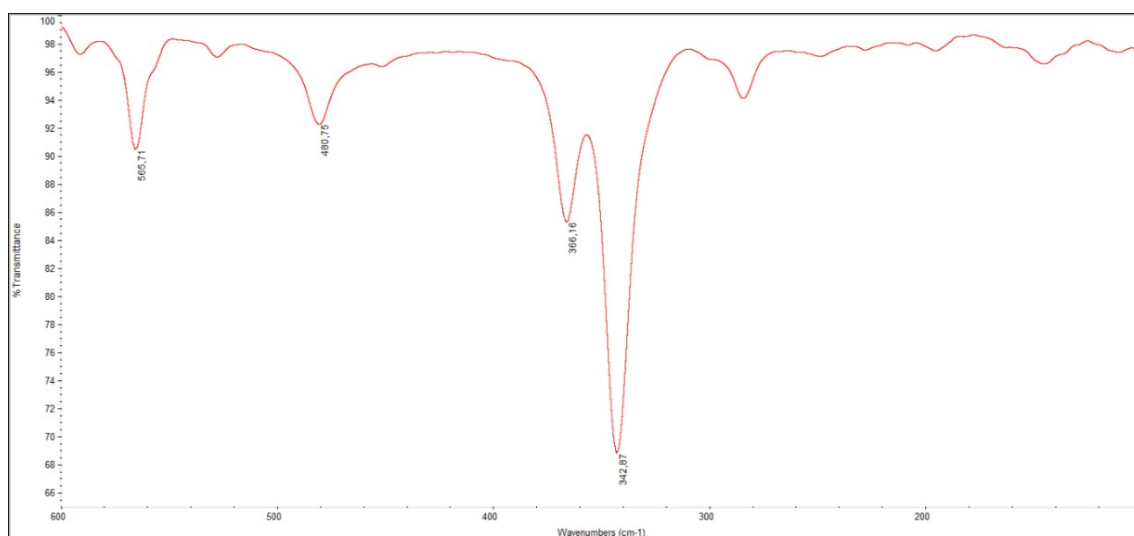


Figure SI 46. Far FT-IR (600-100 cm⁻¹, nujol) spectrum of bis(L-proline methyl ester dithiocarbamate)copper(II), [Cu(ProOMeDTC)₂].

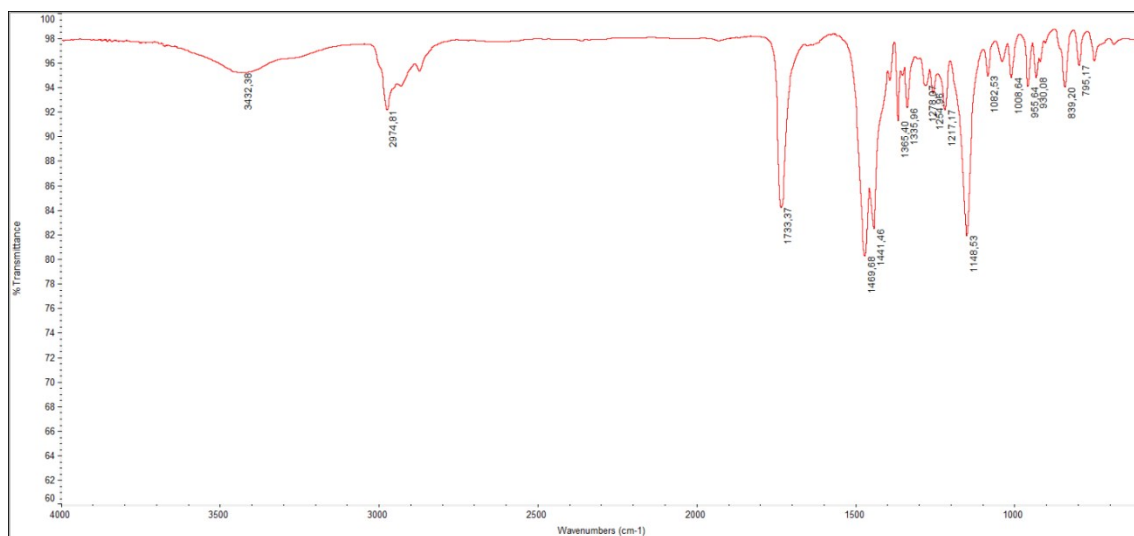


Figure SI 47. Medium FT-IR (4000-600 cm⁻¹, KBr) spectrum of bis(L-proline *tert*-butyl ester dithiocarbamate)copper(II), [Cu(ProOtBuDTC)₂].

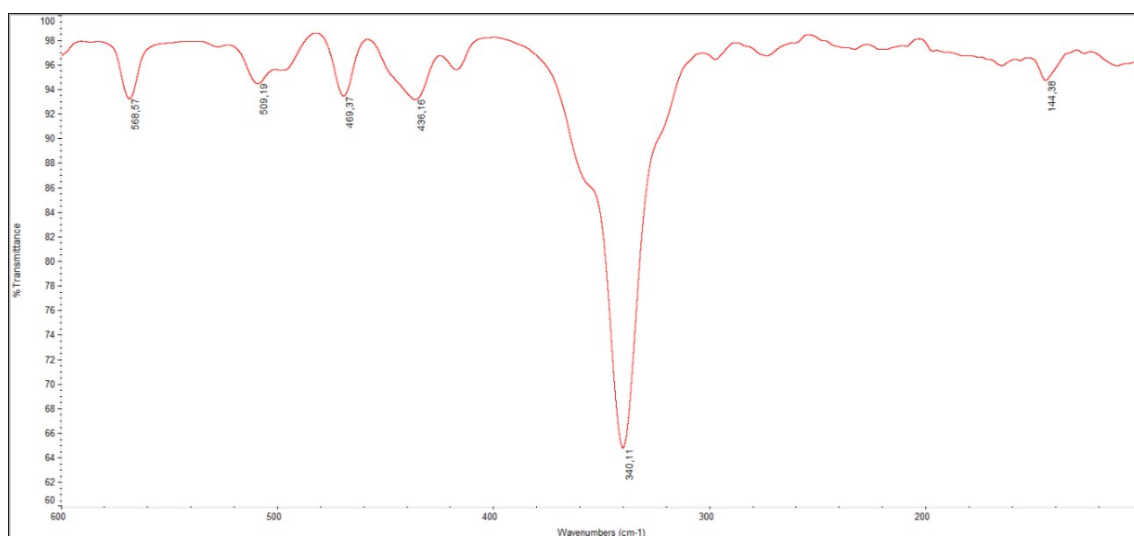


Figure SI 48. Far FT-IR (600-100 cm⁻¹, nujol) spectrum of bis(L-proline *tert*-butyl ester dithiocarbamate)copper(II), [Cu(ProOtBuDTC)₂].

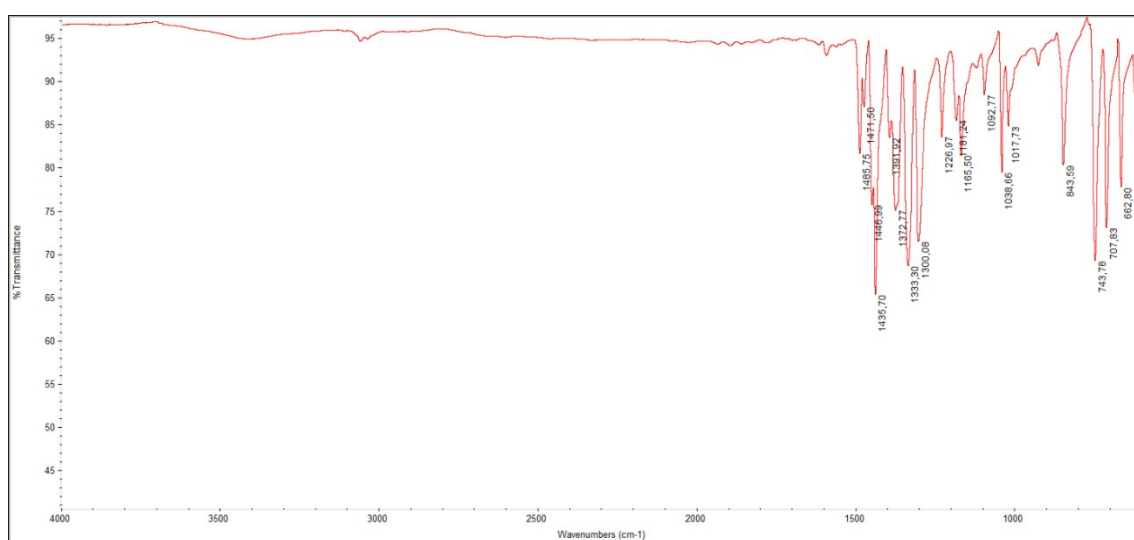


Figure SI 49. Medium FT-IR (4000-600 cm⁻¹, KBr) spectrum of bis(carbazole dithiocarbamate)copper(II), [Cu(CDT)₂].

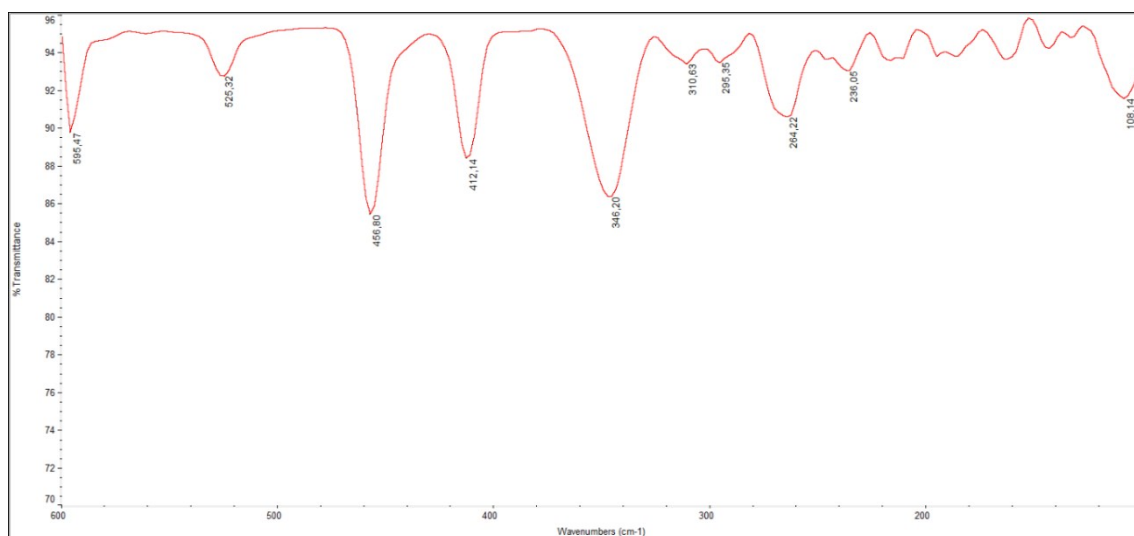


Figure SI 50. Far FT-IR (600-100 cm⁻¹, nujol) spectrum of bis(carbazole dithiocarbamate)copper(II), [Cu(CDT)₂].

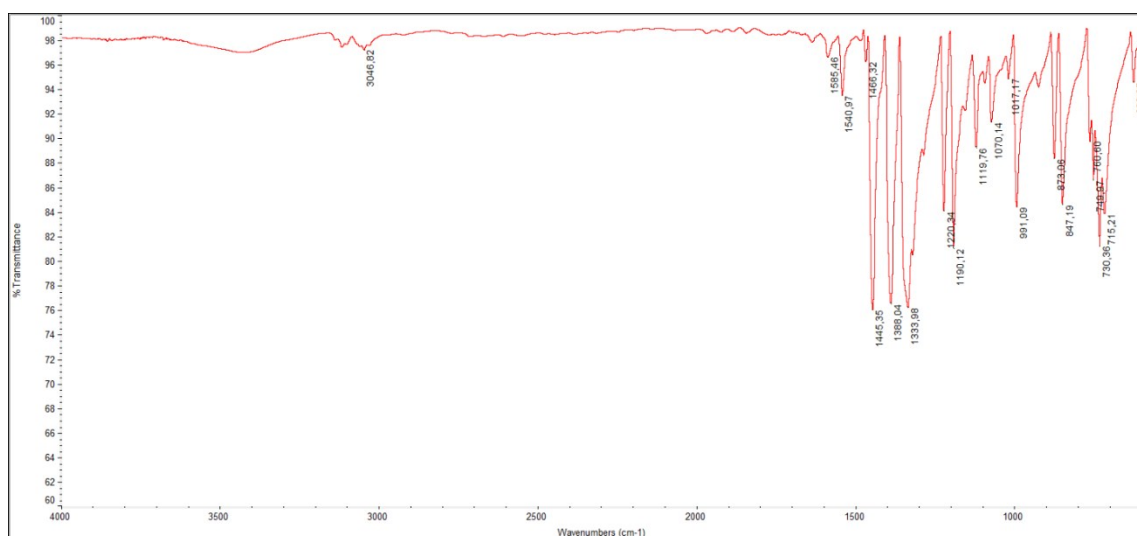


Figure SI 51. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of bis(indole dithiocarbamate)copper(II), $[\text{Cu}(\text{IndDTC})_2]$.

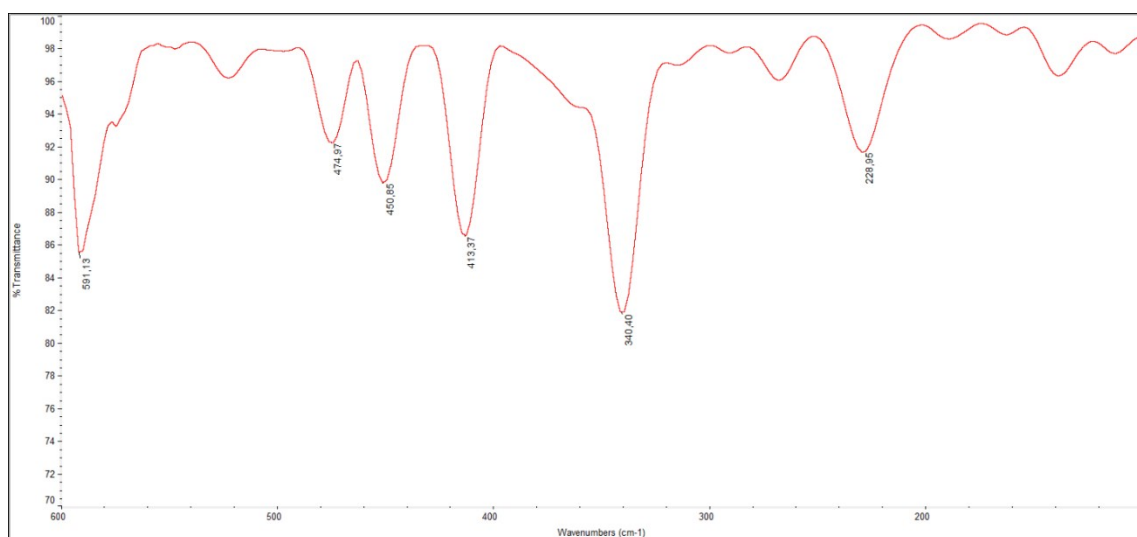


Figure SI 52. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of bis(indole dithiocarbamate)copper(II), $[\text{Cu}(\text{IndDTC})_2]$.

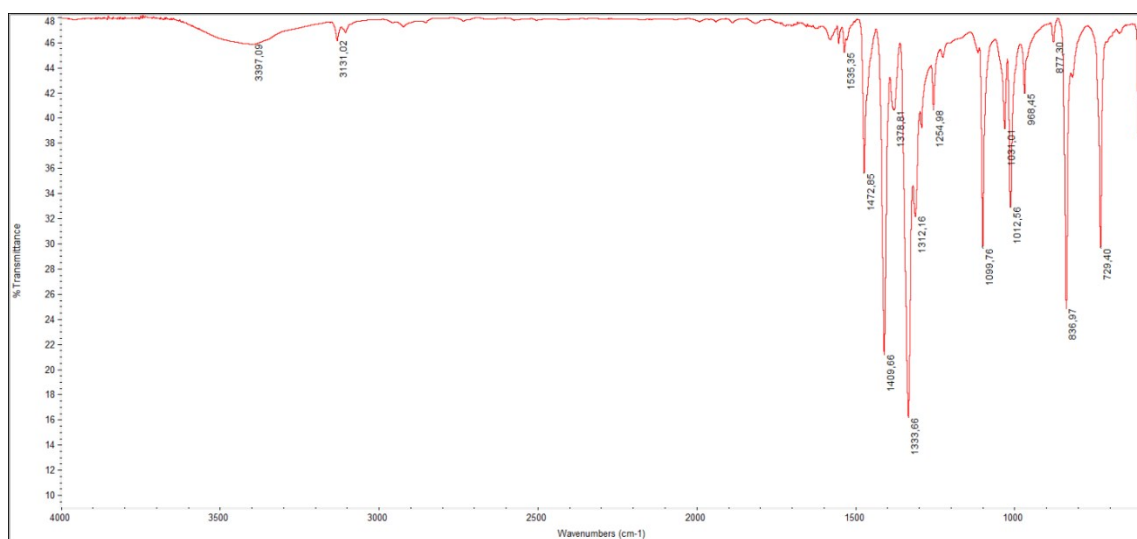


Figure SI 53. Medium FT-IR (4000-600 cm^{-1} , KBr) spectrum of bis(pyrrole dithiocarbamate)copper(II), $[\text{Cu}(\text{PyrroldTC})_2]$.

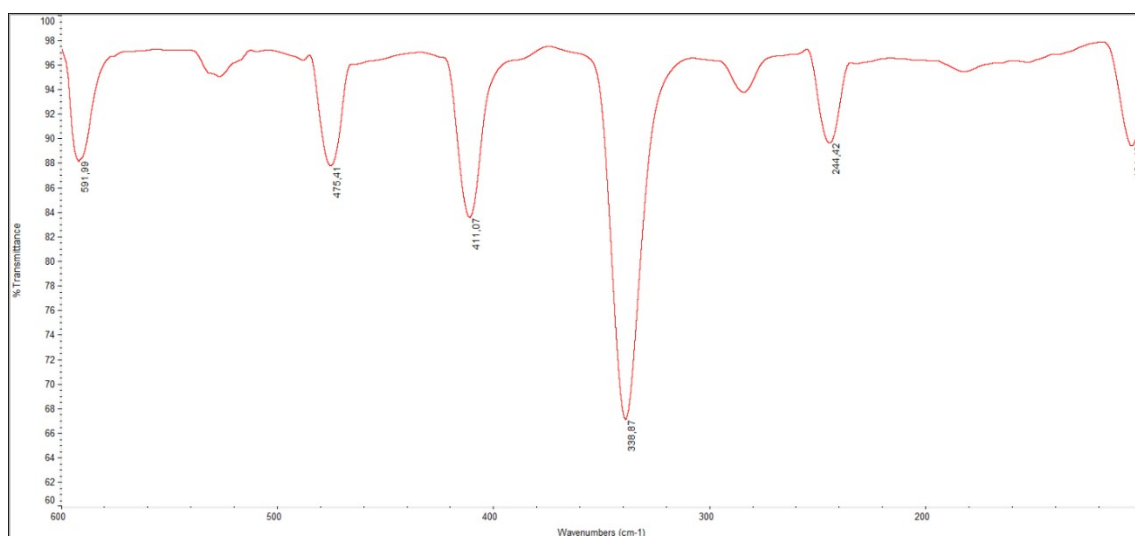


Figure SI 54. Far FT-IR (600-100 cm^{-1} , nujol) spectrum of bis(pyrrole dithiocarbamate)copper(II), $[\text{Cu}(\text{PyrroleDTC})_2]$.

¹H-NMR spectra

¹H-NMR spectra of the synthesized dithiocarbamate ligands

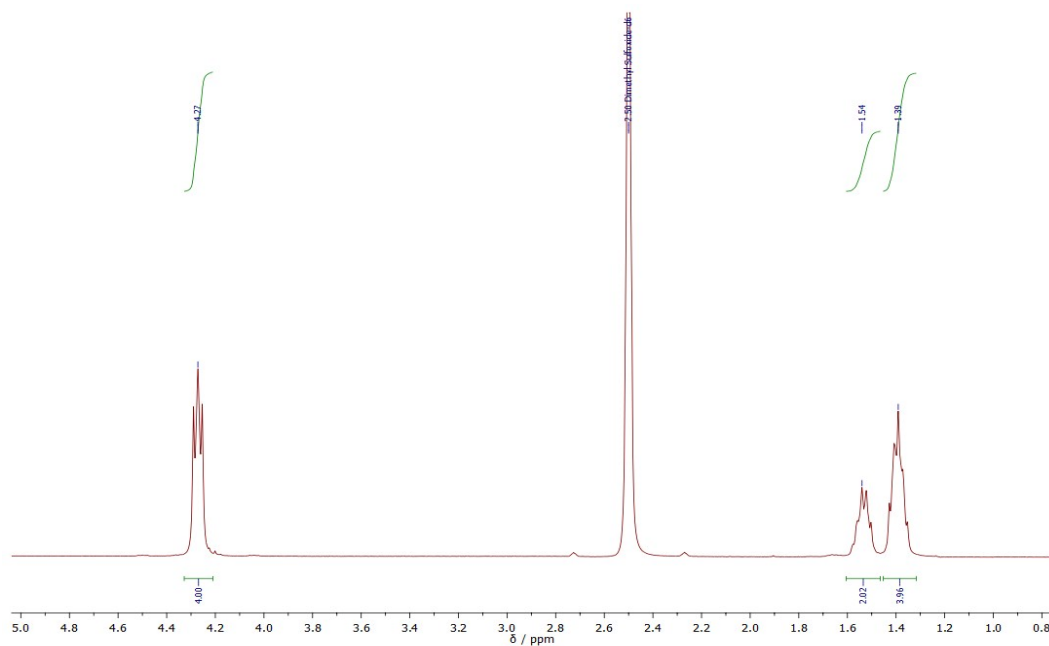


Figure SI 55. ^1H -NMR (DMSO-d_6 , 298 K, 300.13 MHz) spectrum of piperidine dithiocarbamate potassium salt (K PipeDTC).

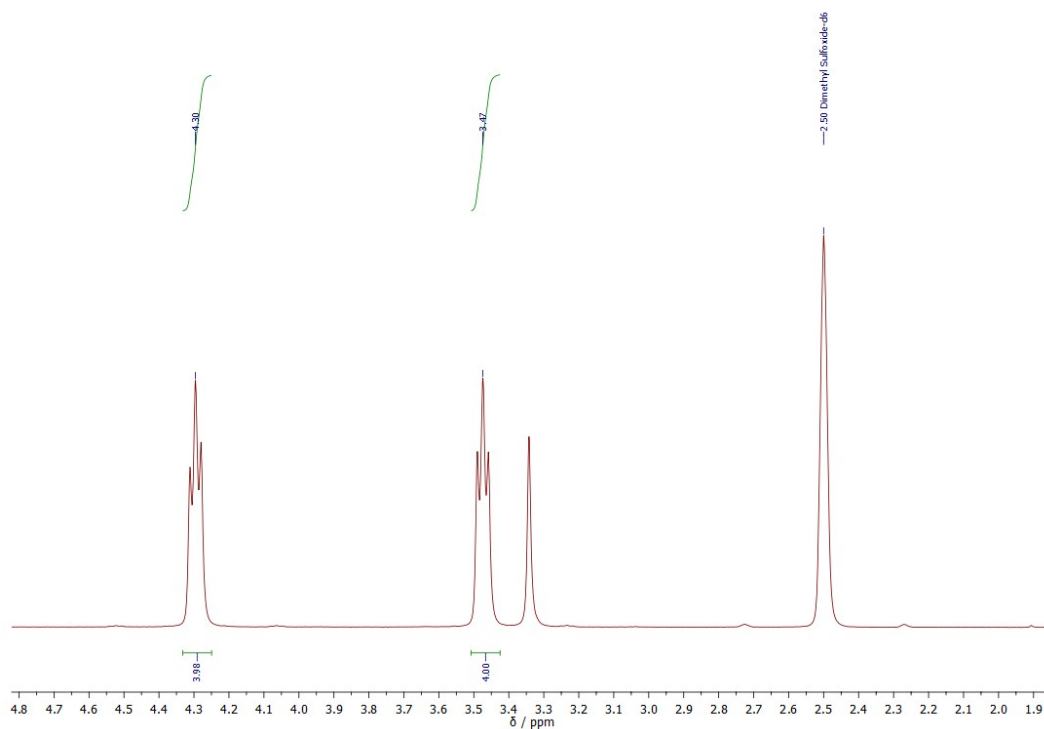


Figure SI 56. ^1H -NMR (DMSO-d_6 , 298 K, 300.13 MHz) spectrum of morpholine dithiocarbamate potassium salt (K MorphDTC).

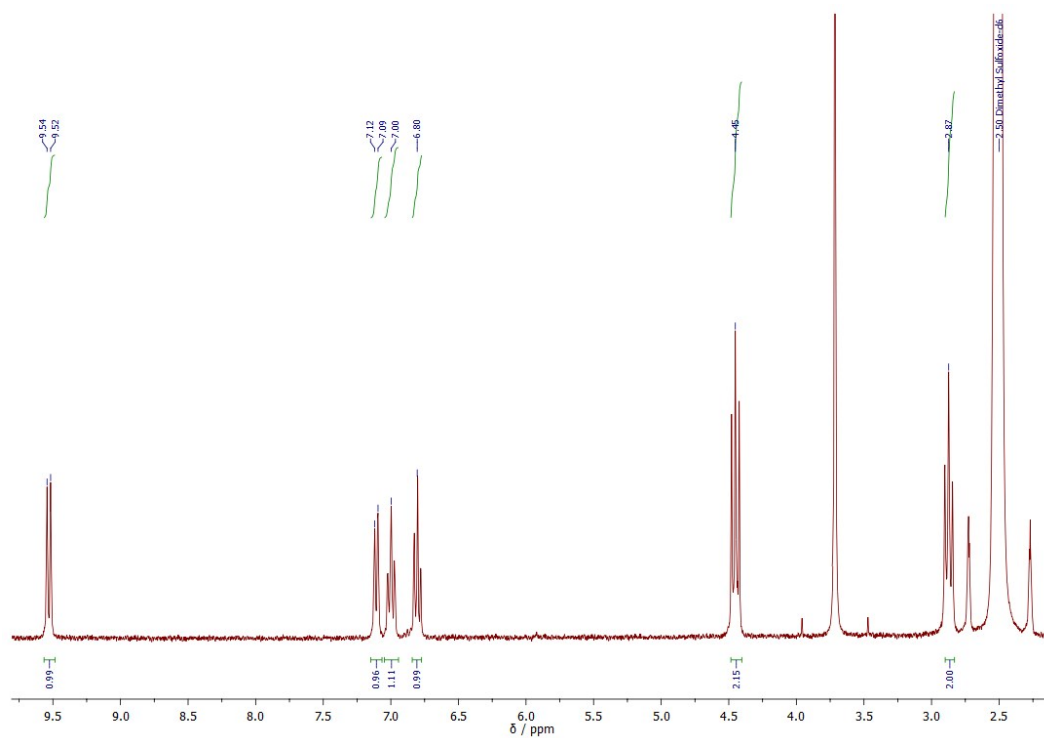


Figure SI 57. ^1H -NMR (DMSO-d_6 , 298 K, 300.13 MHz) spectrum of indoline dithiocarbamate potassium salt (K IndolineDTC).

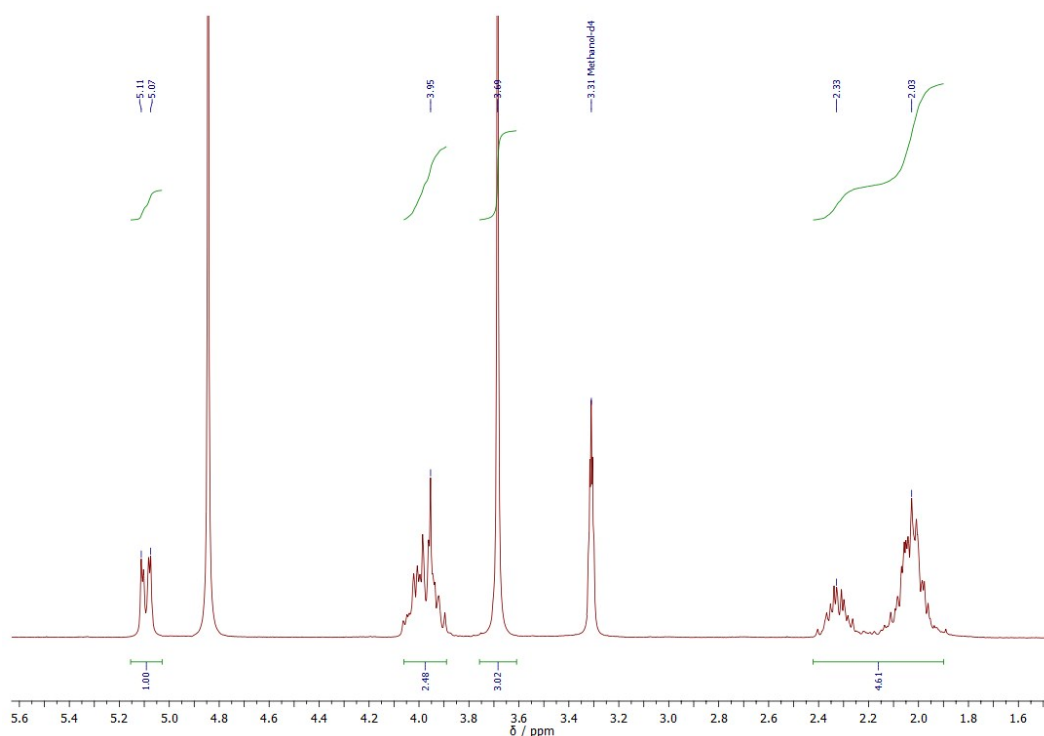


Figure SI 58. ^1H -NMR (CD₃OD, 298 K, 300.13 MHz) spectrum of L-proline methyl ester dithiocarbamate sodium salt (Na ProOMeDTC).

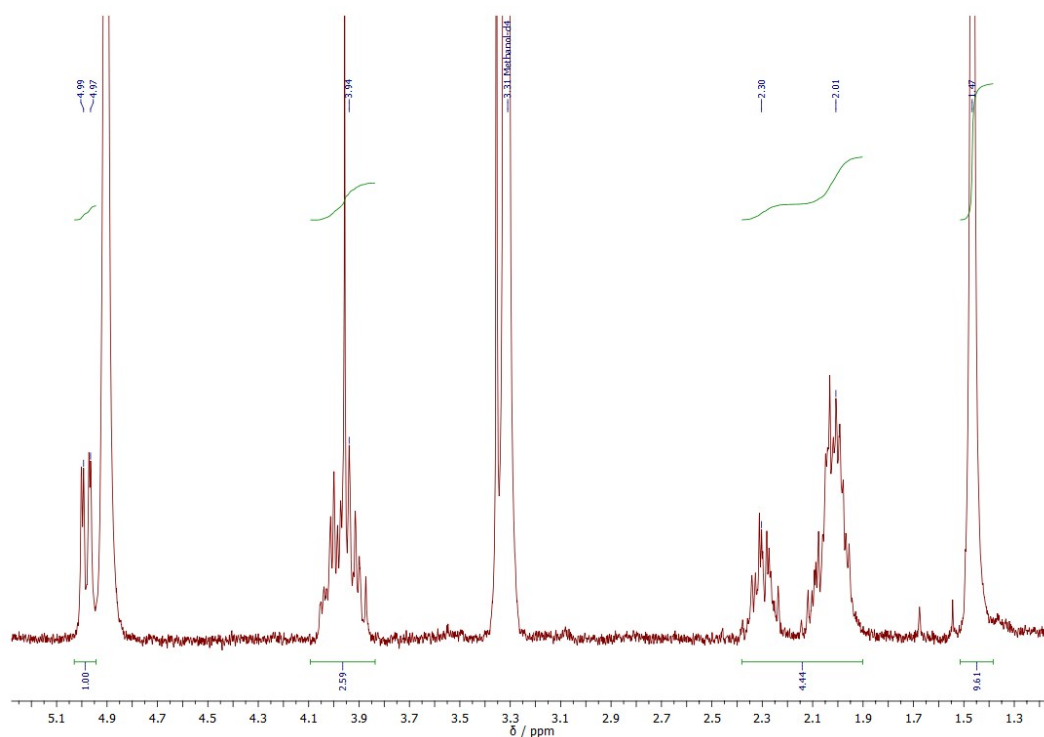


Figure SI 59. ^1H -NMR (CD₃OD, 298 K, 300.13 MHz) spectrum of L-proline *tert*-butyl ester dithiocarbamate sodium salt (Na ProOtBuDTC).

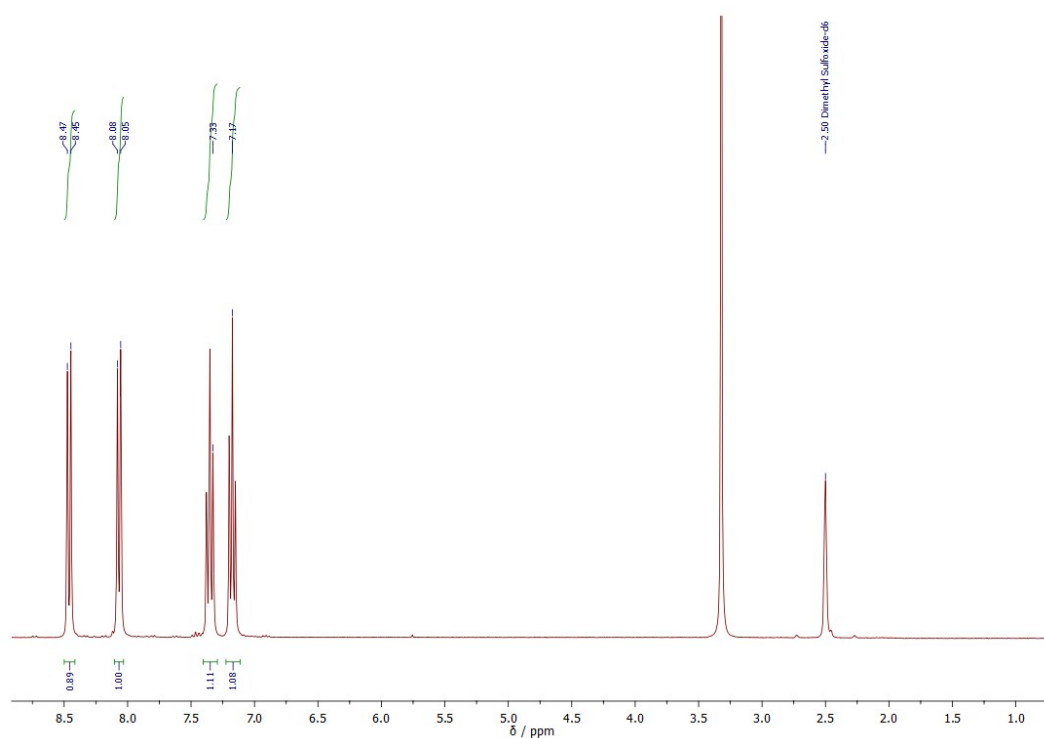


Figure SI 60. ¹H-NMR (DMSO-d₆, 298 K, 300.13 MHz) spectrum of carbazole dithiocarbamate sodium salt (Na CDT).

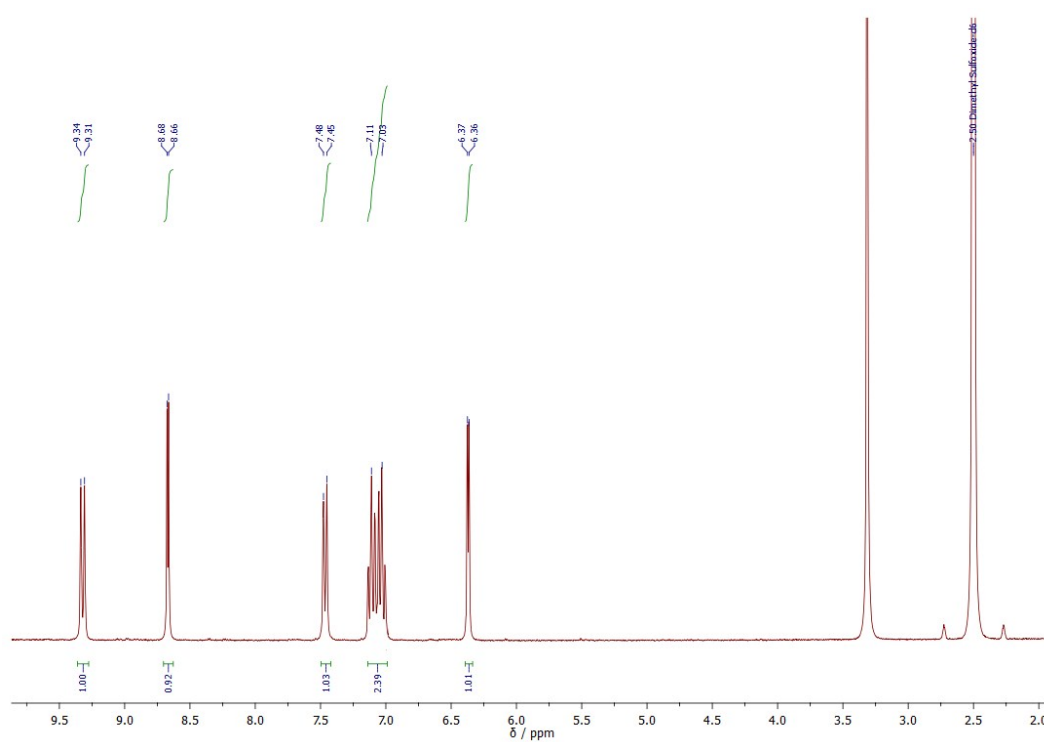


Figure SI 61 ¹H-NMR (DMSO-d₆, 298 K, 300.13 MHz) spectrum of indole dithiocarbamate sodium salt (Na IndDTC).

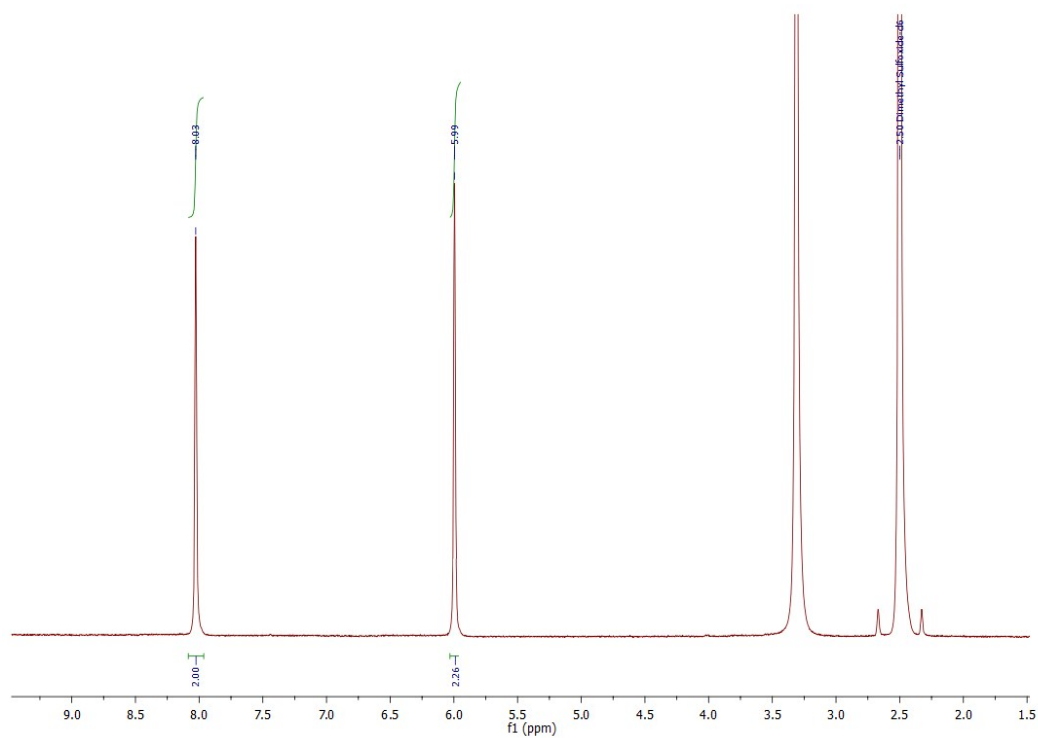


Figure SI 62. ^1H -NMR (DMSO- d_6 , 298 K, 300.13 MHz) spectrum of pyrrole dithiocarbamate sodium salt (Na PyrrDTC).

^1H -NMR spectra of the synthesized Ru(III) dithiocarbamate complexes

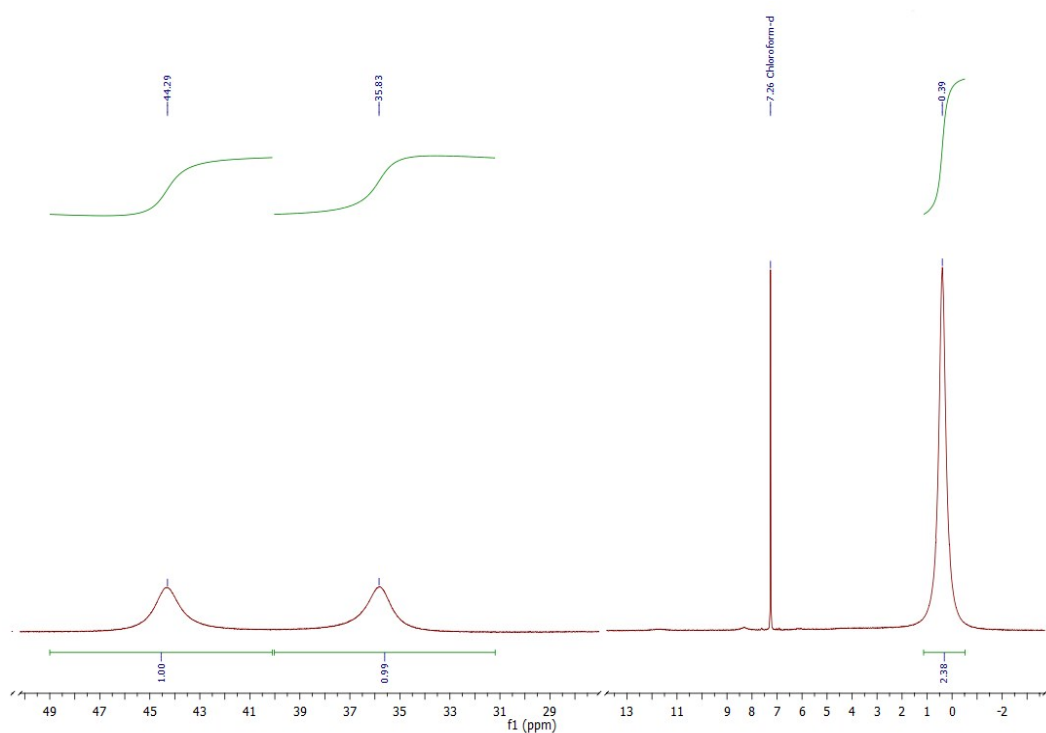


Figure SI 63. ^1H -NMR (CDCl_3 , 298 K, 300.13 MHz) spectrum of tris(pyrrolidine dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{PDT})_3]$.

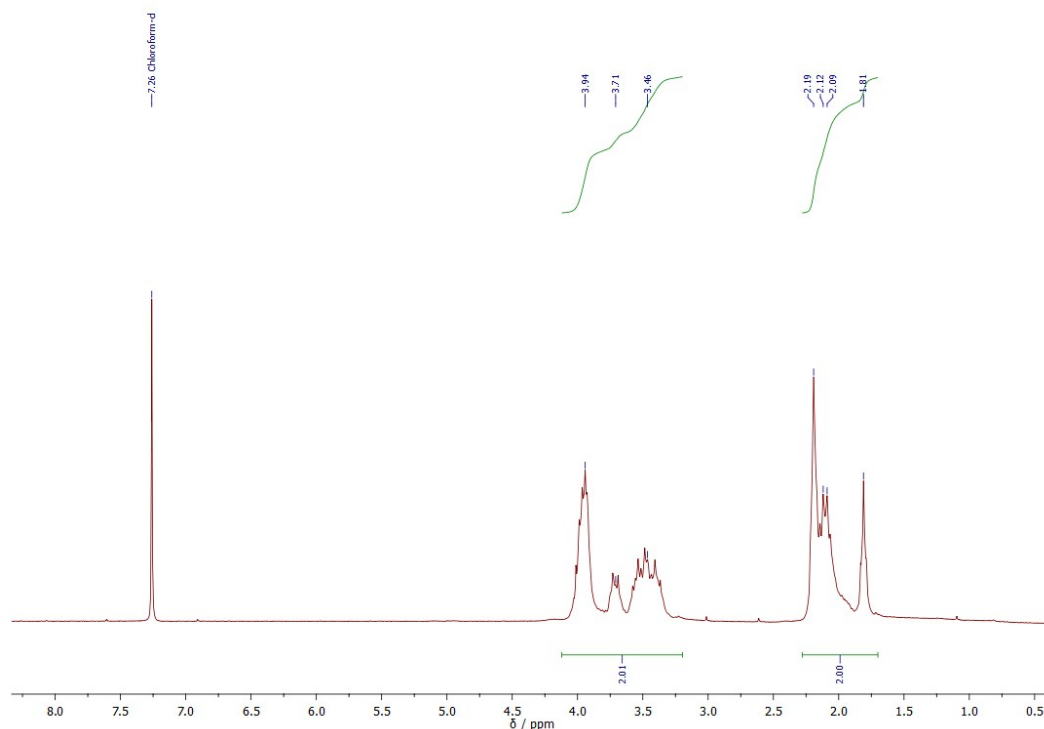


Figure SI 64. ^1H -NMR (CDCl₃, 298 K, 300.13 MHz) spectrum of β -pentakis(pyrrolidine dithiocarbamate)diruthenium(III) chloride, β -[Ru₂(PDT)₅]Cl.

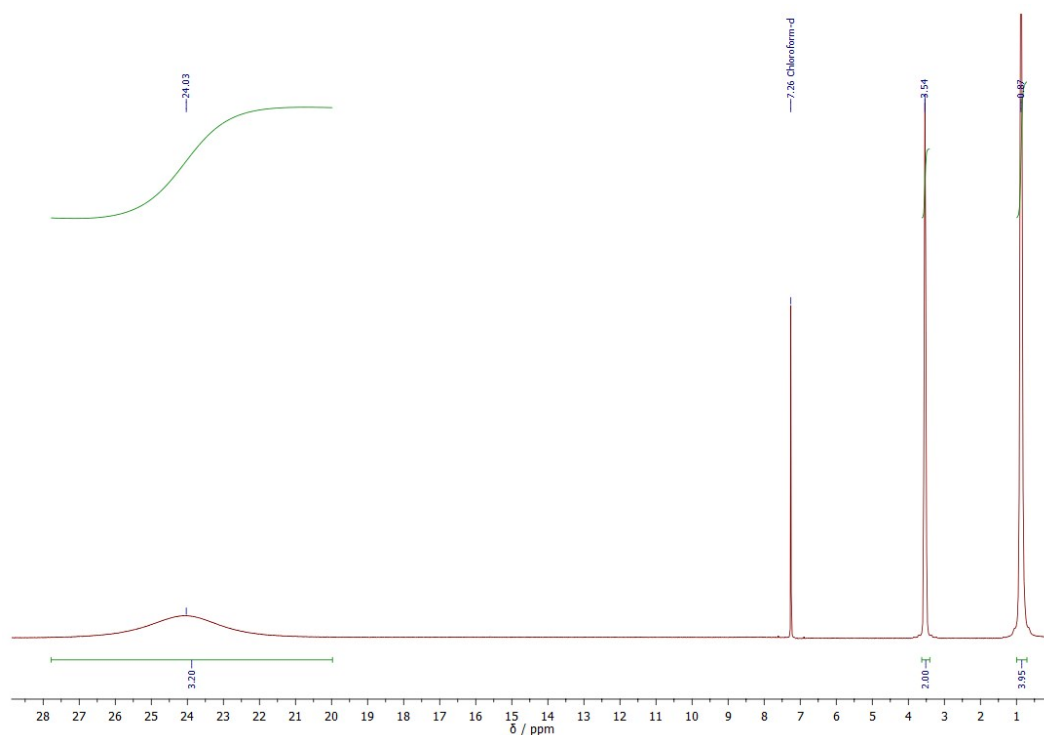


Figure SI 65. ^1H -NMR (CDCl₃, 298 K, 300.13 MHz) spectrum of tris(piperidine dithiocarbamate)ruthenium(III), [Ru(PipeDTC)₃].

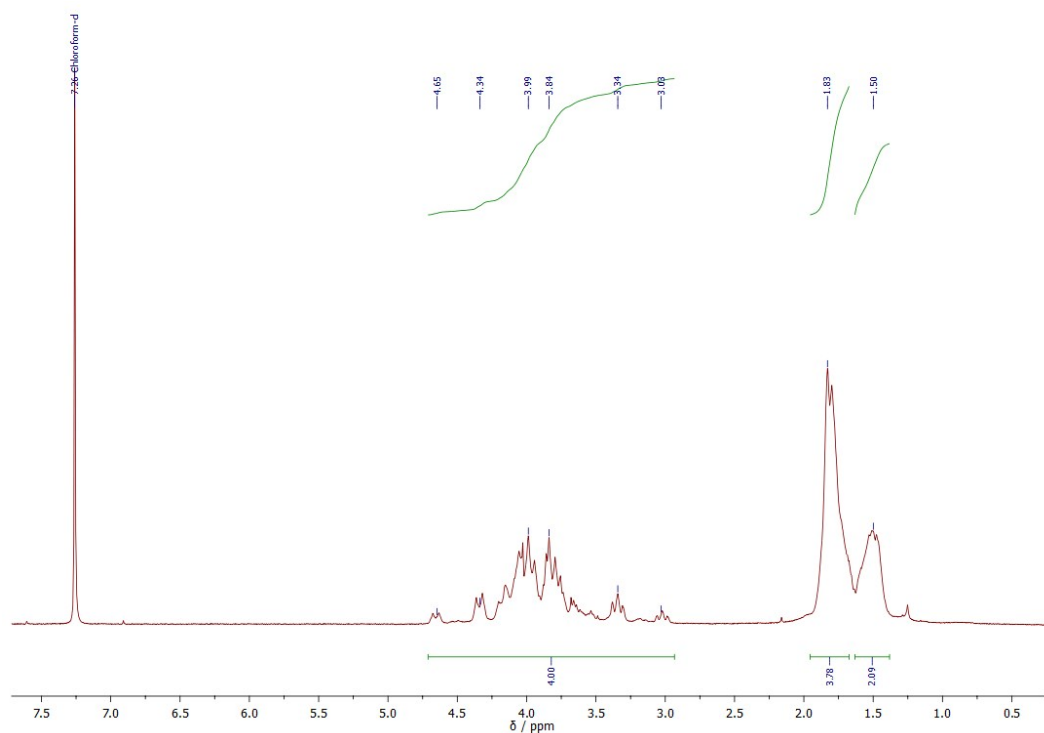


Figure SI 66. ^1H -NMR (CDCl₃, 298 K, 300.13 MHz) spectrum of β -pentakis(piperidine dithiocarbamate)diruthenium(III) chloride, β -[Ru₂(PipeDTC)₅]Cl.

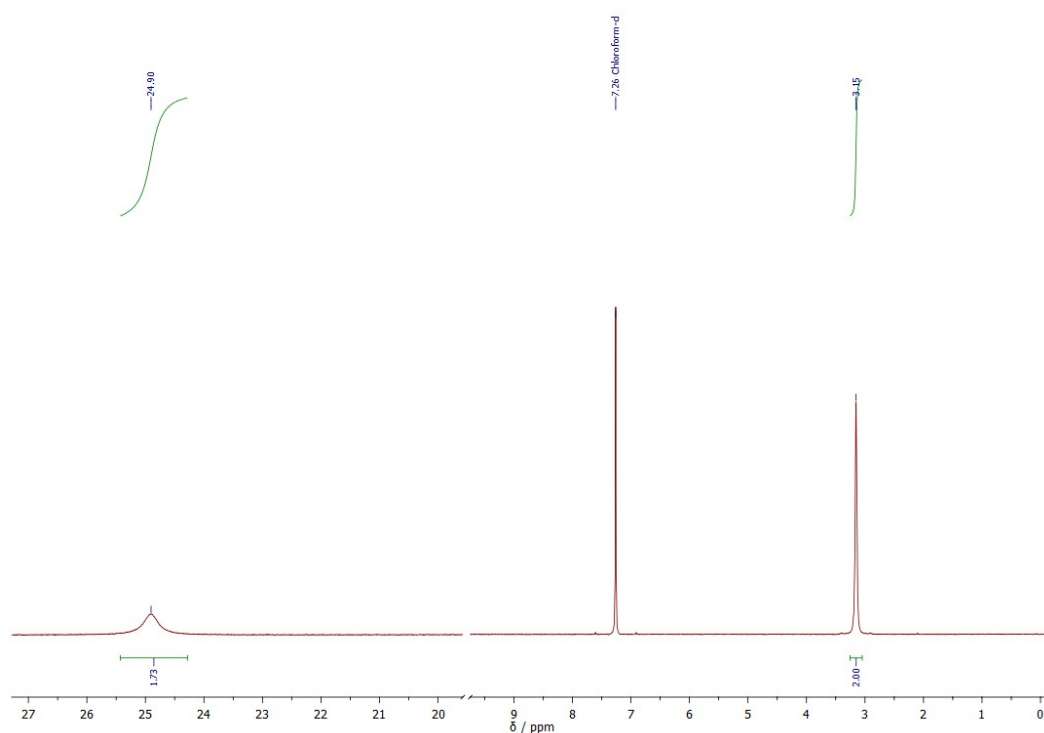


Figure SI 67. ^1H -NMR (CDCl₃, 298 K, 300.13 MHz) spectrum of tris(morpholine dithiocarbamate)ruthenium(III), [Ru(MorphDTC)₃].

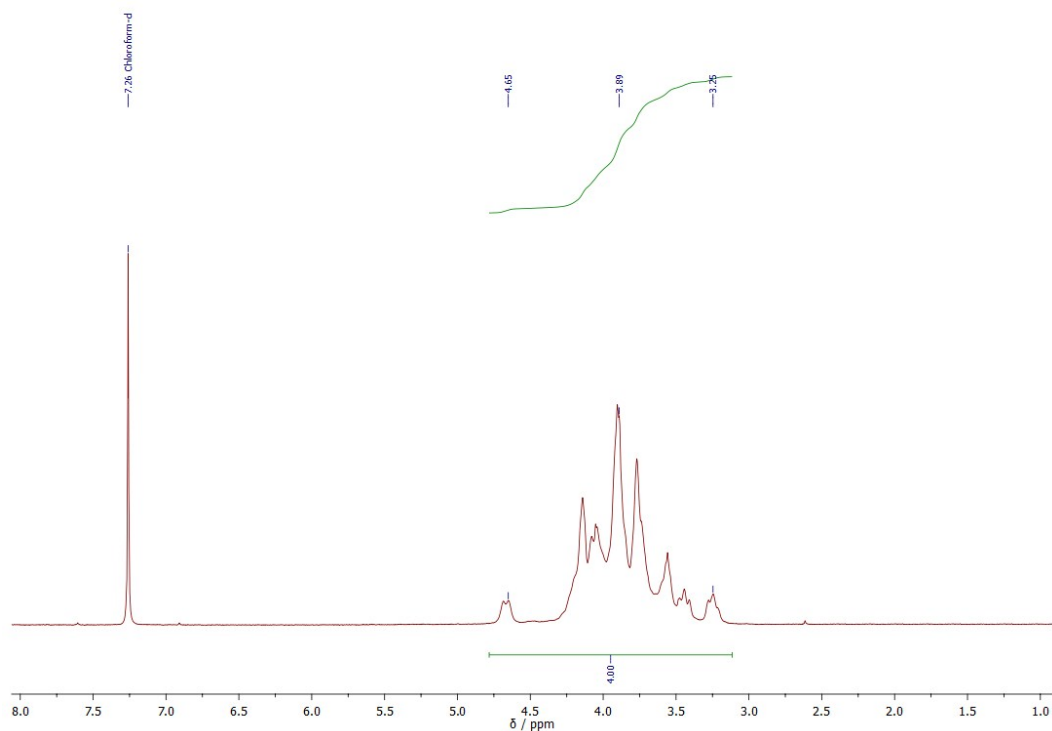


Figure SI 68. ^1H -NMR (CDCl_3 , 298 K, 300.13 MHz) spectrum of β -pentakis(morpholine dithiocarbamate)diruthenium(III) chloride, β - $[\text{Ru}_2(\text{MorphDTC})_5]\text{Cl}$.

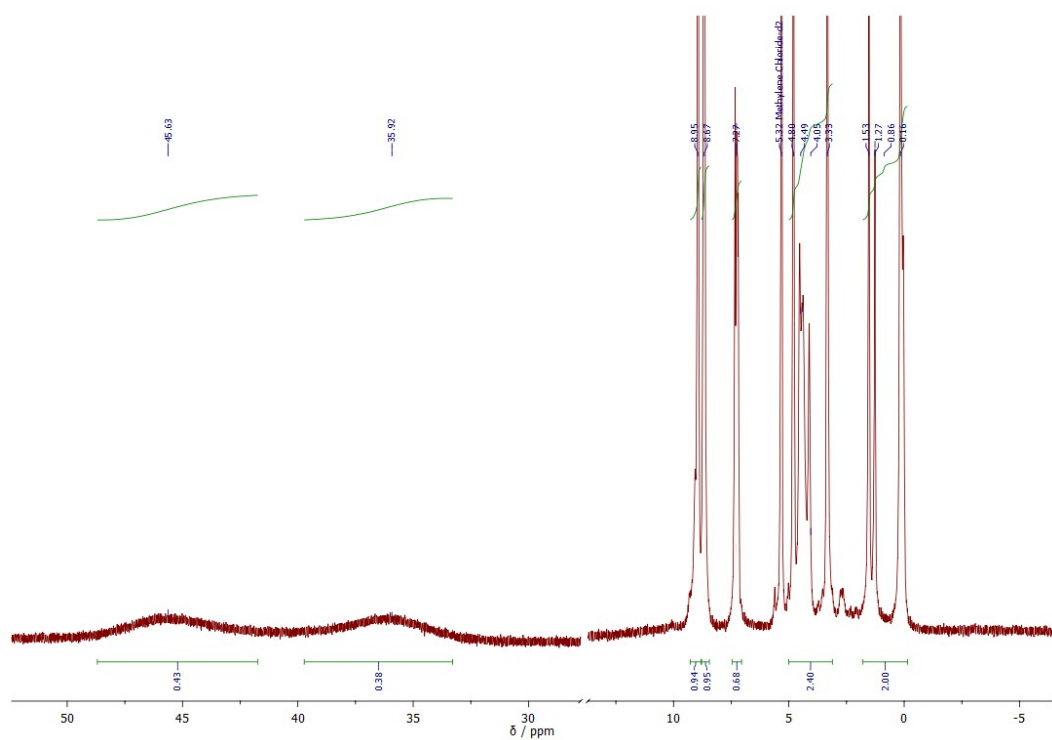


Figure SI 69. ^1H -NMR (CD_2Cl_2 , 298 K, 300.13 MHz) spectrum of tris(indoline dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{IndolineDTC})_3]$.

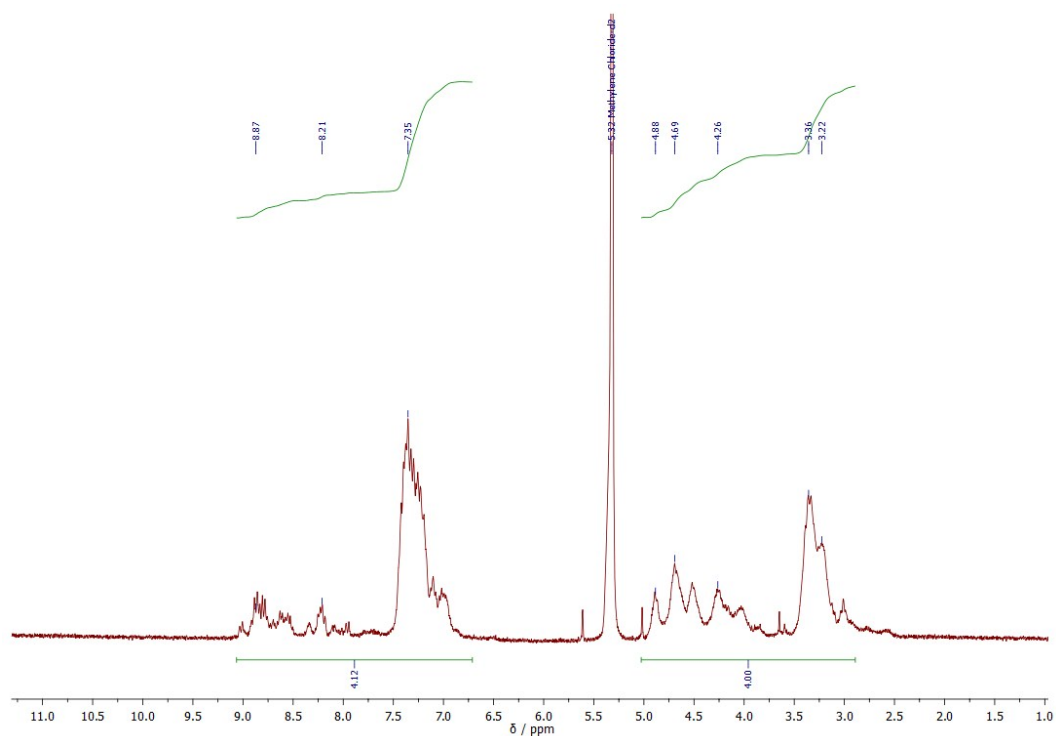


Figure SI 70. ^1H -NMR (CD_2Cl_2 , 298 K, 300.13 MHz) spectrum of β -pentakis(indoline dithiocarbamate)diruthenium(III) chloride, $\beta\text{-}[\text{Ru}_2(\text{IndolineDTC})_5]\text{Cl}$.

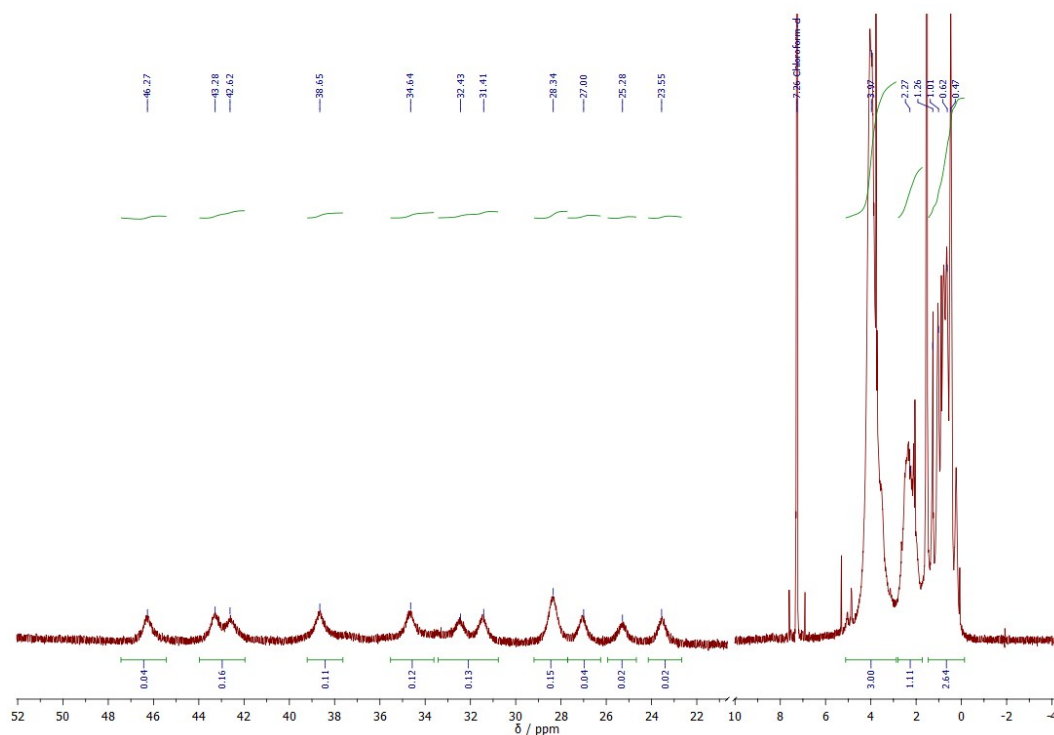


Figure SI 71. ^1H -NMR (CDCl_3 , 298 K, 300.13 MHz) spectrum of tris(L-proline methyl ester dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{ProOMeDTC})_3]$.

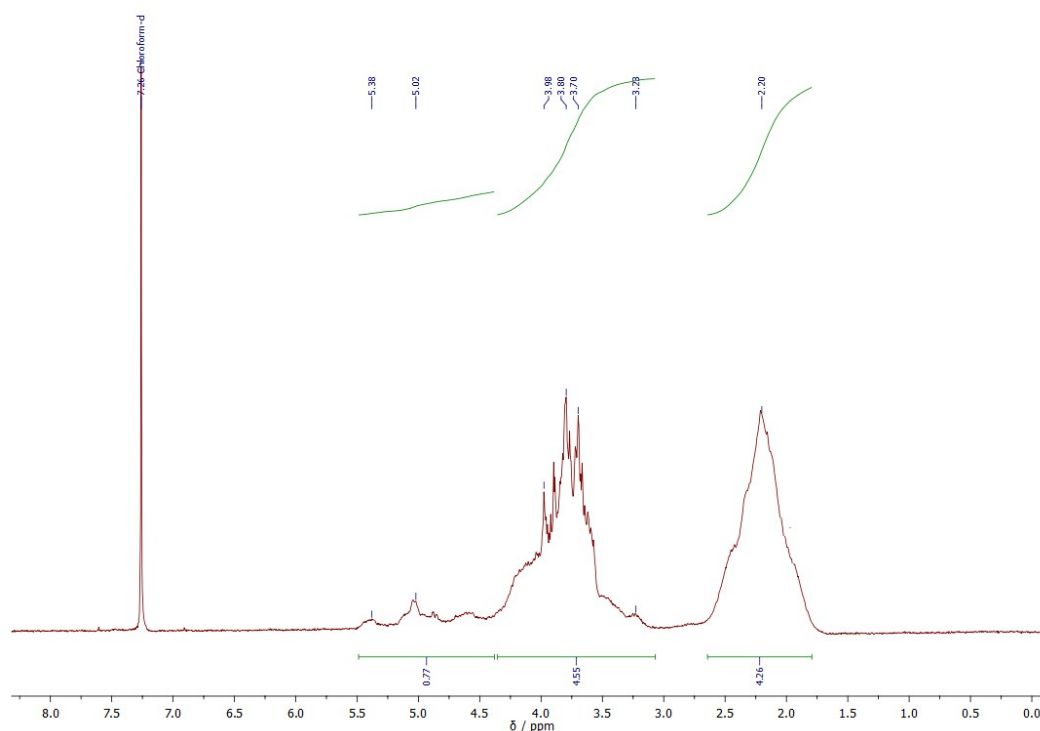


Figure SI 72. ¹H-NMR (CDCl₃, 298 K, 300.13 MHz) spectrum of β-pentakis(L-proline methyl ester dithiocarbamate)diruthenium(III) chloride, β-[Ru₂(ProOMeDTC)₅]Cl.

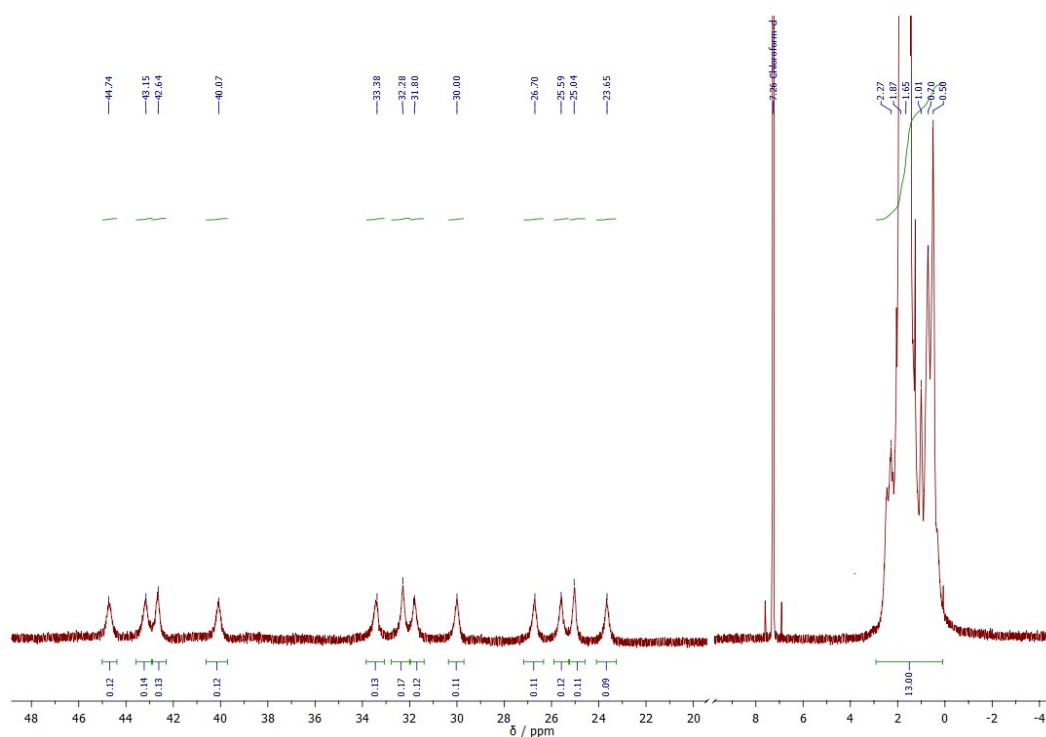


Figure SI 73. ¹H-NMR (CDCl₃, 298 K, 300.13 MHz) spectrum of tris(L-proline *tert*-butyl ester dithiocarbamate)ruthenium(III), [Ru(ProOtBuDTC)₃].

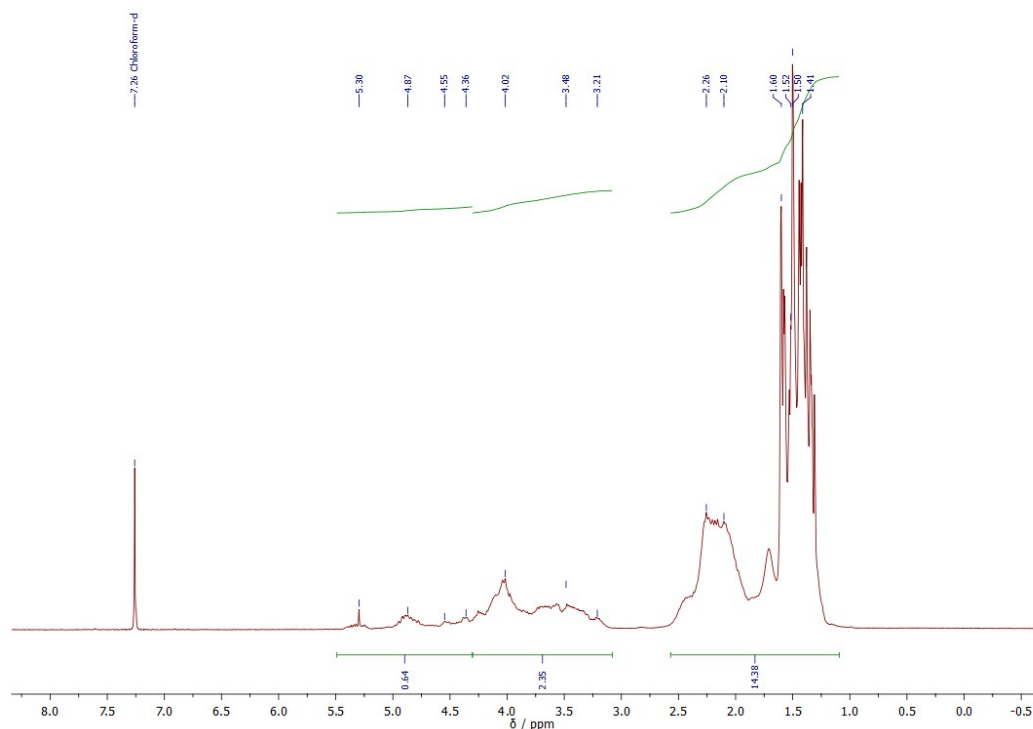


Figure SI 74. ^1H -NMR (CDCl_3 , 298 K, 300.13 MHz) spectrum of β -pentakis(L-proline *tert*-butyl ester dithiocarbamate)diruthenium(III) chloride, β - $[\text{Ru}_2(\text{ProOtBuDTC})_5]\text{Cl}$.

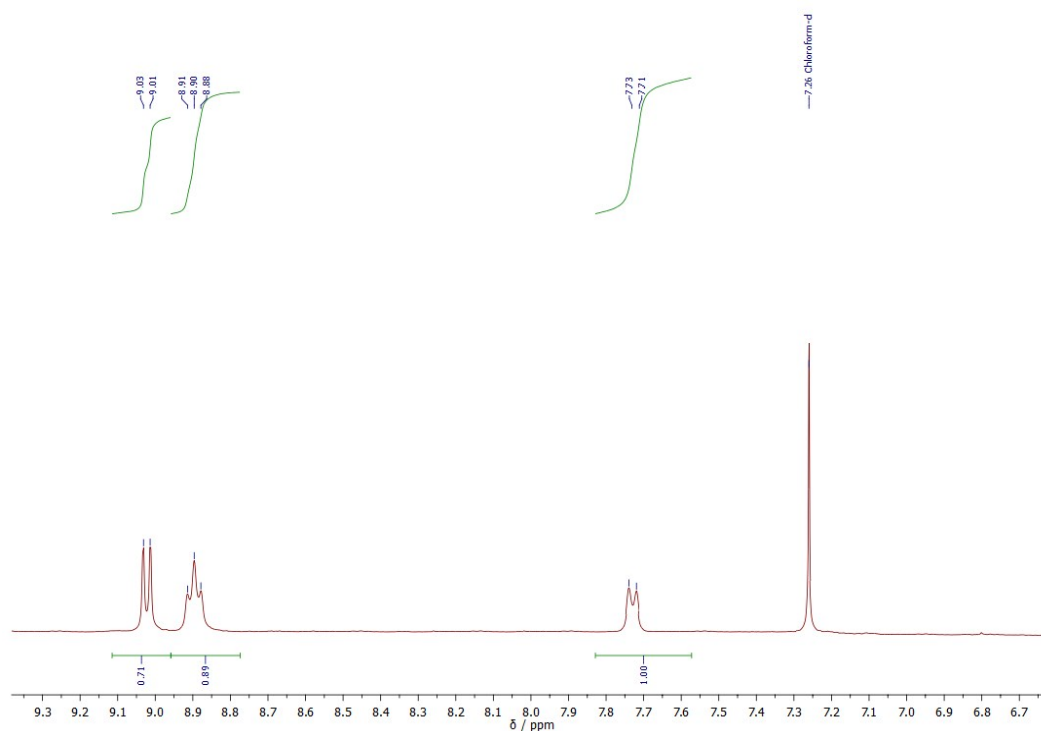


Figure SI 75. ^1H -NMR (CDCl_3 , 298 K, 300.13 MHz) spectrum of tris(carbazole dithiocarbamate)ruthenium(III), $[\text{Ru}(\text{CDT})_3]$.

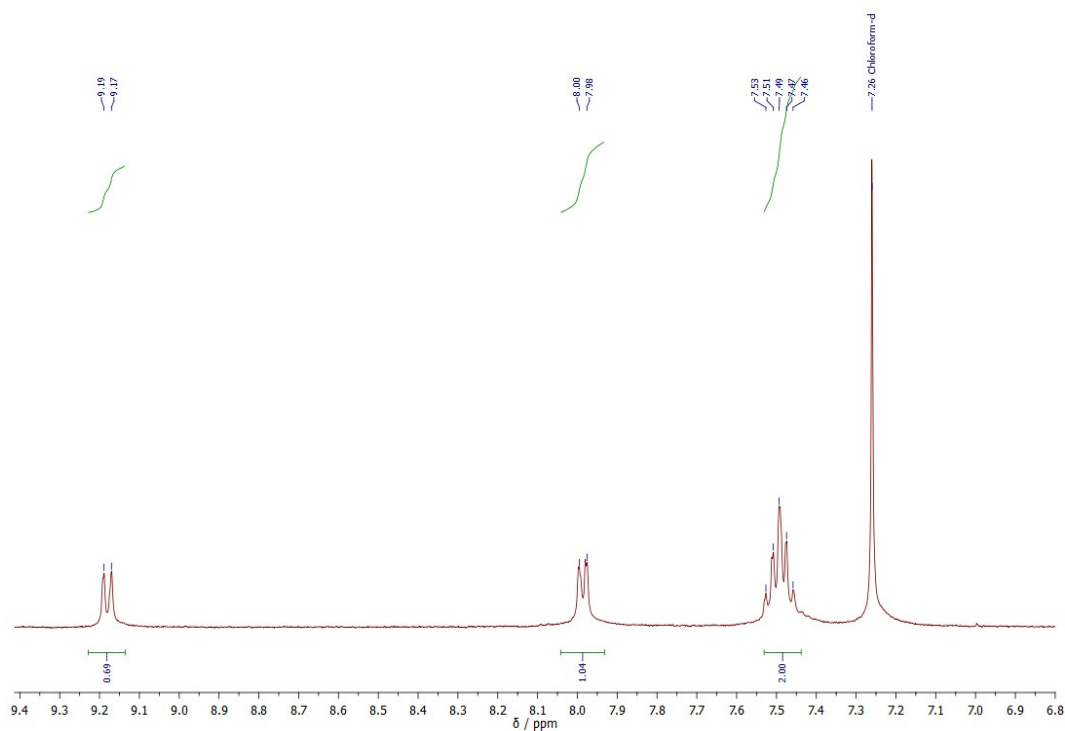


Figure SI 76. ^1H -NMR (CDCl_3 , 298 K, 300.13 MHz) spectrum of β -pentakis(carbazole dithiocarbamate)diruthenium(III) chloride, $\beta\text{-}[\text{Ru}_2(\text{CDT})_5]\text{Cl}$.

^1H -NMR spectra of the synthesized Cu(II) dithiocarbamate complexes

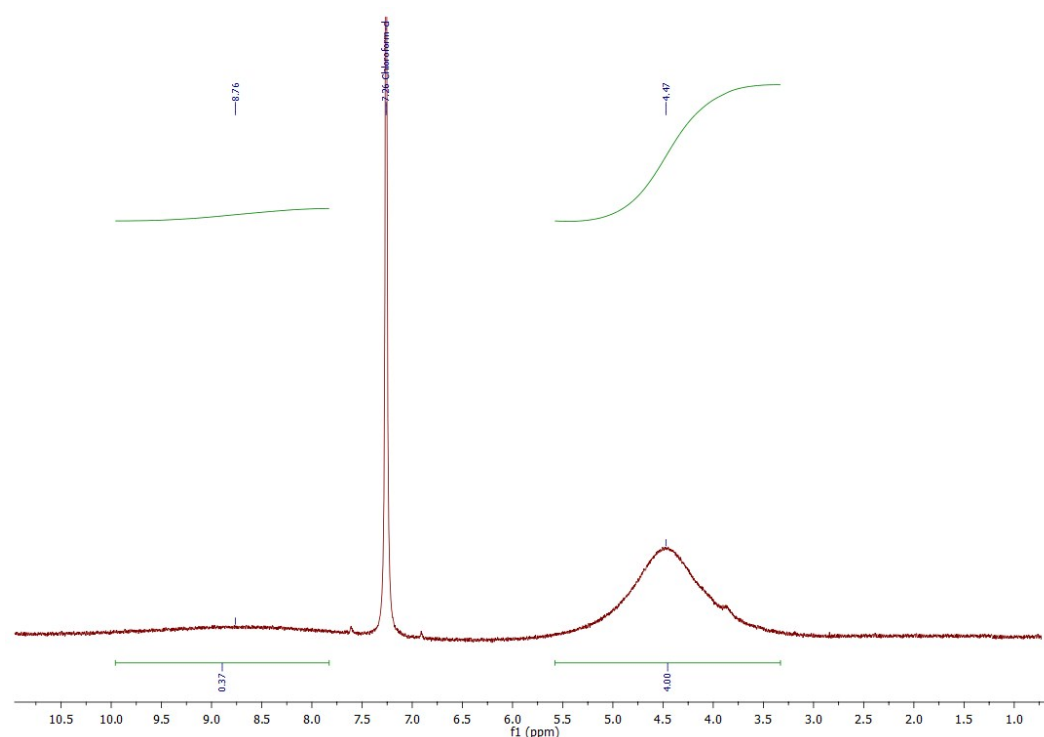


Figure SI 77. ^1H -NMR (CDCl_3 , 298 K, 300.13 MHz) spectrum of bis(pyrrolidine dithiocarbamate)copper (II), $[\text{Cu}(\text{PDT})_2]$.

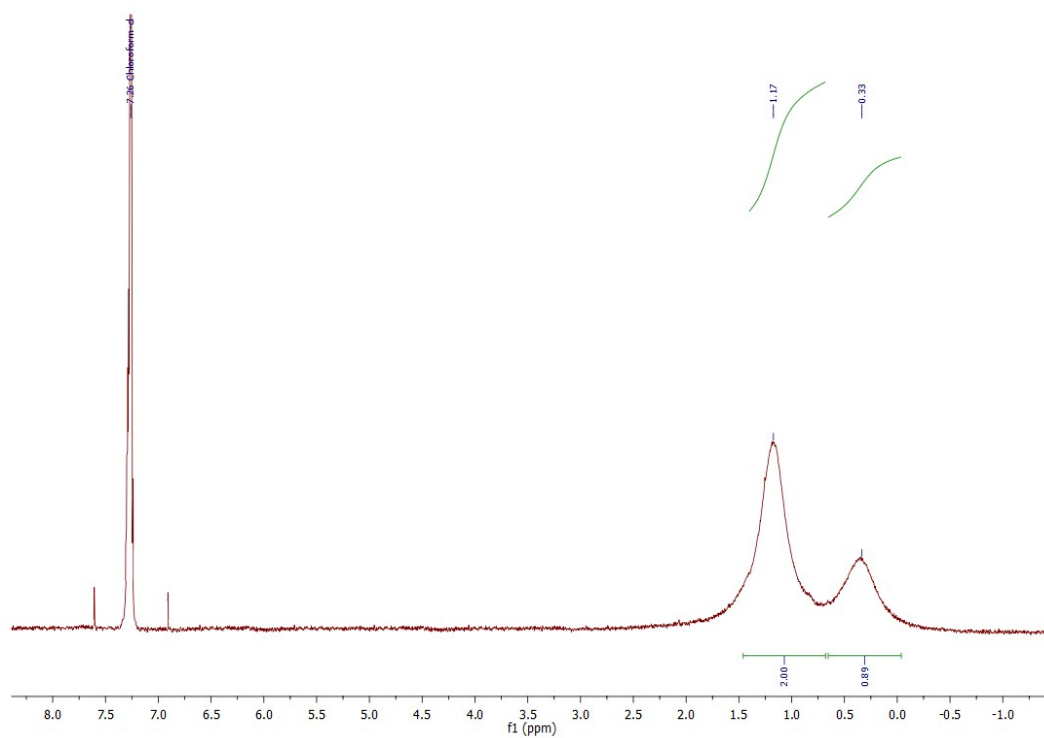


Figure SI 78. ^1H -NMR (CDCl_3 , 298 K, 300.13 MHz) spectrum of bis(piperidine dithiocarbamate)copper(II), $[\text{Cu}(\text{PipeDTC})_2]$.

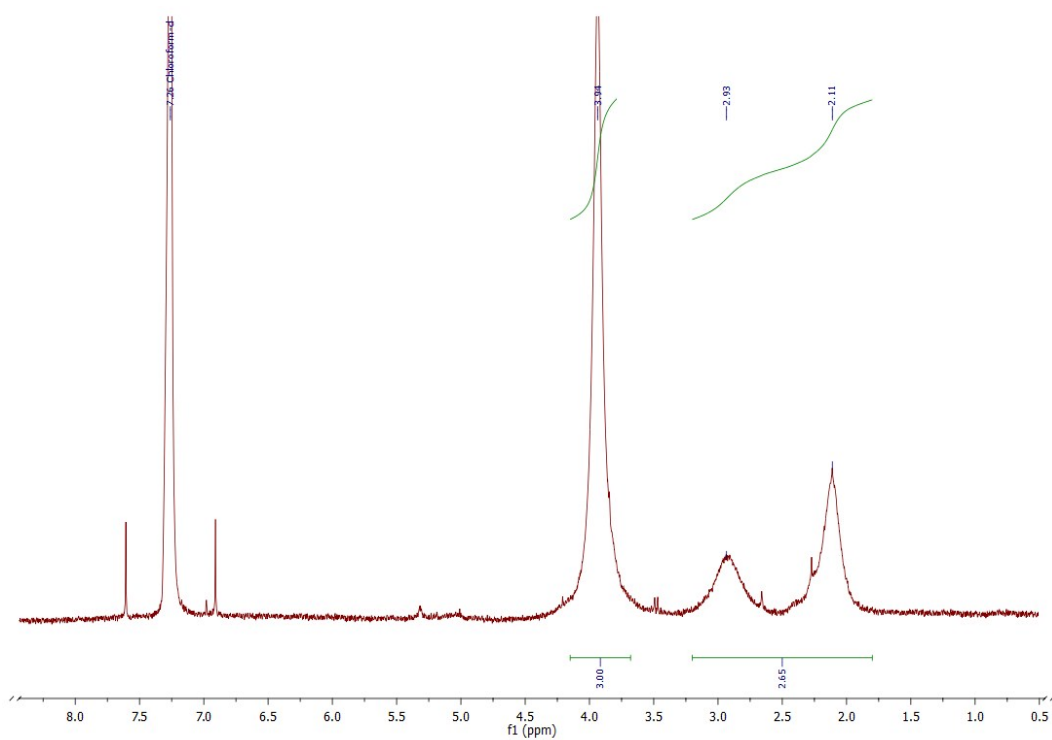


Figure SI 79. ^1H -NMR (CDCl_3 , 298 K, 300.13 MHz) spectrum of bis(L-proline methyl ester dithiocarbamate)copper(II), $[\text{Cu}(\text{ProOMeDTC})_2]$.

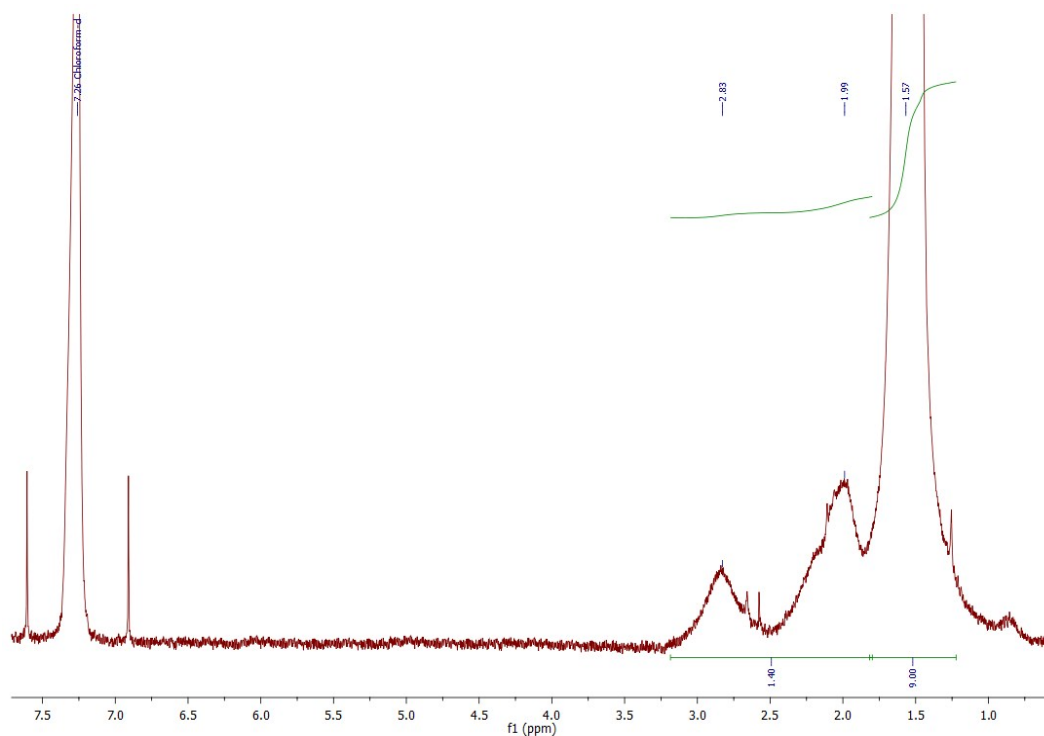


Figure SI 80. ^1H -NMR (CDCl_3 , 298 K, 300.13 MHz) spectrum of bis(L-proline *tert*-butyl ester dithiocarbamate)copper(II), $[\text{Cu}(\text{ProOtBuDTC})_2]$.

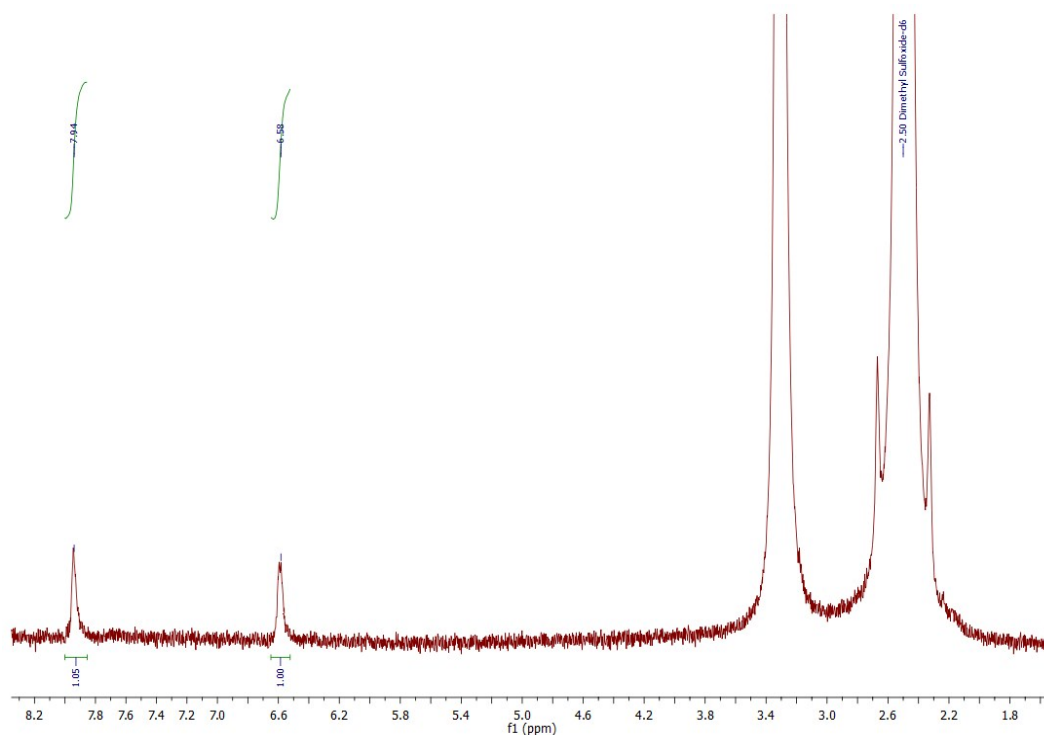
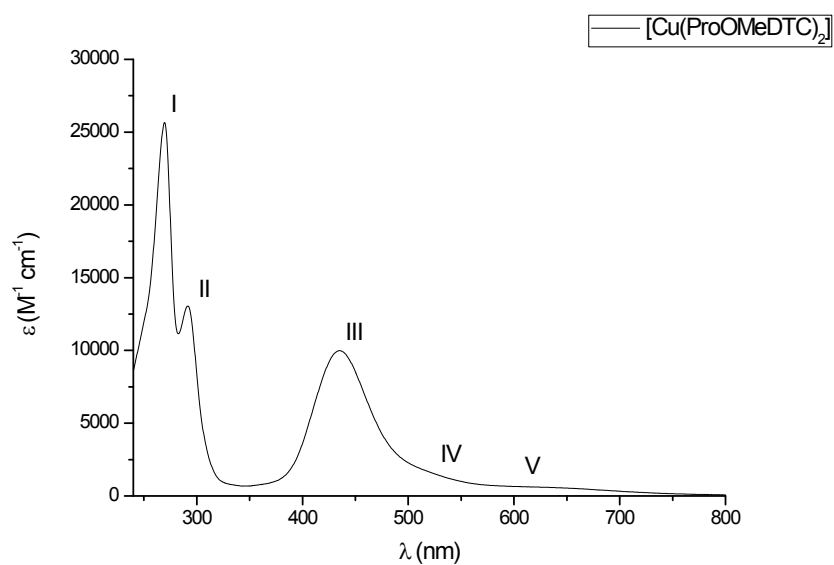
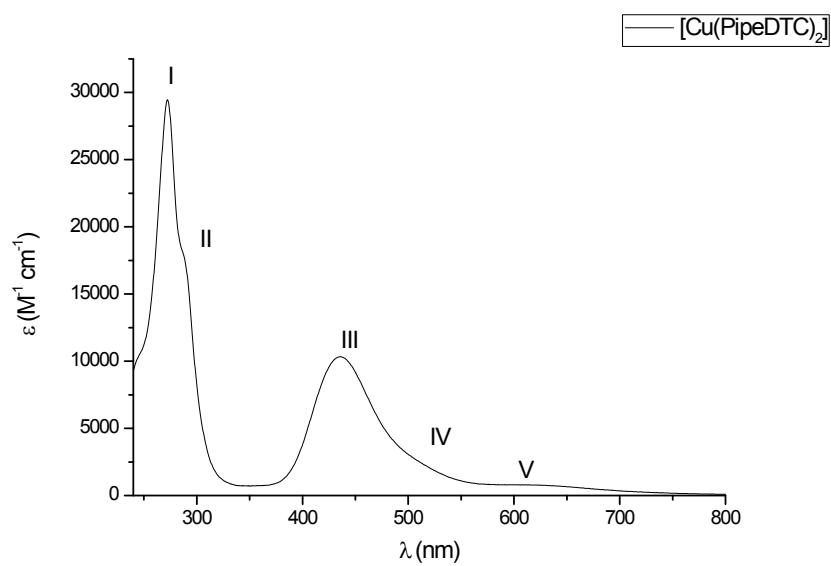
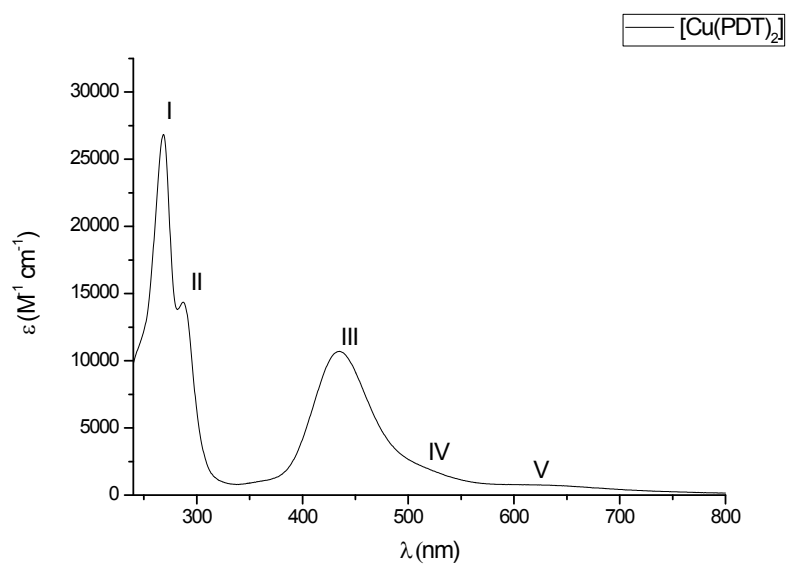
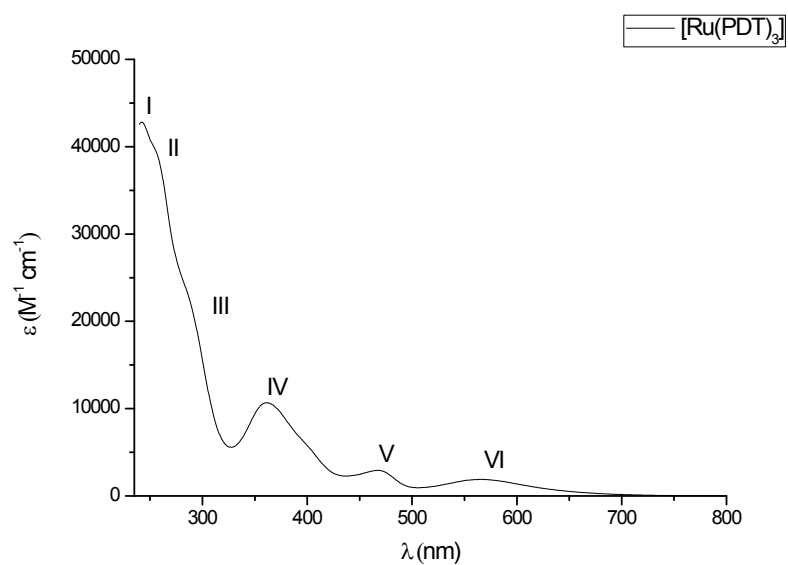
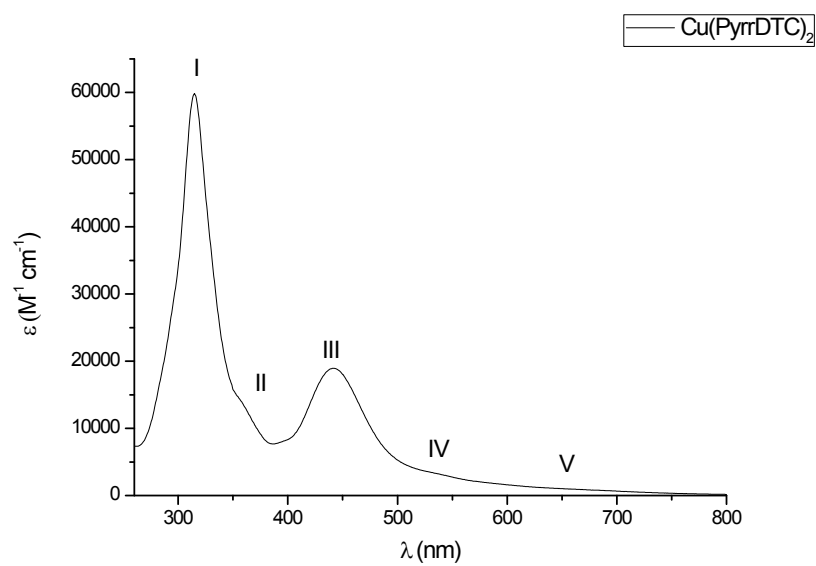
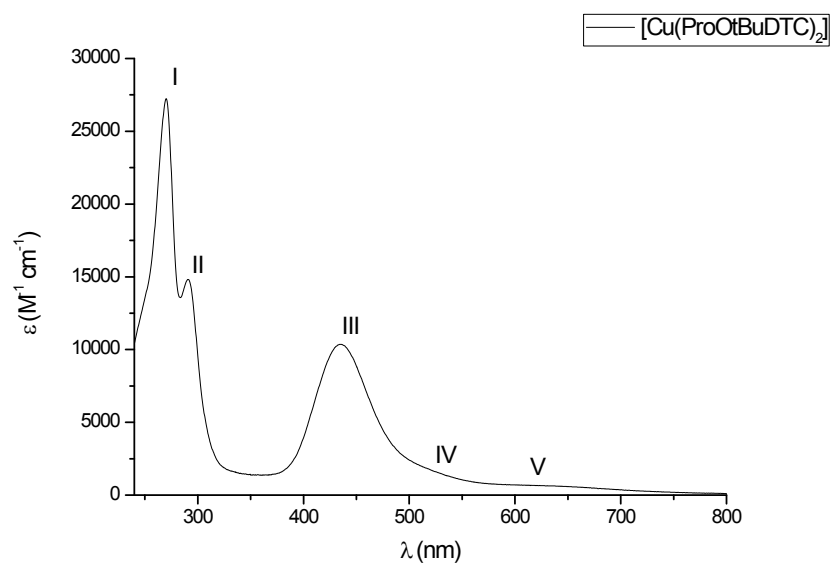


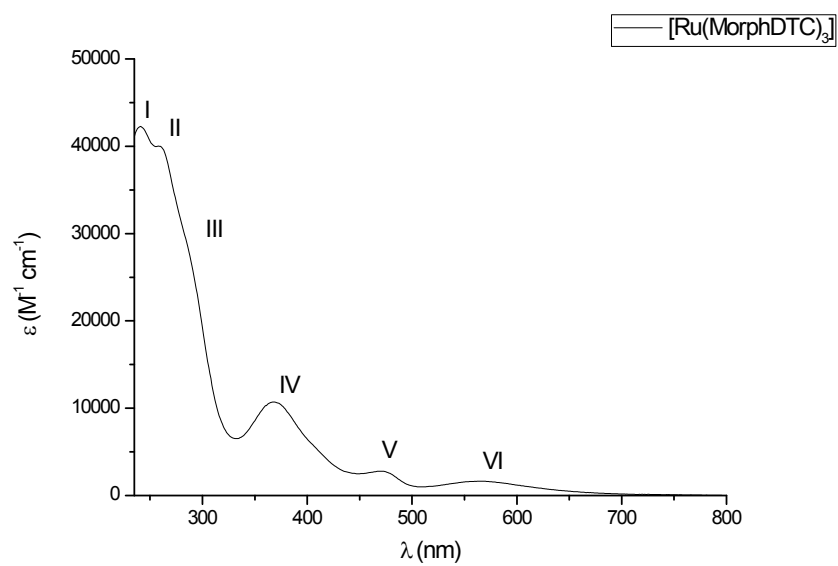
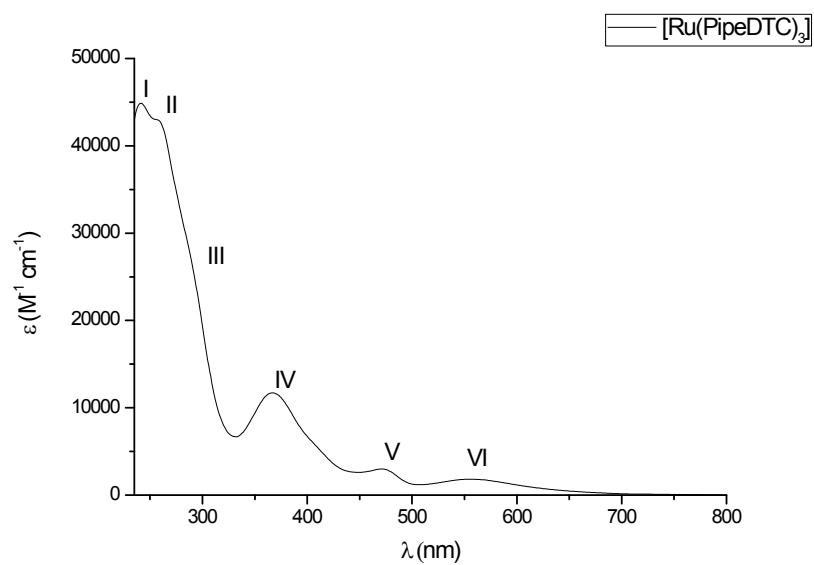
Figure SI 81. ^1H -NMR (DMSO-d_6 , 298 K, 300.13 MHz) spectrum of bis(pyrrole dithiocarbamate)copper(II), $[\text{Cu}(\text{PyrroleDTC})_2]$.

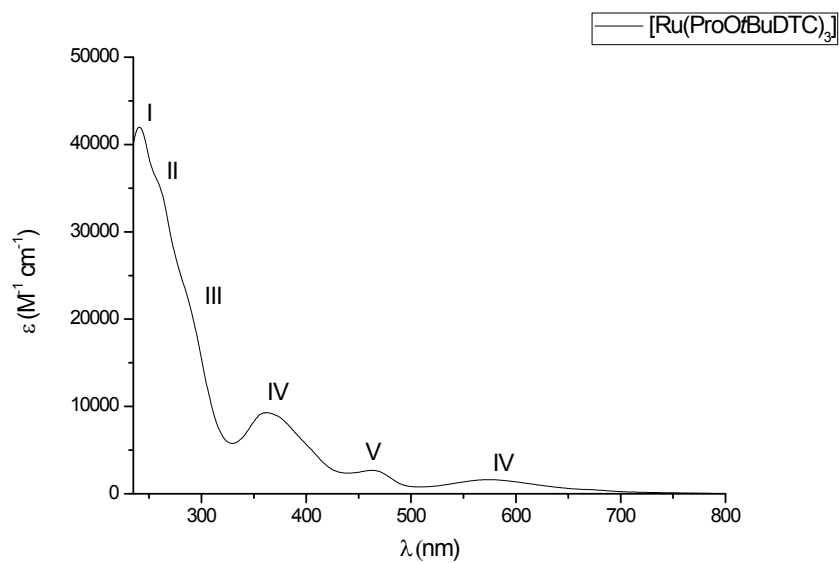
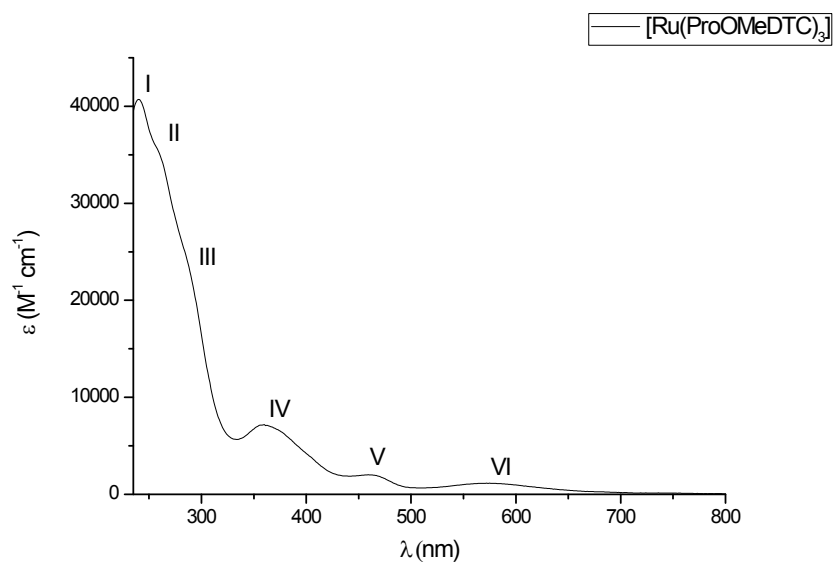
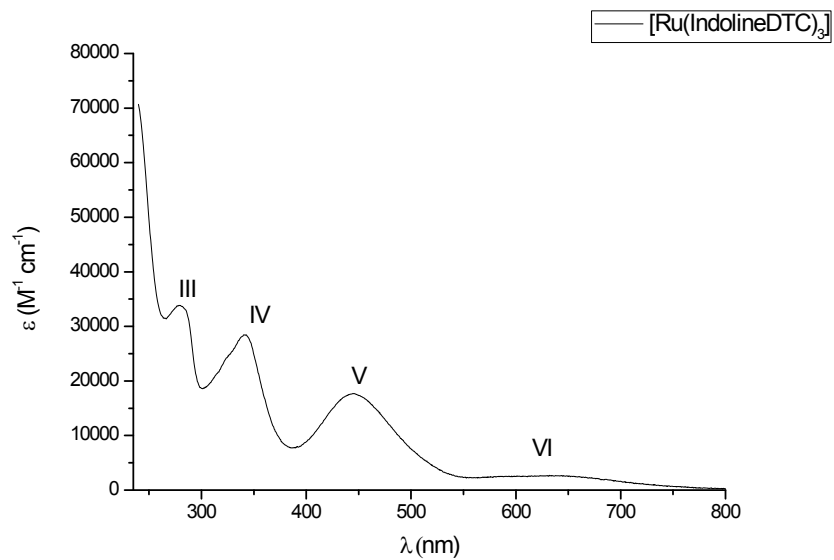
UV-Visible spectra

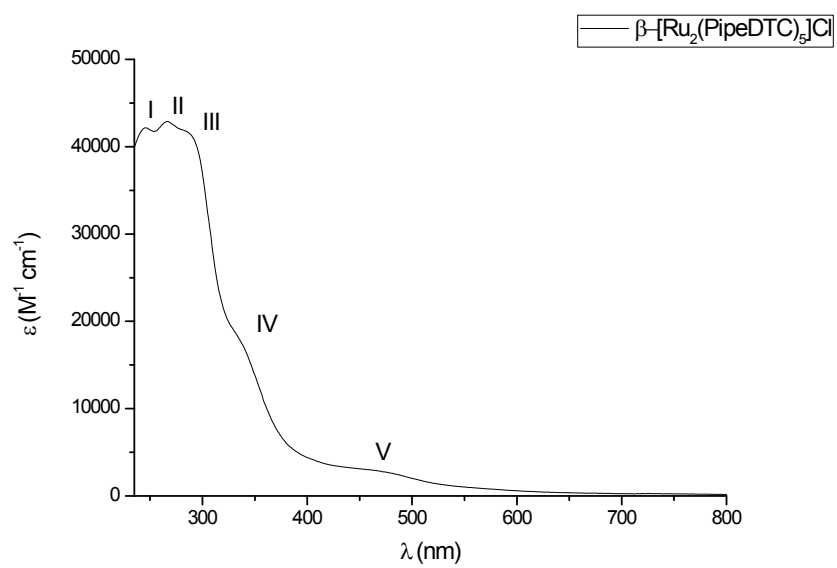
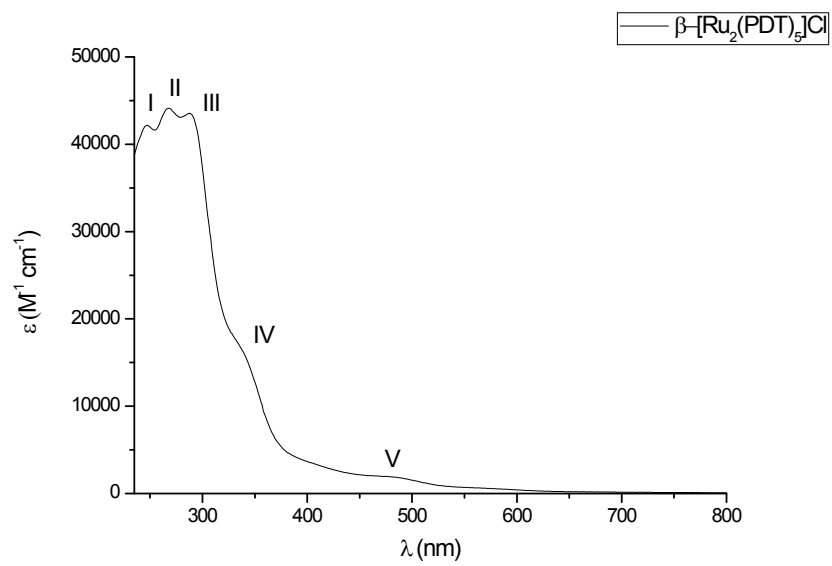
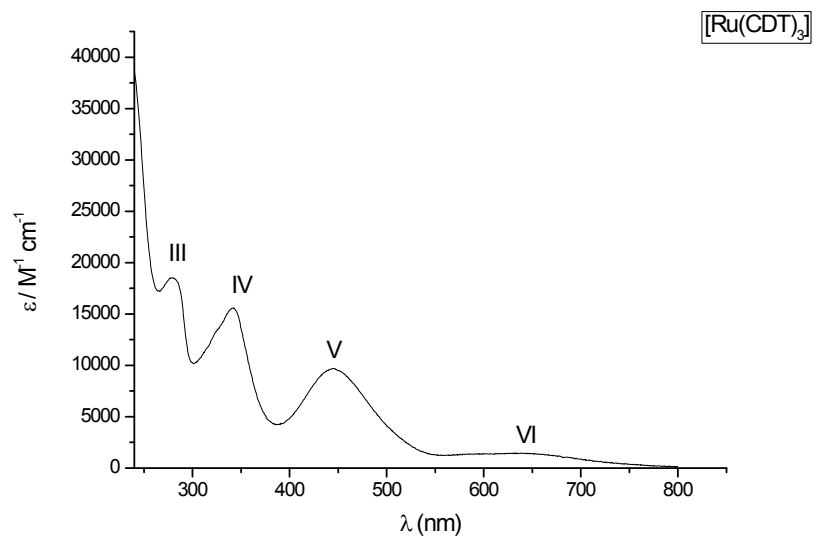
The UV-Vis spectra were obtained in CH_2Cl_2 at 25 °C.

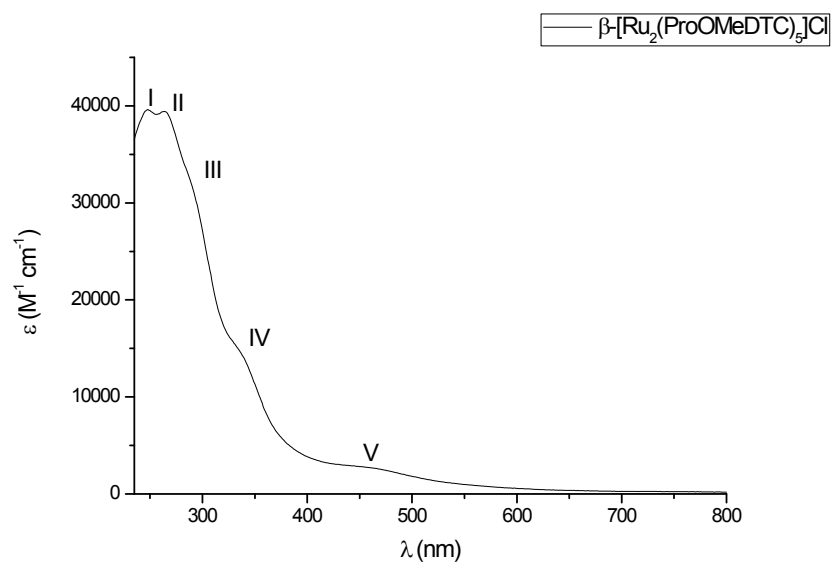
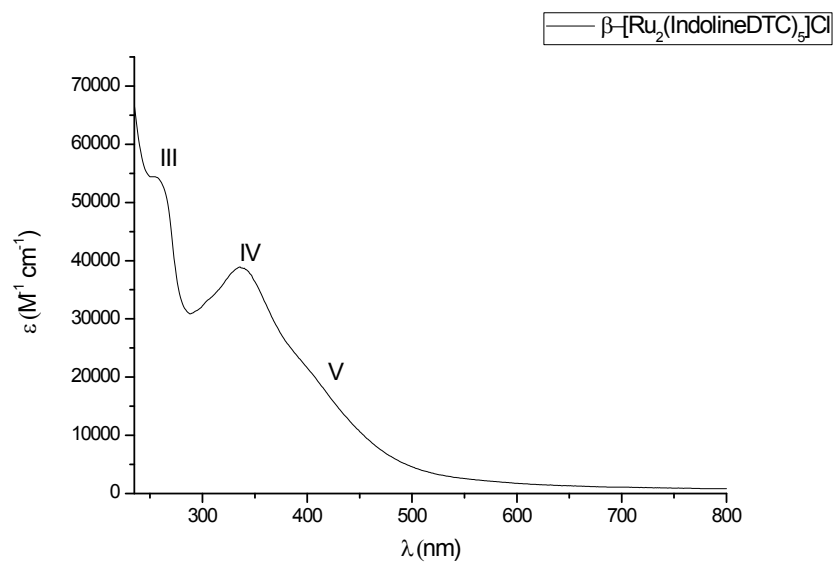
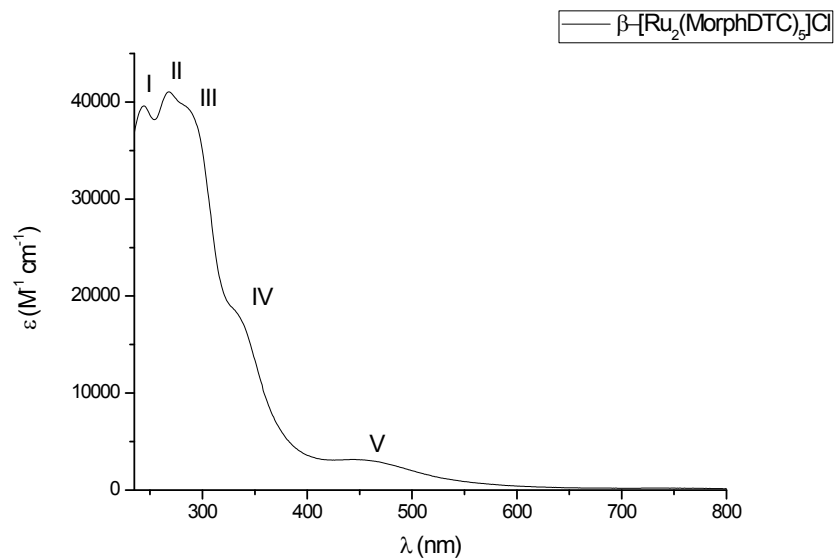


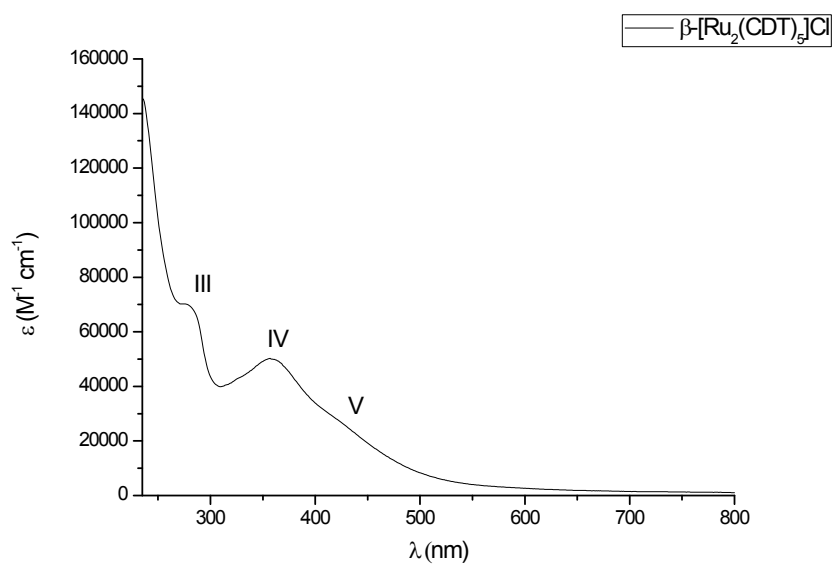
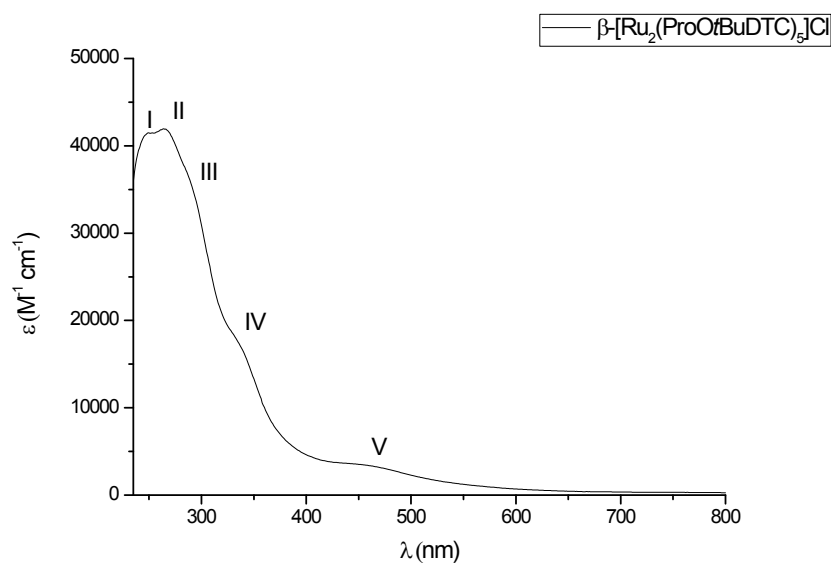










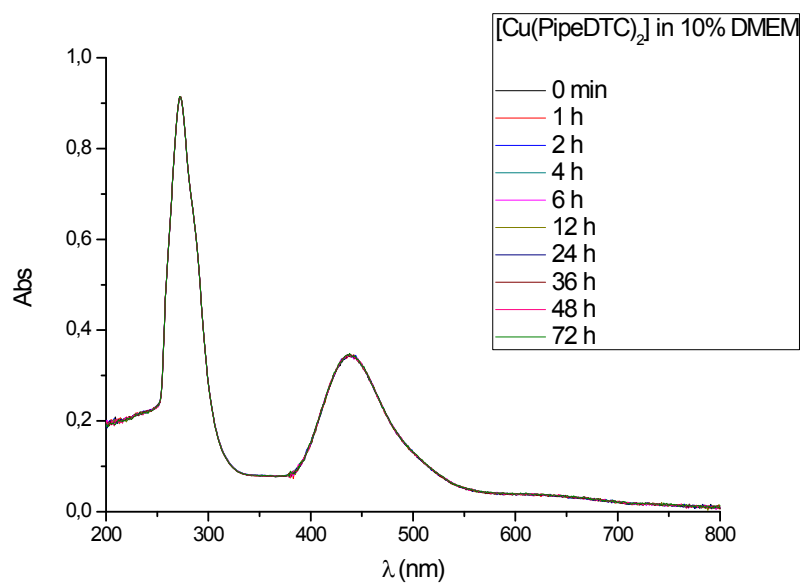
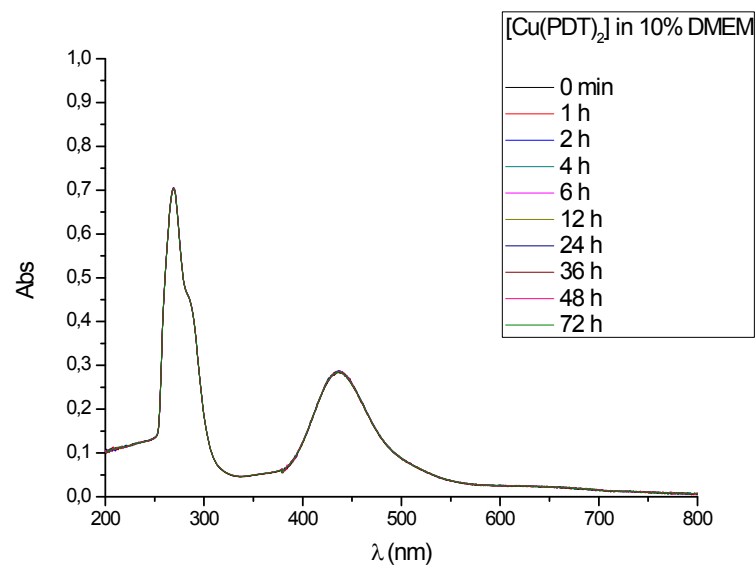


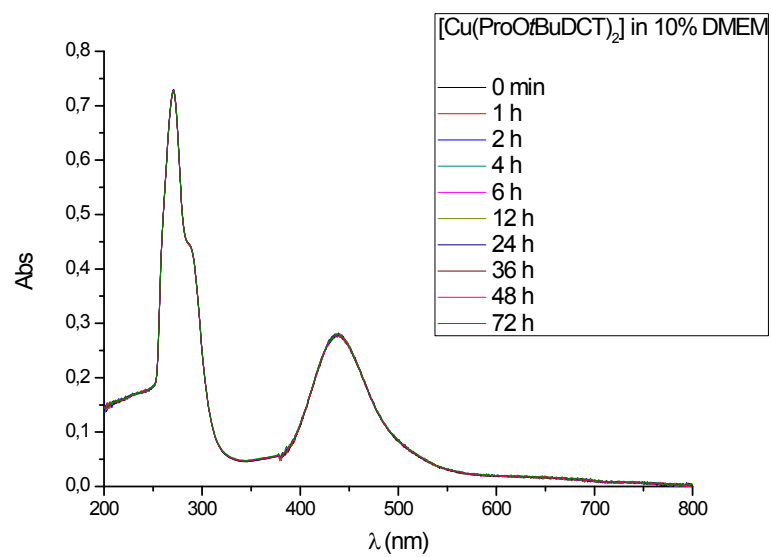
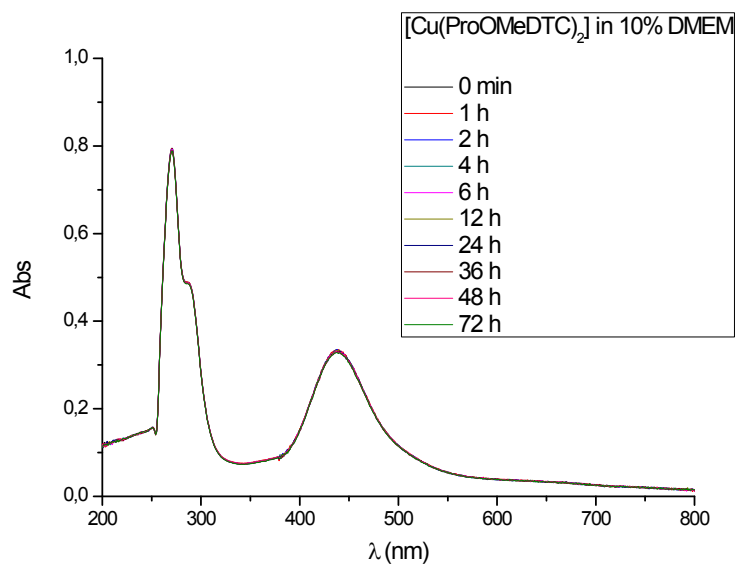
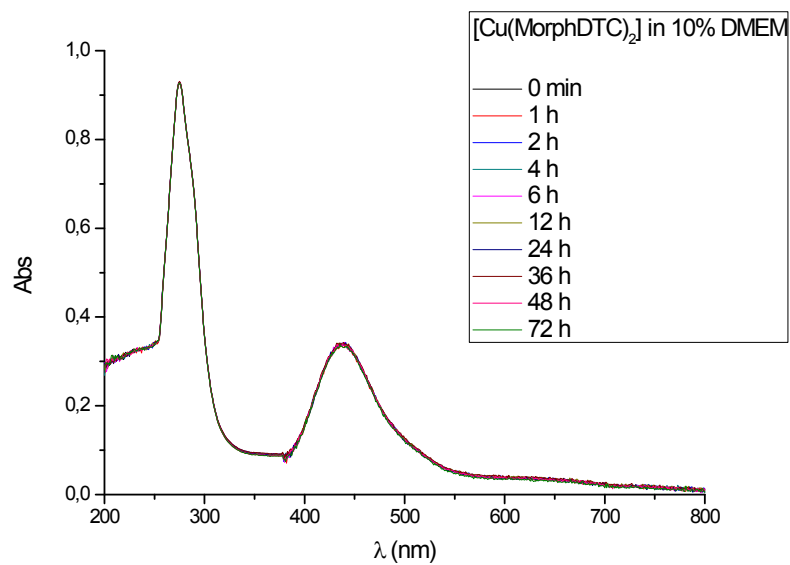
UV-Visible stability studies spectra

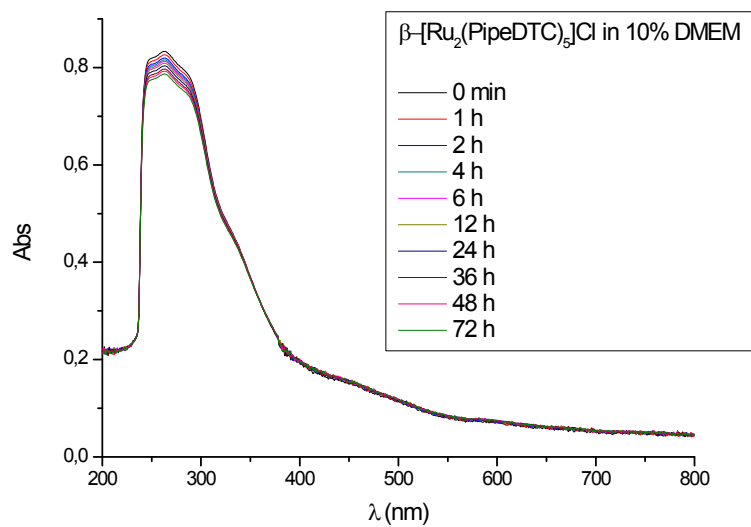
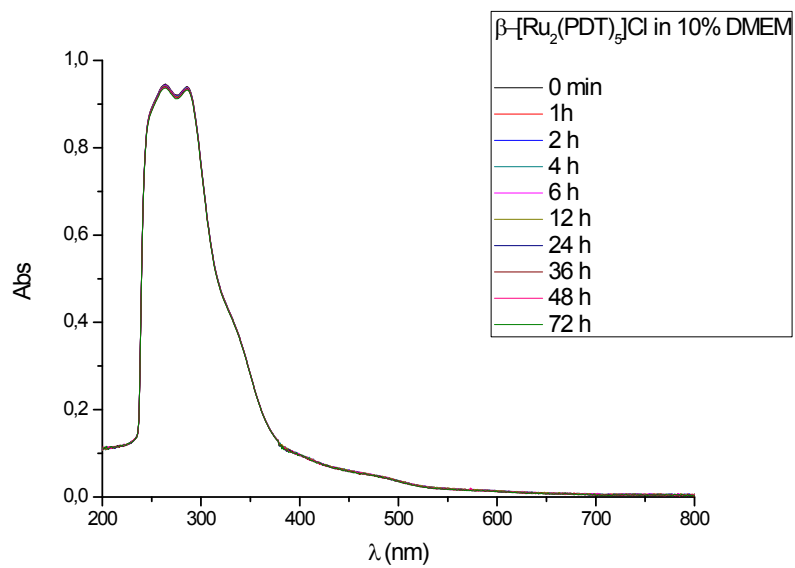
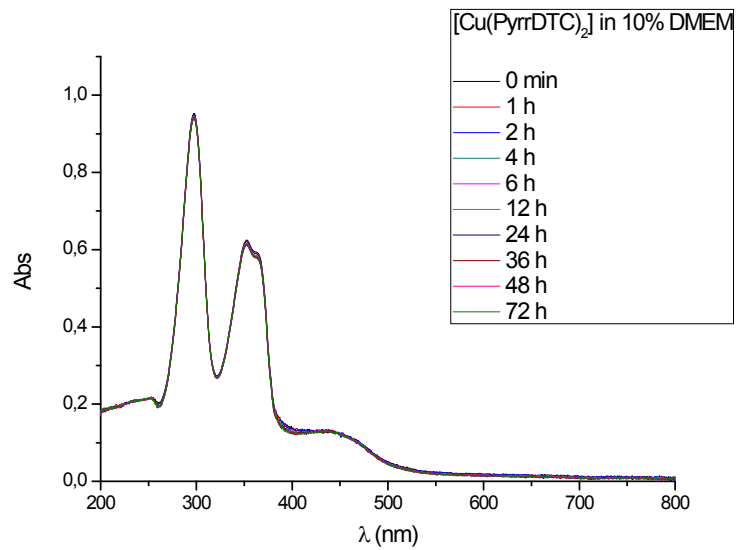
Herein we report the UV-Visible studies of the most interesting coordination compounds in terms of antiproliferative activity.

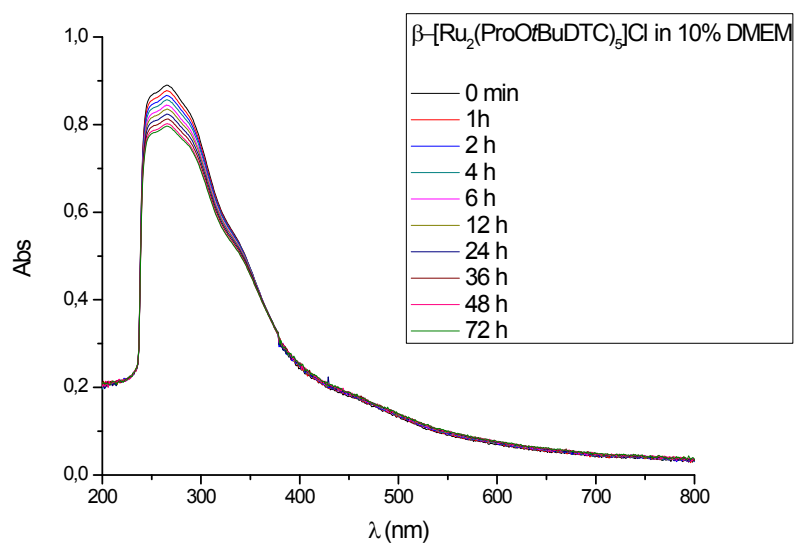
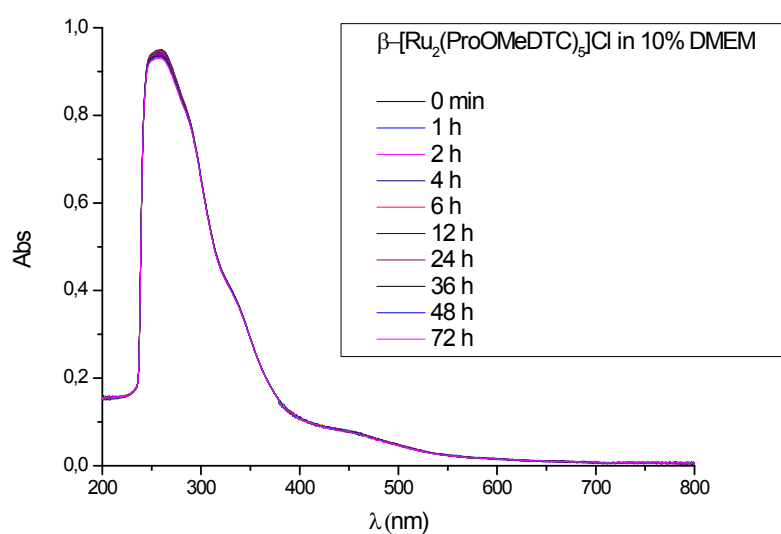
DMEM UV-Visible stability studies

The compounds were previously dissolved in DMSO at a final total volume of 10% v/v in DMEM-PBS 10-80 % v/v at 37 °C.



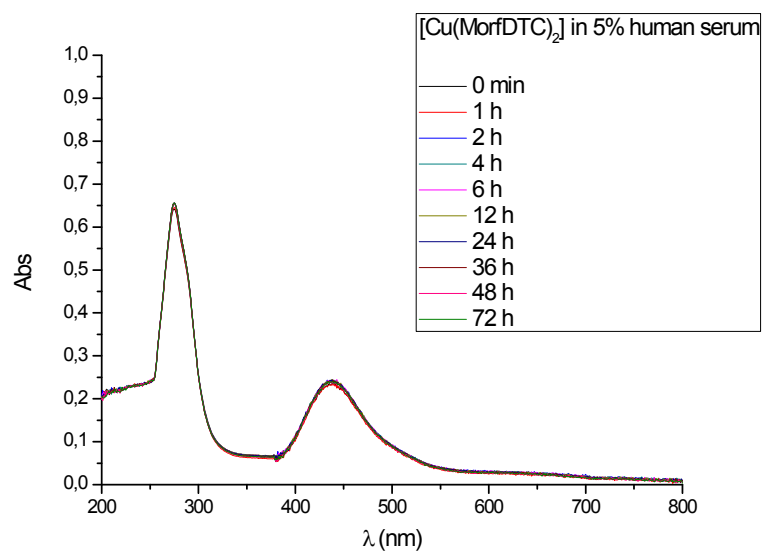
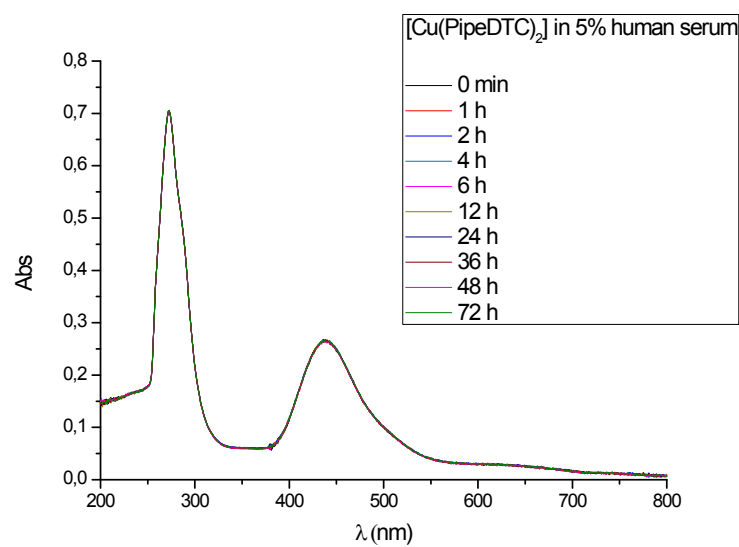
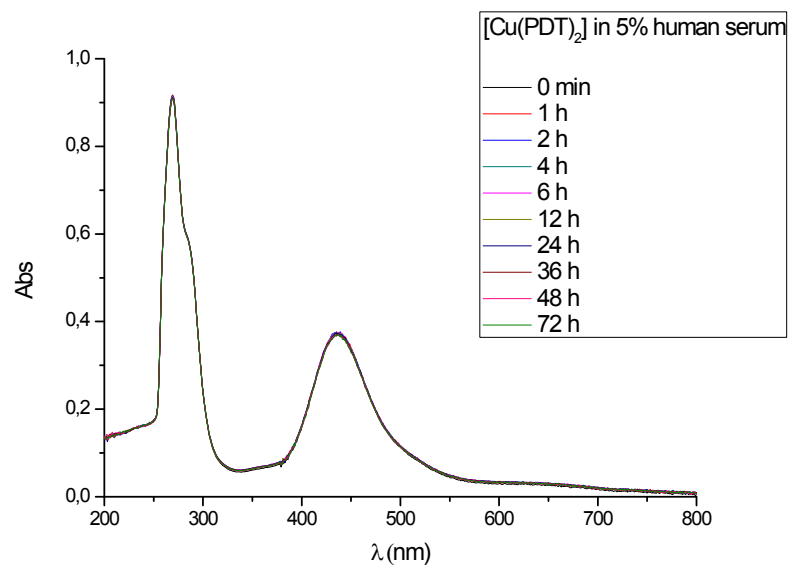


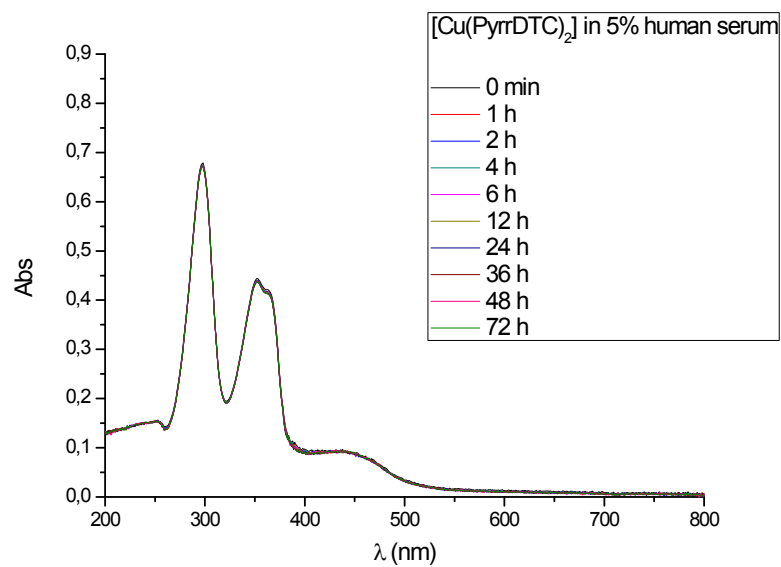
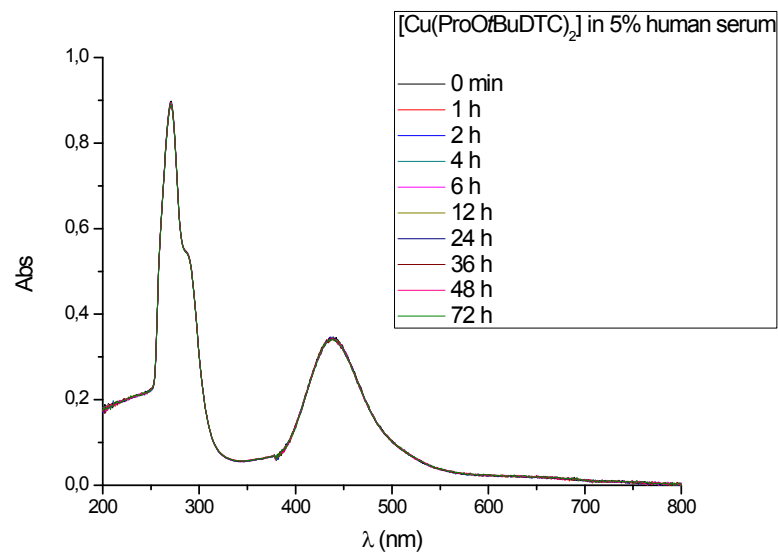
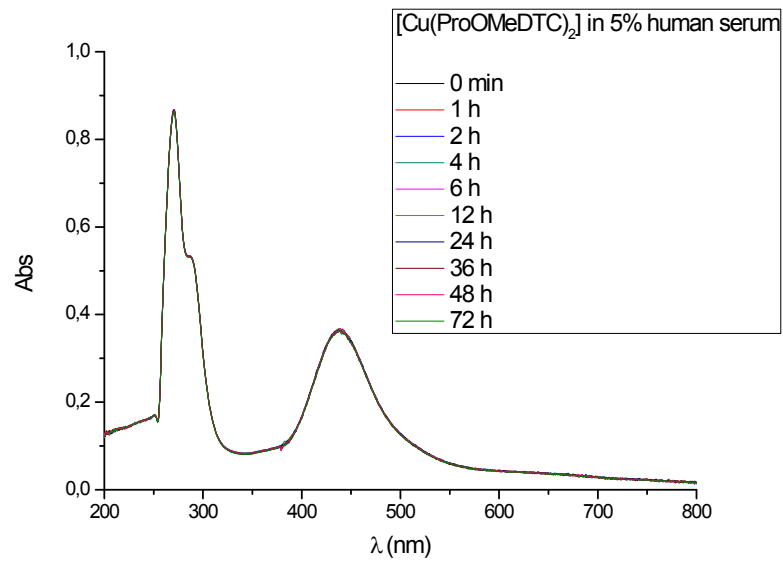


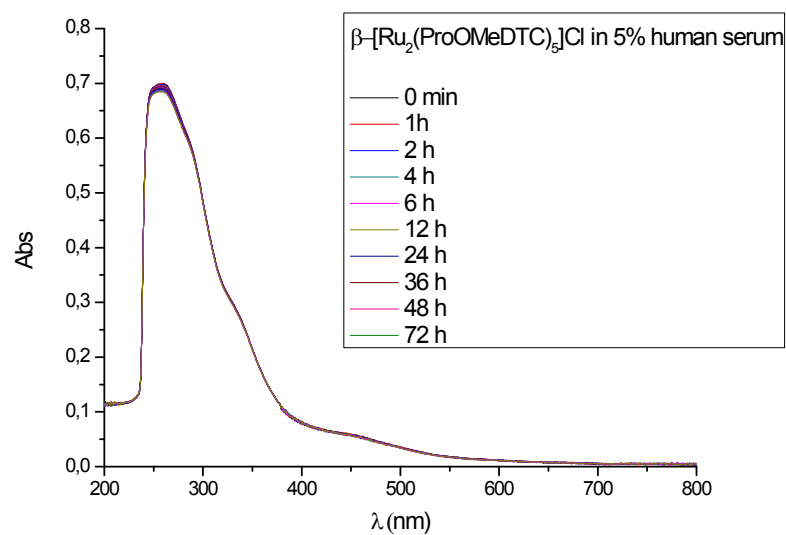
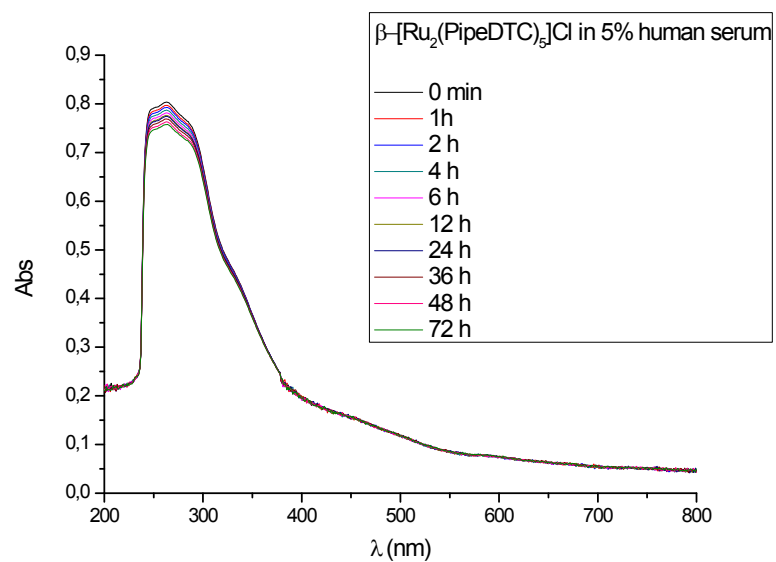
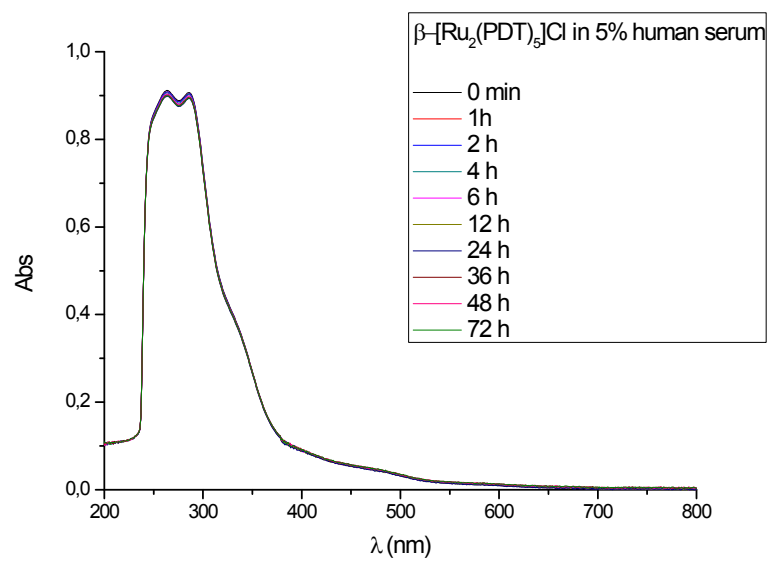


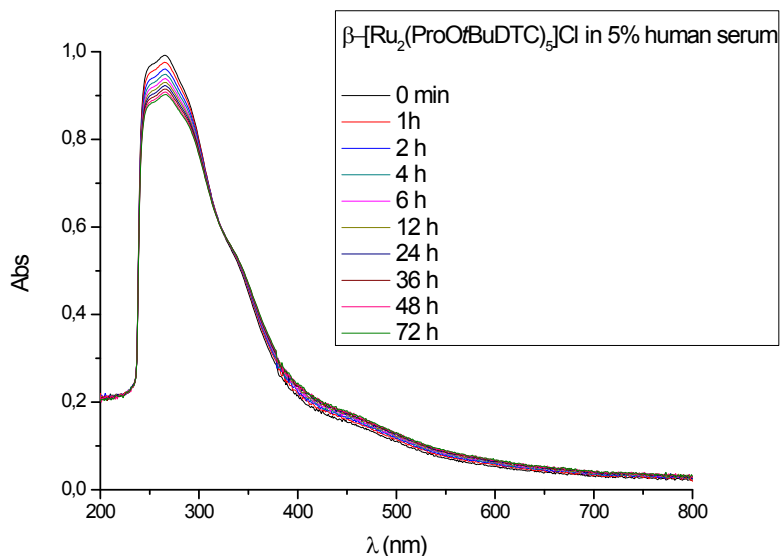
Human serum UV-Visible stability studies

The compounds were previously dissolved in DMSO at a final total volume of 10% v/v in human serum-PBS 5-85 % v/v at 37 °C.









Supporting Information References

1. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallog.*, 2015, **48**, 3.
2. G. M. Sheldrick, *Sect. A Found. Crystallogr.*, 2015, **71**, 3.
3. M. C. Burla, R. Caliendo, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori, R. Spagna, *J. Appl. Crystallog.*, 2012, **45**, 357.
4. G. M. Sheldrick, *Acta crystallogr. , C Struct. Chem.*, 2015, **71**, 3.
5. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. Van De Streek, *J. Appl. Crystallog.*, 2006, **39**, 453.
6. R. D. Bereman and D. Nalewajek, *Inorg. Chem.*, 1978, **17**, 1085.
7. V. Milacic, D. Chen, L. Giovagnini, A. Diez, D. Fregona and Q. P. Dou, *Toxicol. Appl. Pharmacol.*, 2008, **231**, 24.
8. S. Scintilla, L. Brustolin, A. Gambalunga, F. Chiara, A. Trevisan, C. Nardon and D. Fregona, *J. Inorg. Biochem.*, 2017, **166**, 76.
9. S. Quarta, L. Vidalino, C. Turato, M. Ruvoletto, F. Calabrese, M. Valente, S. Cannito, G. Fassina, M. Parola, M. Gatta and P. Pontisso, *J. Pathol.*, 2010, **221**, 343.