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

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**Experimental Section**

**Instruments**

Analytical TLC was carried out on Kieselgel F254; UV light (λ= 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 μL/min flow rate. A mixture of coumarin and 6-methyltriptophan 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 (4000-400 cm⁻¹) were recorded at room temperature (32 scans, resolution 2 cm⁻¹) by Nicolet Nexus 5SXC spectrophotometer. KBr pellets of samples were prepared according to
standard procedures. Far-FTIR spectra (600-50 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).

$^1$H-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 $^1$H-NMR spectra (1H: 300.13 MHz): normal pulse sequence, 64 transients, spectral width 15 ppm (80 ppm in the case of [Ru(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 (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 Log$P = \log \frac{C_1}{(C_0-C_1)}$.

For the X-ray analysis, a summary of data collection and structure refinement for the derivatives [Cu(ProOMeDTC)$_2$], and [Cu(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$_\alpha$: $\lambda = 0.71073$ Å. 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 code$^2$ 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
Table SI 1. Summary of X-ray crystallographic data for [Cu(ProOMeDTC)$_2$] and [Cu(ProO$_t$BuDTC)$_2$].

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<th>[Cu(ProOMeDTC)$_2$]</th>
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Synthesis of the selected cyclic N$_2$N-disubstituted dithiocarbamato 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 dithiocarbamato 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 (CS$_2$) 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 P$_2$O$_5$.

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

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

Aspect: white solid. Yield: 95%. Mp.: 215 °C (dec.). $^1$H-NMR (DMSO-d$_6$, 300.13 MHz): $\delta$ (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 ($\nu_a$, C-H); 1417.12 ($\nu_a$, N-CSS); 965.00 ($\nu_a$, CSS); 516.25 ($\nu_s$, CSS). ESI-MS m/z, [DTC$-$] found (calc.): 160.03 (160.02). Anal. Calc. for C$_6$H$_{10}$KNS$_2$ (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),**

Aspect: white solid. Yield: 85%. Mp.: 323 °C (dec.). $^1$H-NMR (DMSO-d$_6$, 300.13 MHz): $\delta$ (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 ($\nu_a$, C-H); 1410.44 ($\nu_a$, N-CSS); 1109.77 ($\nu_s$, C-O); 989.60 ($\nu_a$, CSS); 546.56 ($\nu_s$, CSS). ESI-MS m/z, [DTC$-$] found (calc.): 162.01 (162.00). Anal. Calc. for C$_5$H$_8$KNOS$_2$ (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 dithiocarbamato ligand derived from indoline**

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 P$_2$O$_5$.

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

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

Aspect: bright yellow solid. Yield: 88%. Mp.: 335 °C (dec.). $^1$H-NMR (DMSO-d$_6$, 300.13 MHz): $\delta$ (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 ($\nu_a$, C-H); 1452.26 (v, C=C ring); 1371.36 ($\nu_{as}$, N-CSS); 931.11 ($\nu_s$, CSS); 743.21 ($\delta$, C-H); 507.81 ($\nu_s$, CSS). ESI-MS m/z, [DTC$-$] found (calc.): 194.02.
(194.01). Anal. Calc. for C₉H₈KNS₂ (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 dithiocarbamato 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 synthetized 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-dithiocarbamato 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, H₃ + H₄), 3.69 (s, 3H, O-CH₃), 3.95 (m, 2H, H₅), 5.07-5.11 (dd, 1H, H₂). Medium FT-IR (KBr): ν (cm⁻¹) = 2953.03 (νₐ, C-H); 1733.20 (ν, C=O); 1392.38 (νₐ, N-CSS); 1177.76 (νₐ, C-OMe); 944.78 (νₛ, CSS); 504.45 (νₛ, 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, H₃ + H₄), 3.94 (m, 2H, H₅), 4.97-4.99 (dd, 1H, H₂). Medium FT-IR (KBr): ν (cm⁻¹) = 2974.63 (νₐ, C-H); 1722.65 (ν, C=O); 1388.27 (νₐ, N-CSS); 1151.18 (νₐ, C-OtBu); 932.89 (νₛ, CSS); 502.02 (νₛ, 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 dithiocarbamato ligand of aromatic N-heterocycles \textit{g-i}

The sodium salts of carbazole dithiocarbamate (Na CDT), indole dithiocarbamate (Na IndDTC), and pyrrole dithiocarbamate (Na PyrrDTC) were synthetized in a Schlenk-line apparatus in a N\textsubscript{2} atmosphere with a modification of literature procedure.\textsuperscript{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 P\textsubscript{2}O\textsubscript{5}. All products were stored under inert atmosphere, as they resulted highly hygroscopic and air sensitive. Analyses are in agreement with literature data.\textsuperscript{6}

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

Carbazole dithiocarbamate sodium salt (Na CDT), \textit{g}

Aspect: orange hygroscopic solid. Yield: 88\%. Mp.: n.d. \textsuperscript{1}H-NMR (DMSO-d\textsubscript{6}, 300.13 MHz): \(\delta\) (ppm) = 7.17 (t, 2H, H\textsubscript{(3)} + H\textsubscript{(6)}), 7.33 (t, 2H, H\textsubscript{(2)} + H\textsubscript{(7)}), 8.05-8.08 (d, 2H, H\textsubscript{(4)} + H\textsubscript{(5)}), 8.45-8.47 (d, 2H, H\textsubscript{(1)} + H\textsubscript{(8)}). Medium FT-IR (KBr): \(\tilde{\nu}\) (cm\textsuperscript{-1}) = 1435.84 (\(\nu\), C=C ring); 1281.47 (\(\nu\)\textsubscript{a}, N-CSS); 1040.03 (\(\nu\)\textsubscript{a}, CSS); 832.62 (\(\omega\), C-H); 742.53 (\(\delta\), C-H); 569.77 (\(\nu\)\textsubscript{s}, CSS). ESI-MS \textit{m/z}, [DTC\textsuperscript{-}] found (calc.): 242.01 (242.01).

Anal. Calc. for C\textsubscript{13}H\textsubscript{8}NNaS\textsubscript{2} (MW = 265.33 g·mol\textsuperscript{-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), \textit{h}

Aspect: yellow-orange hygroscopic solid. Yield: 71\%. Mp.: n.d. \textsuperscript{1}H-NMR (DMSO-d\textsubscript{6}, 300.13 MHz): \(\delta\) (ppm) = 6.36-6.37 (d, 1H, H\textsubscript{(3)}), 7.03-7.11 (m, 2H, H\textsubscript{(5)} + H\textsubscript{(6)}), 7.45-7.48 (d, 1H, H\textsubscript{(4)}), 8.66-8.68 (d, 1H, H\textsubscript{(1)}), 9.31-9.34 (d, 1H, H\textsubscript{(7)}). Medium FT-IR (KBr): \(\tilde{\nu}\) (cm\textsuperscript{-1}) = 2923.17 (\(\nu\)\textsubscript{a}, C-H); 1439.44 (\(\nu\), C=C ring); 1289.94 (\(\nu\)\textsubscript{a}, N-CSS); 997.91 (\(\nu\)\textsubscript{a}, CSS); 824.65 (\(\nu\)\textsubscript{a}, C-H); 752.33 (\(\nu\)\textsubscript{s}, C-H); 550.32 (\(\nu\)\textsubscript{s}, CSS). ESI-MS \textit{m/z}, [DTC\textsuperscript{-}] found (calc.): 192.00 (191.99).

Anal. Calc. for C\textsubscript{9}H\textsubscript{6}NNaS\textsubscript{2} (MW = 215.27 g·mol\textsuperscript{-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), \textit{i}

Aspect: dark yellow hygroscopic solid. Yield: 66\%. Mp.: n.d. \textsuperscript{1}H-NMR (DMSO-d\textsubscript{6}, 300.13 MHz): \(\delta\) (ppm) = 5.99 (s, 2H, H\textsubscript{(3)} + H\textsubscript{(4)}), 8.03 (s, 2H, H\textsubscript{(2)} + H\textsubscript{(5)}). Medium FT-IR (KBr): \(\tilde{\nu}\) (cm\textsuperscript{-1}) = 2923.10 (\(\nu\)\textsubscript{a}, C-
H); 1457.21 (v, C=C ring); 1259.12 (va, N-CSS); 1012.45 (va, CSS); 815.10 (δ, C-H); 746.04 (δ, C-H);
548.16 (va, 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)]

Synthesis of Cu(II) dithiocarbamato complexes of the aliphatic ligands

1.7 mmol (2 eq) of the selected dithiocarbamato 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. 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)]
[Cu(IndolineDTC)] are in agreement with literature data.

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

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): υ (cm⁻¹) = 2965.40, 2871.44
(νa, C-H); 1497.92 (νa, N-CSS); 947.33 (νa, CSS). Far FT-IR (nujol): υ (cm⁻¹) = 559.05 (νa, CSS); 338.54 (νa, Cu-
S); 291.40 (νs, 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)]

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): υ (cm⁻¹) = 2941.17, 2850.28 (νa, C-H);
1501.54 (νa, N-CSS); 947.25 (νa, CSS). Far FT-IR (nujol): υ (cm⁻¹) = 563.41 (νa, CSS); 353.57 (νa, Cu-
S); 291.76 (νs, 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 35.94. Found: C 37.54; H 4.77; N 7.10; S 35.18.
Solubility: chloroform, dichloromethane, DMSO, acetonitrile.

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

Aspect: brown solid. Yield: 94%. Mp.: 296 °C (dec.). Medium FT-IR (KBr): υ (cm⁻¹) = 2968.97, 2853.40
(νa, C-H); 1485.33 (νa, N-CSS); 1110.23 (νa, C-O); 1010.40 (νa, CSS). Far FT-IR (nujol): υ (cm⁻¹) = 558.69
(νs, CSS); 338.25 (νa, Cu-S); 291.38 (νa, Cu-S). ESI-MS m/z, [M⁺] found (calc.): 386.94 (386.94). Anal.
Calc. for C₁₀H₁₂CuN₂O₂S₄ (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 (\( \nu_a \), C-H); 1481.41 (\( \nu_s \), C=C ring); 1422.33 (\( \nu_a \), N-CSS); 1038.58 (\( \nu_a \), CSS); 739.18 (\( \delta \), C-H). Far FT-IR (nujol): \( \tilde{\nu} \) (cm\(^{-1}\)) = 556.43 (\( \nu_s \), CSS); 343.83 (\( \nu_a \), Cu-S); 271.35 (\( \nu_s \), Cu-S). ESI-MS \( m/z \), [M+]+ found (calc.): 450.96 (450.95). Anal. Calc. for C\(_{18}\)H\(_{16}\)CuN\(_2\)S\(_4\) (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) dithiocarbamato 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 dithiocarbamato salt dissolved in ethanol (5 mL) to an ethanol solution containing 0.70 mmol of CuCl\(_2\)·2H\(_2\)O. 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 P\(_2\)O\(_5\).

Bis(L-proline methyl ester dithiocarbamate)copper(II), [Cu(ProOMeDTC)₂]
Aspect: dark green solid. Yield: 80%. Mp.: 215 °C. \(^1\)H-NMR (CDCl\(_3\), 300.13 MHz): \( \delta \) (ppm) = 2.11-2.93 (m, 8H, H\(_3\) + H\(_4\)); 3.94 (m, 6H, O-C\(_3\)H\(_3\)). Medium FT-IR (KBr): \( \tilde{\nu} \) (cm\(^{-1}\)) = 2951.87 (\( \nu_a \), C-H); 1750.79 (\( \nu \), C=O); 1471.56 (\( \nu_a \), N-CSS); 1153.76 (\( \nu_a \), C-OMe); 939.75 (\( \nu_a \), CSS). Far FT-IR (nujol): \( \tilde{\nu} \) (cm\(^{-1}\)) = 565.71 (\( \nu_s \), CSS); 342.87 (\( \nu_a \), Cu-S); 279.96 (\( \nu_s \), Cu-S). ESI-MS \( m/z \), [M]+ found (calc.): 470.97 (470.96). Anal. Calc. for C\(_{14}\)H\(_{20}\)CuN\(_2\)O\(_4\)S\(_4\) (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. \(^1\)H-NMR (CDCl\(_3\), 300.13 MHz): \( \delta \) (ppm) = 1.57 (s, 18H, O-C(C\(_3\)H\(_3\))), 1.99-2.83 (m, 8H, H\(_3\) + H\(_4\)). Medium FT-IR (KBr): \( \tilde{\nu} \) (cm\(^{-1}\)) = 2974.81 (\( \nu_a \), C-H); 1733.37 (\( \nu \), C=O); 1469.68 (\( \nu_a \), N-CSS); 1148.53 (\( \nu_a \), C-OtBu); 930.08 (\( \nu_a \), CSS). Far FT-IR (nujol): \( \tilde{\nu} \) (cm\(^{-1}\)) = 568.57 (\( \nu_s \), CSS); 340.11 (\( \nu_a \), Cu-S); 276.11 (\( \nu_s \), Cu-S). ESI-MS \( m/z \), [M]+ found (calc.): 555.06 (555.05). Anal. Calc. for C\(_{20}\)H\(_{32}\)CuN\(_2\)O\(_4\)S\(_4\) (MW = 556.29 g·mol\(^{-1}\)): C 43.18; H 4.27; N 5.69; S 23.71. Found: C 43.83; H 4.90; S 23.21. Solubility: methanol, ethanol, ethyl acetate, chloroform, dichloromethane, DMSO, acetonitrile.
Synthesis of Cu(II) dithiocarbamato complexes of aromatic N-heterocycles g-i

The copper(II) complexes involving the aromatic ligands g-i were obtained according to literature procedure\(^6\) by dropwise addition of 1.5 mmol (2 eq) of the dithiocarbamato salt (dissolved in 5 mL of tetrahydrofuran) to a solution containing 0.75 mmol of CuCl\(_2\)·2H\(_2\)O 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 P\(_2\)O\(_5\). 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): \(\tilde{\nu} (\text{cm}^{-1}) = 3011.02 (\nu_{\text{a}}, \text{C-H}); 1485.75, 1446.99, 1435.70 (\nu, \text{C=C ring}); 1333.30 (\nu_{\text{a}}, \text{N-CSS}); 1038.66 (\nu_{\text{a}}, \text{CSS}); 843.59 (\omega, \text{C-H}); 743.78, 707.83 (\delta, \text{C-H}).\)

Far FT-IR (nujol): \(\tilde{\nu} (\text{cm}^{-1}) = 595.47 (\nu_{\text{s}}, \text{CSS}); 412.14 (\nu_{\text{a}}, \text{Cu-S}); 346.20 (\nu_{\text{a}}, \text{Cu-S}).\)

ESI-MS m/z, [M\(^{+}\)] found (calc.): 546.98 (546.95). Anal. Calc. for C\(_{26}\)H\(_{16}\)CuN\(_2\)S\(_4\) (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): \(\tilde{\nu} (\text{cm}^{-1}) = 3046.82 (\nu_{\text{a}}, \text{C-H}); 1445.35, 1388.04 (\nu, \text{C=C ring}); 1333.98 (\nu_{\text{a}}, \text{N-CSS}); 1017.17 (\nu_{\text{a}}, \text{CSS}); 847.19 (\omega, \text{C-H}); 749.97, 730.36 (\delta, \text{C-H}).\)

Far FT-IR (nujol): \(\tilde{\nu} (\text{cm}^{-1}) = 591.13 (\nu_{\text{s}}, \text{CSS}); 413.37 (\nu_{\text{a}}, \text{Cu-S}); 340.40 (\nu_{\text{a}}, \text{Cu-S}).\)

ESI-MS m/z, [M\(^{+}\)] found (calc.): 446.94 (446.92). Anal. Calc. for C\(_{18}\)H\(_{12}\)CuN\(_2\)S\(_4\) (MW = 448.11 g·mol\(^{-1}\)): C 48.25; H 2.70; N 6.25; S 28.62. Found: C 48.07; H 2.45; N 4.94; 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): \(\tilde{\nu} (\text{cm}^{-1}) = 3131.02 (\nu_{\text{a}}, \text{C-H}); 1472.85, 1409.66 (\nu, \text{C=C ring}); 1333.66 (\nu_{\text{a}}, \text{N-CSS}); 1012.56 (\nu_{\text{a}}, \text{CSS}); 836.97 (\omega, \text{C-H}); 729.40 (\delta, \text{C-H}).\)

Far FT-IR (nujol): \(\tilde{\nu} (\text{cm}^{-1}) = 591.99 (\nu_{\text{s}}, \text{CSS}); 411.07 (\nu_{\text{a}}, \text{Cu-S}); 338.87 (\nu_{\text{a}}, \text{Cu-S}).\)

ESI-MS m/z, [M\(^{+}\)] found (calc.): 346.90 (346.89). Anal. Calc. for C\(_{10}\)H\(_{8}\)CuN\(_2\)S\(_4\) (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 a-i ligands, the neutral [Ru\textsuperscript{III}DTC\textsubscript{3}], and the ionic dinuclear β-[Ru\textsuperscript{III}\textsubscript{2}DTC\textsubscript{5}]Cl

Synthesis of Ru(III) dithiocarbamato complexes of the aliphatic ligands a-i

According to a literature procedure, a solution of RuCl\textsubscript{3}·3H\textsubscript{2}O (1.5 mmol) in water (4 mL), 10 mL of an aqueous solution of the dithiocarbamato 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\textsubscript{2}Cl\textsubscript{2} to be purified by silica gel chromatography. A gradient from pure CH\textsubscript{2}Cl\textsubscript{2} to CH\textsubscript{2}Cl\textsubscript{2}/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-[Ru\textsubscript{2}(PDT)\textsubscript{5}]Cl was isomerized to the thermodynamically stable β-[Ru\textsubscript{2}(PDT)\textsubscript{5}]Cl by reflux in methanol for 8 hours. All the compounds were re-precipitated from CH\textsubscript{2}Cl\textsubscript{2} - diethyl ether, washed with n-pentane, and dried in vacuum pump in the presence of P\textsubscript{2}O\textsubscript{5}. Analyses for Ru(III)-PDT derivatives are in agreement with literature data.

Tris(pyrrolidine dithiocarbamate)ruthenium(III), [Ru(PDT)\textsubscript{3}]

Aspect: dark green solid. Yield: 31%. R.f. (on silica gel, CH\textsubscript{2}Cl\textsubscript{2}): 0.85. Mp.: 256 °C. \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 300.13 MHz): \(\delta\) (ppm) = 0.39 (s, 12H, H(3) + H(4)), 35.83 (s br, 6H, H(2) + H(5)), 44.29 (s br, 6H, H(2) + H(5)). Medium FT-IR (KBr): \(v\) (cm\textsuperscript{-1}) = 2945.32, 2865.58 (\(v_a\), C-H); 1487.12, 1469.76, 1444.15 (\(v_a\), N-CSS); 942.18 (\(v_s\), CSS). Far FT-IR (nujol): \(v\) (cm\textsuperscript{-1}) = 565.37 (\(v_s\), CSS); 447.75 (\(v_a\), Ru-S); 318.90 (\(v_s\), Ru-S). ESI-MS \(m/z\), [M\textsuperscript{+}] found (calc.): 539.96 (539.93). Anal. Calc. for C\textsubscript{15}H\textsubscript{24}N\textsubscript{3}RuS\textsubscript{6} (MW = 539.83 g·mol\textsuperscript{-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-[Ru\textsubscript{2}(PDT)\textsubscript{5}]Cl

Aspect: dark red solid. Yield: 32%. R.f. (on silica gel, CH\textsubscript{2}Cl\textsubscript{2}/MeOH 92:8): 0.23. Mp.: 236 °C.

\textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 300.13 MHz): \(\delta\) (ppm) = 1.81-2.19 (m, 20H, H(3) + H(4)), 3.46-3.94 (m, 20H, H(2) + H(5)). Medium FT-IR (KBr): \(v\) (cm\textsuperscript{-1}) = 2947.10, 2667.69 (\(v_a\), C-H); 1505.71, 1473.13, 1447.94 (\(v_a\), N-CSS); 946.59 (\(v_s\), CSS). Far FT-IR (nujol): \(v\) (cm\textsuperscript{-1}) = 563.86 (\(v_s\), CSS); 445.81 (\(v_a\), Ru-S); 347.83 (\(v_s\), Ru-S). ESI-MS \(m/z\), [M-Cl\textsuperscript{+}] found (calc.): 932.87 (932.86). Anal. Calc. for C\textsubscript{25}H\textsubscript{40}Cl\textsubscript{5}Ru\textsubscript{2}S\textsubscript{10} (MW = 968.86 g·mol\textsuperscript{-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), [Ru(PipeDTC)\textsubscript{3}]

Aspect: dark green solid. Yield: 31%. R.f. (on silica gel, CH\textsubscript{2}Cl\textsubscript{2}/MeOH 92:8): 0.23. Mp.: 236 °C.
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): ν (cm⁻¹) = 2936.08, 2850.82 (νₐ, C-H); 1487.83, 1455.07, 1439.06 (νₐ, N-CS); 1001.97 (νₐ, CSS). Far FT-IR (nujol): ν (cm⁻¹) = 538.14 (νₛ, CSS); 405.74 (νₐ, Ru-S); 330.99 (νₛ, 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, acetone, 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): ν (cm⁻¹) = 2933.43 (νₐ, C-H); 1503.23, 1441.03 (νₐ, N-CS); 1001.63 (νₐ, CSS). Far FT-IR (nujol): ν (cm⁻¹) = 544.23 (νₛ, CSS); 406.62 (νₐ, Ru-S); 321.88 (νₛ, 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): ν (cm⁻¹) = 2859.46 (νₐ, C-H); 1486.03, 1430.57 (νₐ, N-CS); 994.13 (νₐ, CSS). Far FT-IR (nujol): ν (cm⁻¹) = 541.55 (νₛ, CSS); 412.70 (νₐ, Ru-S); 324.59 (νₛ, 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) = 3.15 (s, 12H, H(2) + H(6)), 24.90 (s br, 12H, H(3) + H(5)). Medium FT-IR (KBr): ν (cm⁻¹) = 2859.46 (νₐ, C-H); 1486.03, 1430.57 (νₐ, N-CS); 994.13 (νₐ, CSS). Far FT-IR (nujol): ν (cm⁻¹) = 541.55 (νₛ, CSS); 412.70 (νₐ, Ru-S); 324.59 (νₛ, 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 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.

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): ν (cm⁻¹) = 2842.06 (vₐ, C-H); 1475.67 (ν, C=C ring); 1387.37, 1347.88, 1322.11 (νₐ, N-CSS); 947.54 (νₐ, CSS); 750.41 (δ, C-H). Far FT-IR (nujol): ν (cm⁻¹) = 546.68 (νₛ, CSS); 424.20 (νₐ, Ru-S); 333.12 (νₛ, 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): ν (cm⁻¹) = 2850.49 (νₐ, C-H); 1484.25 (ν, C=C ring); 1431.19, 1323.61 (νₐ, N-CSS); 952.20 (νₐ, CSS); 750.98 (δ, C-H). Far FT-IR (nujol): ν (cm⁻¹) = 558.76 (νₛ, CSS); 421.19 (νₐ, Ru-S); 323.76 (νₛ, 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) dithiocarbamato 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 redissolved 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 reprecipitated 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): ν (cm⁻¹) = 2949.05 (vₐ, C-H); 1742.31 (ν, C=O); 1439.74 (νₐ, N-CSS); 1169.25 (νₐ, C-OMe); 942.14 (νₐ, CSS). Far FT-IR (nujol): ν (cm⁻¹) = 546.88 (vₛ, CSS); 453.06 (vₐ, Ru-S); 323.86 (vₛ, Ru-S). ESI-MS m/z, [M⁺] found
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): ʋ (cm⁻¹) = 2950.23 (ʋₐ, C-H); 1741.36 (ʋ, C=O); 1480.37, 1447.83 (ʋₐ, N-CSS); 1170.04 (ʋₐ, C-OMe); 944.45 (ʋₐ, CSS). Far FT-IR (nujol): ʋ (cm⁻¹) = 546.95 (ʋₕ, CSS); 461.98 (ʋₐ, Ru-S); 335.16 (ʋₕ, Ru-S). ESI-MS m/z, [M-Cl⁺] found (calc.): 1223.92 (1223.89). Anal. Calc. for C₃₀H₅₀ClN₅Ru₂S₁₀ (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.

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

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(C₃H₃))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): ʋ (cm⁻¹) = 2975.22, 2872.34 (ʋₐ, C-H); 1736.11 (ʋ, C=O); 1440.10 (ʋₐ, N-CSS); 1148.66 (ʋₕ, C-OtBu); 933.50 (ʋₐ, CSS). Far FT-IR (nujol): ʋ (cm⁻¹) = 547.60 (ʋₕ, CSS); 470.56 (ʋₐ, Ru-S); 320.98 (ʋₕ, Ru-S). ESI-MS m/z, [M⁺] found (calc.): 840.12 (840.09). Anal. Calc. for C₃₀H₅₀Cl₃O₃Ru₂S₁₀ (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.

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

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): ʋ (cm⁻¹) = 2975.16 (ʋₐ, C-H); 1735.39 (ʋ, C=O); 1481.10, 1450.06 (ʋₐ, N-CSS); 1148.87 (ʋₕ, C-OtBu); 935.12 (ʋₐ, CSS). Far FT-IR (nujol): ʋ (cm⁻¹) = 551.30 (ʋₕ, CSS); 471.19 (ʋₐ, Ru-S); 325.69 (ʋₕ, Ru-S). ESI-MS m/z, [M-Cl⁺] found (calc.): 1434.16 (1434.12). Anal. Calc. for C₅₀H₈₀Cl₃O₁₀Ru₂S₁₀ (MW = 1469.64 g·mol⁻¹): C 40.87; H 5.49; N 4.77; S
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) dithiocarbamato complex of the aromatic N-heterocycles**

The synthesis was carried out in a Schlenk-line apparatus under N$_2$ atmosphere according to literature procedure. Briefly, 2.7 mmol of synthesized carbazole dithiocarbamate Na(CDT) and 0.9 mmol of RuCl$_3$·3H$_2$O 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 [Ru$_2$(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 CH$_2$Cl$_2$ for 8 hours to obtain the isomer β-[Ru$_2$(CDT)$_3$]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 CH$_2$Cl$_2$/n-hexane 40:60 to elute the mononuclear complex. All the complexes have been re-precipitated in CH$_2$Cl$_2$-n-hexane, washed with n-pentane and dried in vacuum over P$_2$O$_5$. Analyses are in agreement with literature data.

Tris(carbazole dithiocarbamate)ruthenium(III), [Ru(CDT)$_3$]

Aspect: dark green solid. Yield: 20%. R.f. (on silica gel, CH$_2$Cl$_2$/hexane 1:1): 0.88. Mp.: 218 °C. $^1$H-NMR (CDCl$_3$, 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$_a$, CSS); 459.76 (ν$_a$, Ru-S); 413.25 (ν$_a$, Ru-S). ESI-MS m/z, [M$^+$] found (calc.): 827.97 (827.94). Anal. Calc. for C$_{39}$H$_{24}$N$_3$RuS$_6$ (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-[Ru$_2$(CDT)$_3$]Cl

Aspect: brown solid. Yield: 22%. R.f. (on silica gel, CH$_2$Cl$_2$/hexane 1:1): 0.60. Mp.: 230 °C. $^1$H-NMR (CDCl$_3$, 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$_a$, CSS); 466.20 (ν$_a$, Ru-S); 415.14 (ν$_a$, Ru-S). ESI-MS m/z, [M$^+$Cl]$^-$ found (calc.): 1490.89 (1490.87). Anal. Calc. for C$_{65}$H$_{40}$ClN$_5$Ru$_2$S$_{10}$ (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 Dulbecco’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. 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 (2·10^4 cells/well), and incubated at 37 °C in a 5% CO_2 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 μM, 5 μM, 2 μM, 1 μM, 0.5 μM and in some cases lower) for 72 hours. Cell viability was evaluated via MTT assay, according to standard procedures.

**IR resuming tables**

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<th>ν(C=C)</th>
<th>ν(N-CSS)</th>
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<th>ν_a(CSS)</th>
<th>ω(C-H)</th>
<th>δ(C-H)</th>
<th>ν_s(CSS)</th>
<th>ν_a(Cu-S)</th>
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**Table SI 2.** Collection of diagnostic IR-vibrations (4000-500 cm⁻¹) of the synthetized dithiocarbamato salts.
Table SI 3. Collection of the fundamental IR-vibrations (4000-200 cm$^{-1}$) of the analyzed Cu(II)-DTC complexes.

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<th>$\nu$($\alpha$(CSS))</th>
<th>$\omega$(C-H)</th>
<th>$\delta$(C-H)</th>
<th>$\nu$($s$(CSS))</th>
<th>$\nu$($\alpha$(Ru-S))</th>
<th>$\nu$($\alpha$(Ru-S))</th>
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<td>446 cm$^{-1}$</td>
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<td>547 cm$^{-1}$</td>
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<td>-</td>
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<td>471 cm$^{-1}$</td>
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Table SI 4. Collection of the main IR-vibrations (4000-200 cm⁻¹) of the analyzed Ru(III)-DTC complexes.

**¹H-NMR resuming tables**

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Table SI 5. Comparison between proton chemical shifts (ppm) of the dithiocarbamato salts and the parent amine (reported in brackets). The H-signal 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-d₆ except for those of L-proline esters, obtained in CD₃OD, with a 300.13 MHz NMR spectrometer.

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<th>H (6)</th>
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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 CDCl$_3$ with a 300.13 MHz spectrometer at 298 K.

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<th>$H_{(4)}$</th>
<th>$H_{(5)}$</th>
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<th>OMe</th>
<th>OtBu</th>
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Table SI 7: List of the proton chemical shifts (ppm) of Ru(III)-DTC derivatives, both mono- and dinuclear, synthetized 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

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<th>band III</th>
<th>band IV</th>
<th>band V</th>
<th>band VI</th>
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<td>453 nm (10760)</td>
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Table SI 8. UV-visible spectral data (800-240 nm) of soluble Cu(II) dithiocarbamato complexes in CH₂Cl₂ at 25 °C; sh= shoulder.

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<th>band V</th>
<th>band VI</th>
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<td>286 nm (26096)</td>
<td>368 nm (10078)</td>
<td>470 nm (2236)</td>
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<td>-a</td>
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<td>460 nm (1693)</td>
<td>575 nm (956)</td>
</tr>
<tr>
<td>β[Ru₂(ProOMeDTC)₅]Cl</td>
<td>248 nm (39500)</td>
<td>262 nm (39371)</td>
<td>288 nm (32752)</td>
<td>323 nm (14706)</td>
<td>453 nm (2533)</td>
<td>-</td>
</tr>
<tr>
<td>[Ru(ProOtBuDTC)₃]</td>
<td>241 nm (41996)</td>
<td>260 nm (35400)</td>
<td>283 nm (23840)</td>
<td>362 nm (9297)</td>
<td>463 nm (2076)</td>
<td>577 nm (1626)</td>
</tr>
<tr>
<td>β[Ru₂(ProOtBuDTC)₅]Cl</td>
<td>249 nm</td>
<td>264 nm</td>
<td>287 nm</td>
<td>322 nm</td>
<td>449 nm</td>
<td>-</td>
</tr>
</tbody>
</table>
Table SI 9. UV-Visible spectral data (800-240 nm) of the synthetized Ru(III) dithiocarbamato complexes in CH₂Cl₂ at 25 °C; sh= shoulder; ≠= the band is not reported since it is placed below the solvent cut-off (240 nm).

**IR spectra**

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

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

Figure SI 11. Medium FT-IR (4000-600 cm$^{-1}$, KBr) spectrum of β-pentakis(pyrrolidine dithiocarbamate)diruthenium(III) chloride, β-[Ru$_2$(PDT)$_5$]Cl.
Figure SI 12. Far FT-IR (600-100 cm$^{-1}$, nujol) spectrum of β-pentakis(pyrrolidine dithiocarbamate)diruthenium(III) chloride, β-[Ru$_2$(PDT)$_5$]Cl.

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

Figure SI 14. Far FT-IR (600-100 cm$^{-1}$, nujol) spectrum of tris(piperidine dithiocarbamate)ruthenium(III), [Ru(PipeDTC)$_3$].
Figure SI 15. Medium FT-IR (4000-600 cm\(^{-1}\), KBr) spectrum of \(\beta\)-pentakis(piperidine dithiocarbamate)diruthenium(III) chloride, \(\beta\)-\([\text{Ru}_2(\text{PipeDTC})_5]\)Cl.

Figure SI 16. Far FT-IR (600-100 cm\(^{-1}\), nujol) spectrum of \(\beta\)-pentakis(piperidine dithiocarbamate)diruthenium(III) chloride, \(\beta\)-\([\text{Ru}_2(\text{PipeDTC})_5]\)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), [Ru(MorphDTC)$_3$].

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

Figure SI 20. Far FT-IR (600-100 cm$^{-1}$, nujol) spectrum of β-pentakis(morpholine dithiocarbamate)diruthenium(III) chloride, β-[Ru$_2$(MorphDTC)$_5$]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-[Ru$_2$(IndolineDTC)$_3$]Cl.
Figure SI 24. Far FT-IR (600-100 cm$^{-1}$, nujol) spectrum of β-pentakis(indoline dithiocarbamate)diruthenium(III) chloride, β-[Ru$_2$(IndolineDTC)$_5$]Cl.

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

Figure SI 26. Far FT-IR (600-100 cm$^{-1}$, nujol) spectrum of tris(l-proline methyl ester dithiocarbamate)ruthenium(III), [Ru(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, β-$\text{[Ru}_2\text{(ProOMeDTC)}_5\text{]}\text{Cl.}$

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

Figure SI 29. Medium FT-IR (4000-600 cm$^{-1}$, KBr) spectrum of tris(L-proline tert-butyl ester dithiocarbamate)ruthenium(III), [Ru(ProOtBuDTC)$_3$].
Figure SI 30. Far FT-IR (600-100 cm$^{-1}$, nujol) spectrum of tris(L-proline tert-butyl ester dithiocarbamate)ruthenium(III), [Ru(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, β-[Ru$_2$(ProOtBuDTC)$_5$]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, β-[Ru$_2$(ProOtBuDTC)$_5$]Cl.
Figure SI 33. Medium FT-IR (4000-600 cm\(^{-1}\), KBr) spectrum of tris(carbazole dithiocarbamate)ruthenium(III), [Ru(CDT)\(_3\)].

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

Figure SI 35. Medium FT-IR (4000-600 cm\(^{-1}\), KBr) spectrum of β-pentakis(carbazole dithiocarbamate)diruthenium(III) chloride, β-[Ru\(_2\)(CDT)\(_5\)]Cl.
Figure SI 36. Far FT-IR (600-1000 cm$^{-1}$, nujol) spectrum of β-pentakis(carbazole dithiocarbamate)diruthenium(III) chloride, β-[Ru$_2$(CDT)$_5$]Cl.

FT-IR spectra of the synthetized Cu(II) dithiocarbamato complexes

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

Figure SI 38. Far FT-IR (600-100 cm$^{-1}$, nujol) spectrum of bis(pyrrolidine dithiocarbamate)copper(II), [Cu(PDT)$_2$].
Figure SI 39. Medium FT-IR (4000-600 cm\(^{-1}\), KBr) spectrum of bis(piperidine dithiocarbamate)copper(II), [Cu(PipeDTC)\(_2\)].

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

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

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

Figure SI 53. Medium FT-IR (4000-600 cm$^{-1}$, KBr) spectrum of bis(pyrrole dithiocarbamate)copper(II), [Cu(PyrroleDTC)$_2$].
Figure SI 54. Far FT-IR (600-100 cm\(^{-1}\), nujol) spectrum of bis(pyrrole dithiocarbamate)copper(II), [Cu(PyrroleDTC)\(_2\)].

\(^1\)H-NMR spectra

\(^1\)H-NMR spectra of the synthetized dithiocarbamato ligands

Figure SI 55. \(^1\)H-NMR (DMSO-\(d_6\), 298 K, 300.13 MHz) spectrum of piperidine dithiocarbamate potassium salt (K PipeDTC).
Figure SI 56. $^1$H-NMR (DMSO-d$_6$, 298 K, 300.13 MHz) spectrum of morpholine dithiocarbamate potassium salt (K MorphDTC).

Figure SI 57. $^1$H-NMR (DMSO-d$_6$, 298 K, 300.13 MHz) spectrum of indoline dithiocarbamate potassium salt (K IndolineDTC).
Figure SI 58. $^1$H-NMR (CD$_3$OD, 298 K, 300.13 MHz) spectrum of L-proline methyl ester dithiocarbamate sodium salt (Na ProOMeDTC).

Figure SI 59. $^1$H-NMR (CD$_3$OD, 298 K, 300.13 MHz) spectrum of L-proline tert-butyl ester dithiocarbamate sodium salt (Na ProO$t$BuDTC).
Figure SI 60. $^1$H-NMR (DMSO-d$_6$, 298 K, 300.13 MHz) spectrum of carbazole dithiocarbamate sodium salt (Na CDT).

Figure SI 61.$^1$H-NMR (DMSO-d$_6$, 298 K, 300.13 MHz) spectrum of indole dithiocarbamate sodium salt (Na IndDTC).
**Figure SI 62.** $^1$H-NMR (DMSO-d$_6$, 298 K, 300.13 MHz) spectrum of pyrrole dithiocarbamate sodium salt (Na PyrDTC).

$^1$H-NMR spectra of the synthetized Ru(III) dithiocarbamato complexes

**Figure SI 63.** $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of tris(pyrrolidine dithiocarbamate)ruthenium(III), [Ru(PDT)$_3$].
Figure SI 64. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of β-pentakis(pyrrolidine dithiocarbamate)diruthenium(III) chloride, $\beta$-[Ru$_2$(PDT)$_5$]Cl.

Figure SI 65. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of tris(piperidine dithiocarbamate)ruthenium(III), [Ru(PipeDTC)$_3$].
Figure SI 66. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of $\beta$-pentakis(piperidine dithiocarbamate)diruthenium(III) chloride, $\beta$-$[\text{Ru}_2(\text{PipeDTC})_5]\text{Cl}$.

Figure SI 67. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of tris(morpholine dithiocarbamate)ruthenium(III), $[\text{Ru}\{\text{MorphDTC}\}_3]$.
Figure SI 68. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of β-pentakis(morpholine dithiocarbamate)diruthenium(III) chloride, β-[Ru$_2$(MorphDTC)$_5$]Cl.

Figure SI 69. $^1$H-NMR (CD$_2$Cl$_2$, 298 K, 300.13 MHz) spectrum of tris(indoline dithiocarbamate)ruthenium(III), [Ru(IndolineDTC)$_3$].
Figure SI 70. $^1$H-NMR (CD$_2$Cl$_2$, 298 K, 300.13 MHz) spectrum of $\beta$-pentakis(indoline dithiocarbamate)diruthenium(III) chloride, $\beta$-[Ru$_2$(IndolineDTC)$_5$]Cl.

Figure SI 71. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of tris(1-proline methyl ester dithiocarbamate)ruthenium(III), [Ru(ProOMeDTC)$_3$].
Figure SI 72. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of β-pentakis(L-proline methyl ester dithiocarbamate)diruthenium(III) chloride, β-[Ru$_2$(ProOMeDTC)$_5$]Cl.

Figure SI 73. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of tris(L-proline tert-butyl ester dithiocarbamate)ruthenium(III), [Ru(ProOtBuDTC)$_3$].
Figure SI 74. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of β-pentakis(L-proline tert-butyl ester dithiocarbamate)diruthenium(III) chloride, $\beta$-[Ru$_2$(ProO$_6$BuDTC)$_5$]Cl.

Figure SI 75. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of tris(carbazole dithiocarbamate)ruthenium(III), [Ru(CDT)$_3$].
Figure SI 76. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of β-pentakis(carbazole dithiocarbamate)diruthenium(III) chloride, β-[Ru$_2$(CDT)$_3$]Cl.

$^1$H-NMR spectra of the synthetized Cu(II) dithiocarbamato complexes

Figure SI 77. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of bis(pyrrolidine dithiocarbamate)copper (II), [Cu(PDT)$_2$].
Figure SI 78. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of bis(piperidine dithiocarbamate)copper(II), [Cu(PipeDTC)$_2$].

Figure SI 79. $^1$H-NMR (CDCl$_3$, 298 K, 300.13 MHz) spectrum of bis(L-proline methyl ester dithiocarbamate)copper(II), [Cu(ProOMeDTC)$_2$].
The UV-Visible spectra were obtained in CH$_2$Cl$_2$ at 25 °C.
\[
\varepsilon(M \cdot cm^{-1})
\]

\[
\lambda_{\text{nm}}
\]

\[
[Ru(IndolineDTC)_3]^{2+}
\]

\[
[Ru(ProOMeDTC)_3]^{2+}
\]

\[
[Ru(ProOBuDTC)_3]^{2+}
\]
**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.
**[Cu(PDT)$_2$] in 10% DMEM**

- 0 min
- 1 h
- 2 h
- 4 h
- 6 h
- 12 h
- 24 h
- 36 h
- 48 h
- 72 h

**[Cu(PipeDTC)$_2$] in 10% DMEM**

- 0 min
- 1 h
- 2 h
- 4 h
- 6 h
- 12 h
- 24 h
- 36 h
- 48 h
- 72 h
[Cu(MorphDTC)]²⁻ in 10% DMEM

- 0 min
- 1 h
- 2 h
- 4 h
- 6 h
- 12 h
- 24 h
- 36 h
- 48 h
- 72 h

[Abs]

\[ \text{Abs} = \frac{\text{Intensity}}{\text{Reference Intensity}} \]

\[ \lambda \text{ (nm)} \]

[0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0]

[Cu(ProOMeDTC)]²⁻ in 10% DMEM

- 0 min
- 1 h
- 2 h
- 4 h
- 6 h
- 12 h
- 24 h
- 36 h
- 48 h
- 72 h

[0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0]

[Cu(ProOButDCT)]²⁻ in 10% DMEM

- 0 min
- 1 h
- 2 h
- 4 h
- 6 h
- 12 h
- 24 h
- 36 h
- 48 h
- 72 h

[0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0]
\[ \text{[Cu(PyrmDTC)] in 10\% DMEM} \]

\[ \text{[\(\beta\)-Ru\(_2\)(PDT)]Cl in 10\% DMEM} \]

\[ \text{[\(\beta\)-Ru\(_3\)(PipeDTC)]Cl in 10\% DMEM} \]
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


