Electronic Supplementary Material (ESI) for CrystEngComm.

Structural study of Mono- Di- and Tetranuclear complexes of the $\{Re(CO)_3\}^+$ fragment with thiosemicarbazones/thiosemicarbazonates ligands containing benzothiazole or benzoxazole groups

Arantxa Pino-Cuevas,[†] Ana Graña,[‡] Ulrich Abram,[§] Rosa Carballo,[†] Ezequiel M. Vázquez-López[*†]*

† Departamento de Química Inorgánica, Facultade de Química, Instituto de Investigación Sanitaria Galicia Sur, Campus Universitario, E-36310 Vigo, Galicia, Spain

‡ Departamento de Química Física, Facultade de Química, Universidade de Vigo, Campus Universitario, E-36310 Vigo, Galicia, Spain

§ Institut für Chemie und Biochemie, Freie Universität Berlin, Baerckstr. 34-36, 14195-Berlin, Germany

Supplementary material

Table of contents

Experimental

Materials and physical measurements

The starting materials and solvents were obtained commercially and were used as supplied. The adducts $[ReX(CO)_3(CH_3CN)_2]$ (X = Cl, Br) were synthesized by following the methods of Farona and Kraus [1] from the corresponding [ReX(CO)5] (X = Cl, Br) [2]. Elemental analyses (C, H, N, S) were carried out on a Fisons EA-1108 microanalyser. IR spectra were recorded from KBr discs (4000–400 cm^{-1}) on a Jasco FT/IR-6100 spectrophotometer. ^{1}H and ^{13}C-NMR spectra were obtained on a Bruker AMX 400 spectrometer. Mass spectra (ESI^{+}) were recorded on a Hewlett-Packard 5989A spectrometer.

Crystallography

The crystallographic data were collected with the Bruker CCD Smart 6000 diffractometer with a Incoatec IμS microsource using a Incoatec Quazar MX multilayer optics-monochromated Cu-Kα radiation, STOE IPDS 2T with graphite monochormated Mo-Kα radiation or a Bruker D8 Venture Photon 100 CMOS with a Incoatec high brillance IμS microsource with Incoatec HeliosTM multilayer optics monochromated Mo- Mo-Kα radiation. Data were corrected for Lorentz, polarization, and absorption effects [3]. The structures were solved by direct methods by using the program SHELXT [4]. All non-hydrogen atoms were refined on F^2 with anisotropic thermal parameters by using SHELXL [5]. Hydrogen atoms were inserted at calculated positions and refined as riding atoms. The graphics were produced with PLATON [6] and MERCURY [7]. The crystallographic data collection and refinement parameters are listed in Tables S1-S3.

The crystal of H_2L^2 suffered radiation damage and the last data set showed unreasonably high R_{int} values (>20%). Consequently, reflections included in that data set were omitted in the data reduction process.

On the other hand, the data for 3c showed some sings of non-merohedral twinning were observed (mainly, high Rint value and Fo is much greater then Fc for all disagreeable reflections). We have unsuccessfully tried to find an alternative domain. In adittion, the crystals contains a disorder solvent molecule (acetone) in the asymmentric unit (with Z' > 1) whose contribution to the reflections was corrected with SQUEEZE [6]. Reflections with values of $\sqrt{w(F_o^2 - F_c^2)^2} \Big/ < w(F_o^2 - F_c^2)^2 >$ ($< w(F_o^2 - F_c^2)^2>$ refers to the average over all reflections) greater than 4.5 were omitted in the refinement. Although the values of the discrepancy factors obtained are high (R1 = 10.87%), the coinciding structure with 2c, as well as with the spectroscopic data and theoretical calculations, does not suggest the presence of relevant errors in the model.

Theoretical Calculation Methods

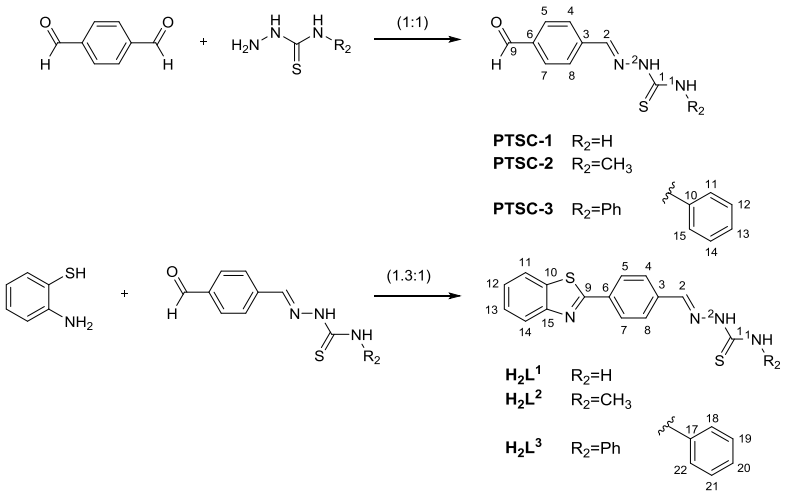
All the structure and wavefunction calculations were performed by using B3LYP method in Gaussian097 [8] with LANLD2Z basis set. The wavefunctions were obtained for the optimized geometries of two symmetries of the molecules **3c** and **6c**. All the optimized structures were confirmed as minima by calculating vibrational frequencies.

We performed QTAIM topological electron density analysis on these wavefunctions by using the AIMAll package [9] and so we obtain bond and atomic properties for the hydrogen bonds

and the atoms involved. This theory is a common tool that allows performing topological analyses of the electron density function, $\rho_{(r)}$ and can be used to identify and to describe the nature of bonds as well as all kinds of intra and intermolecular interactions. The QTAIM formalism considers that two atoms are bonded when a bond path between them could be found. This path should exhibit a so called bond critical point (BCP), a saddle point with two negative eigenvalues of the Hessian matrix of $\rho_{(r)}$. In this study we relate the strength of hydrogen bonds with the value of the electron density at the bond critical points, $\rho_{(rc)}$ and the atomic charge of the atoms

The value of the electron density at the bond critical points, $\rho_{(rc)}$ and the IQA analyses were employed as indicators for hydrogen bond strength. IQA analyses allows to obtain interaction energies (E_{int}) as well as its components, the electrostatic term (V_c) and the exchange-correlation term (V_{xc}). V_c represents the electrostatic, classic term related to the ionic contribution to bonding whereas V_{xc} represents the non-classical component related to pairs of electrons delocalized or shared between atoms.

Synthesis of the ligands H_2L^1-H_2L^3



Scheme S1

Precursors **PTSC-1**, **PTSC-2**, and **PTSC-3** (see Scheme S1) were synthetised by reported methods [10-12]. In short, a solution of the corresponding thiosemicarbazide (TSI) (see table below) was slowly added at 50°C to a solution of terephthalaldehyde (500 mg, 3.73 mmol) in 100 mL water. Then the mixture was stirred at 50°C for 30 min. Once cooled to room temperature, the yellow solid was filtered off and dried under vacuum over $CaCl_2$/KOH.

Amount used in the synthesis of the precursors .

Precursor	R^2	TSI mg (mmol)	Solvent (mL)
PTSC-1	H	342 (3.75)	H_2O (50)
PTSC-2	Me	392 (3.73)	H_2O (50)
PTSC-3	Ph	622 (3.72)	H_2O (70) + EtOH (20)

PTSC-1: Yield: 600 mg (59.9%). M.p.: 216-218°C. IR (KBr): ν(cm^{-1}) = 3329w, 3263w, 3152w (NH), 1686vs (C=O), 1593s, 1533s (C=N), 830m (C-S). ^{1}H-NMR (400 MHz, DMSO): δ (ppm) = 11.61 (s, 1H, NH-2), 10.02 (s, 1H, H9), 8.33 (s, 1H, NH-1), 8.16 (s, 1H, R^2=H), 8.10 (s, 1H, H2), 8.02 (d, 2H, H5 and H7), 7.93 (d, 2H, H4 and H8).

PTSC-2: Yield: 748 mg (90.7%). M.p.: 214-216°C. IR (KBr): ν(cm^{-1}) = 3361w, 3151w (NH), 1691vs (C=O), 1590s, 1523s (C=N), 832m (C-S). ^{1}H-NMR (400 MHz, DMSO): δ (ppm) = 11.72 (s, 1H, NH-2), 10.03 (s, 1H, H9), 8.69 (s, 1H, NH-1), 8.11 (s, 1H, H2), 8.03 (d, 2H, H5 and H7), 7.94 (d, 2H, H4 and H8), 3.03 (s, 3H, R2=CH_3).

PTSC-3: Yield: 909 mg (86.2%). M.p.: 206-208°C. IR (KBr): ν (cm^{-1}) = 3303w, 3137m (NH), 1697vs (C=O), 1595s, 1533s (C=N), 819m (C-S). ^{1}H-NMR (400 MHz, DMSO): δ (ppm)= 12.01 (s, 1H, NH-2), 10.26 (s, 1H, NH-1), 10.05 (s, 1H, H9), 8.23 (s, 1H, H2), 8.15 (d, 2H, H5 and H7), 7.95 (d, 2H, H4 and H8), 7.55 (d, 2H, H11 and H15), 7.40 (t, 2H, H12 and H14), 7.24 (t, 1H, H13).

Synthesis of ligands (H_2L^1, H_2L^2 and H_2L^3). The mixture of the corresponding precursor and 2-aminothiophenol in dry ethanol with some drops of glacial acetic acid (see table below) was heated at reflux for 8 h. The reaction mixture was allowed to cool down to r.t. and the resulting yellow solids were filtered off and dried under vacuum over $CaCl_2$/KOH. Single crystals of H_2L^2 and H_2L^3 were obtained from slow evaporation of the mother liquors.

Amount used in the synthesis of the ligands.

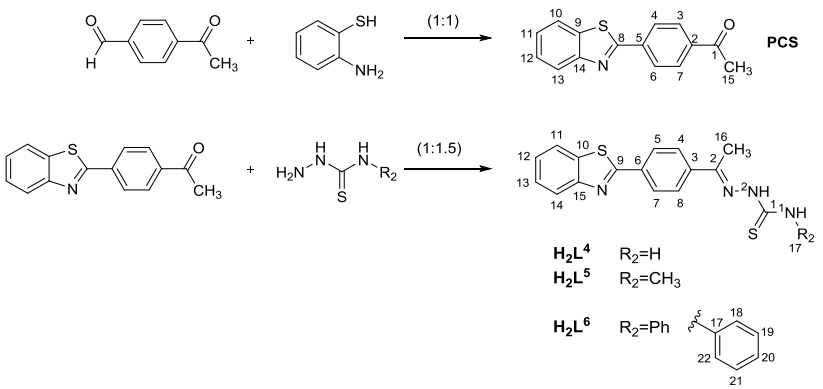
Ligand	R2	PTSC mg (mmol)	2-aminothiophenol mL (mmol)	EtOH (mL)
H_2L^1	H	600 (2.90)	0.40 (3.76)	50
H_2L^2	Me	400 (2.83)	0.25 (2.35)	40
H_2L^3	Ph	800 (1.81)	0.40 (3.67)	90

H_2L^1: Yield: 565 mg (62.8%). M.p.: 240°C (dec.). $C_{15}H_{12}N_4S_2$ (312.05): found C, 56.51; H, 3.67; N, 18.74; S, 20.87; calcd. C, 57.67; H, 3.87; N, 17.93; S, 20.53. MS-ESI: m/z (%) = 313.06 (100) $[M]^+$. IR (KBr): ν (cm^{-1}) = 3428m, 3249m, 3149m (NH), 1590s, 1285m (C=N), 823s, 755s (C-S). UV-Vis solid (λ_{max}, nm): 257, 298 and 390. ^{1}H-NMR (400 MHz, DMSO): δ (ppm) = 11.57 (s, 1H, NH-2), 8.30 (s, 1H, NH-1), 8.18 (d, 1H, J = 7.7 Hz, H11), 8.10 (m, 4H, NH-1, H2, H4 and H8), 8.09 (d, 1H, J=8.7 Hz, H14), 8.06 (d, 1H, J = 8.4 Hz, H5 and H7), 7.58 (t, 1H, J = 7.5 Hz, H12), 7.49 (t, 1H, J=7.5 Hz, H13). ^{13}C-NMR (100 MHz, DMSO): δ (ppm) = 178.7 (C1), 167.1 (C9), 154.1 (C10), 141.5 (C2), 137.5 (C6), 135.0 (C3), 134.0 (C15), 128.6 (C4 and C8), 127.9 (C5 and C7), 127.3 (C12), 126.2 (C13), 123.4 (C14), 122.9 (C11).

H_2L^2: Yield: 432 mg (73.2%). M.p.: 274°C (dec.). $C_{16}H_{14}N_4S_2$ (326.07): found C, 58.28; H, 4.61; N, 16.76; S, 19.28; calcd. C, 58.87; H, 4.32; N, 17.16; S, 19.65. MS-ESI: m/z (%) =327.07 (100) $[M]^+$. IR (KBr): ν (cm^{-1}) = 3262m, 3094m (NH), 1554s, 1252m (C=N), 821m, 754s (C-S). UV-Vis solid (λ_{max}, nm): 295, 358 and 384. ^{1}H-NMR (400 MHz, DMSO): δ (ppm) = 11.67 (s, 1H, NH-2), 8.67 (s, 1H, NH-1), 8.18 (d, 1H, J=7.9 Hz, H11), 8.14 (m, 3H, H2, H4 and H8), 8.10 (d, 1H, J = 8.1 Hz, H14), 8.01 (d, 2H, J = 8.3 Hz, H5 and H7), 7.58 (t, 1H, J = 7.5 Hz, H12), 7.50 (t, 1H, J = 7.5 Hz, H13), 3.05 (s, 3H, H16). ^{13}C-NMR (100 MHz, DMSO): δ (ppm) = 178.3 (C1), 167.1 (C9), 154.1 (C10), 140.9 (C2), 137.6 (C6), 135.0 (C3), 133.9 (C15), 128.4 (C4 and C8), 127.9 (C5 and C7), 127.3 (C12), 126.2 (C13), 123.4 (C14), 122.9 (C11), 31.4 (C17).

H_2L^3: Yield: 825 mg (75.2%). M.p.: 251°C (dec.). $C_{21}H_{16}N_4S_2$ (388.08): found C, 64.23; H, 4.27; N, 14.51; S, 16.27; calcd. C, 64.92; H, 4.15; N, 14.42; S, 16.51. MS-ESI: m/z (%) = 389.09 (100) $[M]^+$. IR (KBr): ν (cm^{-1}) = 3131m, 2983m (NH), 1546vs, 1265m (C=N), 836w, 758m (C-S).UV-Vis solid (λmax, nm): 252, 302 and 396. ^{1}H-NMR (400 MHz, DMSO): δ (ppm)= 11.96 (s, 1H, NH-2), 10.23 (s, 1H, NH-1), 8.23 (s, 1H, H2), 8.16 (m, 6H, H4, H5, H7, H8, H11 and H14), 7.58 (m, 3H, H18, H19 and H20), 7.49 (m, 1H, H12), 7.39 (t, 2H, J = 7.8 Hz, H17 and H21), 7.23 (t, 1H, J = 7.4 Hz, H13). ^{13}C-NMR (100 MHz, DMSO): δ (ppm) = 176.7 (C1), 167.1 (C9), 154.1 (C10), 142.1 (C2), 139.5 (C17), 137.3 (C6), 135.0 (C3), 134.2 (C15), 128.9 (C4 and C8), 128.6 (C19 and C21), 127.9 (C5 and C7), 127.3 (C12), 126.5 (C18 and C22), 126.2 (C20), 125.9 (C13), 123.5 (C14), 122.9 (C11).

Synthesis of the ligands H_2L^4-H_2L^6



Scheme S2

Synthesis of precursor **PCS**: A mixture of 500 mg (3.37 mmol) of 4-acetylbenzaldehyde and 493 µL (4.61 mmol) of 2-aminothiophenol in dry ethanol (20 mL) was refluxed for 12 h under argon atmosphere. The yellow solid formed was filtered off and vacuum dried over $CaCl_2$/KOH.

Yield: 704 mg (82.4%). M.p.: 190-192°C. IR (KBr): ν (cm^{-1}) = 1680vs (C=O), 1269s (C=N), 767s (C-S). UV-Vis (λmax, nm): 212, 254, 298 and 339. ^{1}H-NMR (400 MHz, DMSO): δ (ppm) = 8.24 (d, 2H, J = 8.0 Hz, H3 and H7), 8.20 (d, 1H, J = 8.0 Hz, H10), 8.13 (m, 3H, H4, H6 and H13), 7.59 (t, 1H, J = 7.3 Hz, H11), 7.51 (t, 1H, J = 7.3 Hz, H12), 2.65 (s, 3H, H15).

Synthesis of ligands (H_2L^4, H_2L^5 and H_2L^6): To the mixture of the precursor PCS and the corresponding thiosemicarbazide in dry ethanol was added a few drops of acetic acid (see table bellow). Then the mixture was heated at reflux for 7 h. The resulting yellow solids were filtered off and dried under vacuum over $CaCl_2$/KOH. Single crystals of H_2L^4 and H_2L^5 were obtained after slow evaporation of the mother liquors.

Amount used in the synthesis of the ligands.

Ligand	R2	PCS mg (mmol)	TSI mg (mmol)	EtOH (mL)
H_2L^4	H	200 (0.79)	108 (1.19)	15
H_2L^5	Me	400 (1.58)	249 (2.37)	40
H_2L^6	Ph	200 (0.79)	198 (1.19)	15

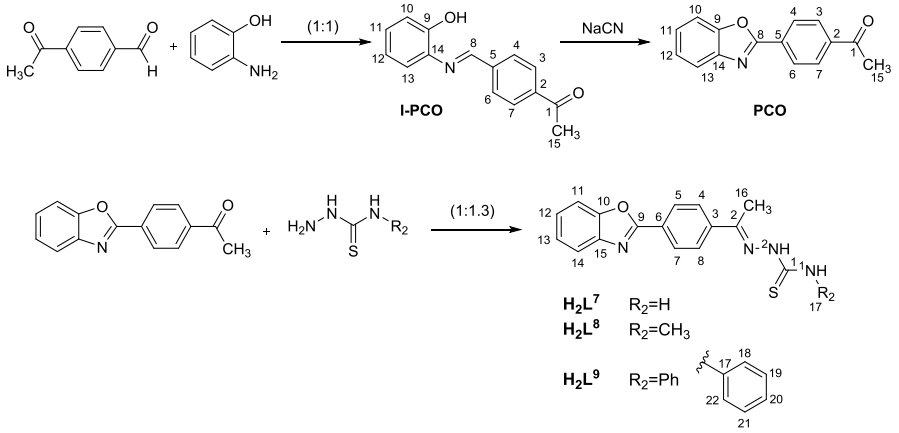
H_2L^4: Yield: 166 mg (64.4%). M.p.: 248°C (dec.). $C_{16}H_{14}N_4S_2$ (326.07): found C, 58.08; H, 4.42; N, 15.56; S, 18.55; calcd. C, 58.87; H, 4.32; N, 17.16; S, 19.65. MS-ESI: m/z (%) = 327.08 (100) $[M]^+$. IR (KBr): ν (cm^{-1}) = 3395m, 3201m, 3146m (NH), 1582s, 1279m (C=N), 835s, 760s (C-S). UV-Vis solid (λ_{max}, nm): 251, 297 and 393. ^{1}H-NMR (400 MHz, DMSO): δ (ppm) = 10.34 (s, 1H, NH-2), 8.39 (s, 1H, NH-1), 8.30 (m, 3H, H4, H8 y H11), 8.22 (m, 4H, NH-1, H5, H7 and H14), 7.56 (t, J = 7.6 Hz, 1H, H12), 7.48 (t, 1H, J = 7.6 Hz, H13), 2.35 (s, 3H, H16). ^{13}C-NMR (100 MHz, DMSO): δ (ppm) = 179.0 (C1), 166.6 (C9), 153.5 (C10), 146.5 (C2), 140.2 (C6), 134.4 (C3), 133.0 (C15), 127.4 (C4 and C8), 126.9 (C5 and C7), 126.7 (C12), 125.6 (C13), 122.9 (C14), 122.3 (C11), 13.8 (C16).

H_2L^5: Yield: 431 mg (80.1%). M.p.: 259°C (dec.). $C_{17}H_{16}N_4S_2$ (340.08): found C, 60.10; H, 4.80; N, 16.37; S, 18.71; calcd. C, 59.97; H, 4.74; N, 16.46; S, 18.84. MS-ESI: m/z (%) = 341.09 (100) $[M]^+$. IR (KBr): ν (cm^{-1}) = 3300m, 3184m (NH), 1540vs, 1258s (C=N), 834m, 751s (C-S).UV-Vis solid (λ_{max}, nm): 249, 300 and 403. ^{1}H-NMR (400 MHz, DMSO): δ (ppm)= 10.39 (s, 1H, NH-2), 8.59 (d, 1H, J= 4.5 Hz, NH-1), 8.11 (d, 3H, J = 8.9 Hz, H4, H8 and H11), 8.06 (m, 3H, H5, H7 and H14), 7.54 (t, 1H, J = 7.4 Hz, H12), 7.45 (t, 1H, J = 7.4 Hz, H13), 3.10 (d, 3H, J= 4.5 Hz, H17), 2.34 (s, 3H, H16). ^{13}C-NMR (100 MHz, DMSO): δ (ppm) = 179.2 (C1), 167.1 (C9), 154.1 (C10), 146.7 (C2), 140.7 (C6), 135.0 (C3), 133.5 (C15), 127.8 (C4 and C8), 127.4 (C5 and C7), 127.2 (C12), 126.1 (C13), 123.4 (C14), 122.8 (C11), 31.7 (C17), 14.4 (C16).

H_2L^6: Yield: 282 mg (88.7%). M.p.: 262°C (dec.). $C_{22}H_{18}N_4S_2$ (402.09): found C, 65.24; H, 4.66; N, 13.78; S, 15.76. calcd. C, 65.64; H, 4.51; N, 13.92; S, 15.93. MS-ESI: m/z (%) = 403.11 (22.2) $[M]^+$. IR (KBr): ν (cm^{-1}) = 3430m, 3304m (NH), 1520vs, 1267m (C=N), 827m, 764s (C-S). UV-Vis solid (λ_{max}, nm): 255, 294 and 390. ^{1}H-NMR (400 MHz, DMSO): δ (ppm)= 10.71 (s, 1H, NH-2), 10.14 (s, 1H, NH-1), 8.22 (d, 2H, J = 8.5 Hz, H4 and H8), 8.17 (d, 1H, J = 7.9 Hz, H11), 8.10 (m, 3H, H5, H7 and H14), 7.58 (m, 3H, H20, H18 and H22), 7.48 (m, 1H, H12), 7.39 (t, 2H, J = 7.4 Hz, H19 and H21), 7.23 (t, 1H, J = 7.9 Hz, H13), 2.44 (s, 3H, H16). ^{13}C-NMR (100 MHz, DMSO): δ (ppm) = 177.6 (C1), 167.1 (C9), 154.1 (C10), 148.1 (C2), 140.6 (C6), 139.6 (C17), 134.9 (C3),

133.7 (C15), 128.6 (C4 and C8), 128.2 (C19 and C21), 127.4 (C5 and C7), 127.3 (C12), 126.5 (C18 and C22), 126.2 (C20), 126.0 (C13), 123.4 (C14), 122.9 (C11), 14.7 (C16).

Synthesis of the ligands H_2L^7-H_2L^9



Scheme S3

The precursor PCO was synthesised by a modification of the method reported by Zahran et al. (Scheme S3) [13] in that a solution of 2-aminophenol (136 mg, 1.25 mmol) in dry ethanol (5 mL) was added dropwise to a solution of 4-acetylbenzaldehyde (185 mg, 1.25 mmol) in dimethylsulfoxide (0.3 mL). The yellow solution was heated at reflux for 9 h. The solution was allowed to cool down at r.t. and the resulting yellow solid (intermediate, I-PCO) was filtered off and dried under vacuum over $CaCl_2$/KOH. Then, a mixture of I-PCO (215 mg, 0.90 mmol) and sodium cyanide (45 mg, 0.90 mmol) in dimethylformamide (2 mL) was stirred for 24 h open to the air. To the reaction mixture was added water (10 mL) and the resulting yellow solid (PCO) was isolated and dried under vacuum over $CaCl_2$/KOH.

I-PCO: Yield: 215 mg (72.3%). M.p.: 136-138°C. IR (KBr): ν (cm^{-1}) = 3244m (OH), 1666vs (C=O), 1626m, 1258m (C=N), 1032m (C-O). ^{1}H-NMR (400 MHz, DMSO): δ (ppm)= 9.14 (s, 1H, OH), 8.81 (s, 1H, H8), 8.16 (d, 2H, J = 8.4 Hz, H3 and H7), 8.06 (d, 2H, J = 8.4 Hz, H4 and H6), 7.25 (dd, 1H, J = 8.0 and 1.3 Hz, H11), 7.10 (ddd, 1H, J = 8.0, 7.5 and 1.3 Hz, H13), 6.90 (dd, 1H, J = 8.0 and 1.3 Hz, H12), 6.84 (td, 1H, J = 7.5, 1.3 Hz, H10), 2.63 (s, 3H, H15).

PCO: Yield: 112 mg (52.5%). M.p.: 159-163°C. IR (KBr): ν (cm^{-1}) = 1678vs (C=O), 1265s (C=N), 1054s (C-O). ^{1}H-NMR (400 MHz, DMSO): δ (ppm) = 8.16 (d, 2H, J = 8.3 Hz, H3 and H7), 7.99 (d, 2H, J = 8.3 Hz, H4 and H6), 7.68 (m, 2H, H10 and H13), 7.35 (m, 2H, H11 and H12), 2.49 (s, 3H, H15).

Synthesis of the ligands (H_2L^7, H_2L^8 and H_2L^9): A solution of corresponding thiosemicarbazide in water was added dropwise to a solution of PCO in methanol with some drops of sulfuric acid

(see table bellow). The mixture was heated at reflux for 5 h. The resulting pale yellow solids were filtered off and dried under vacuum over CaCl2/KOH. Single crystals of **H_2L^7** were obtained from the dimethylsulfoxide solution.

Amount used in the synthesis of the ligands.

Ligand	R2	PCO mg (mmol)	MeOH (mL)	TSI mg (mmol)	Solvent (mL)
H_2L^7	H	100 (0.42)	10	50.0 (0.55)	H_2O (10)
H_2L^8	Me	100 (0.42)	10	57.7 (0.55)	H_2O (10)
H_2L^9	Ph	100 (0.42)	10	103 (0.55)	H_2O (10) + MeOH (5)

H_2L^7: Yield: 106 mg (80.8%). M.p.: 242°C (dec.). $C_{16}H_{14}N_4OS$ (310.09): found C, 61.63; H, 4.95; N, 17.78; S, 9.97; calcd. C, 61.92; H, 4.55; N, 18.06; S, 10.31. MS-ESI: m/z (%) = 311.10 (100) $[M]^+$. IR (KBr): ν (cm^{-1}) = 3408m, 3274m, 3199w (NH), 1591vs, 1490s (C=N), 1090m (C-O), 844m, 736m (C-S). UV-Vis solid (λ_{max}, nm): 301 and 385. ^{1}H-NMR (400 MHz, DMSO): δ (ppm)= 10.38 (s, 1H, NH-2), 8.37 (s, 1H, NH-1), 8.20 (m, 4H, H4, H5, H7 and H8), 8.09 (s, 1H, NH-1), 7.81 (dd, 2H, J = 8.1 and 6.4 Hz, H11 and H14), 7.43 (m, 2H, H12 and H13), 2.34 (s, 3H, H16). ^{13}C-NMR (100 MHz, DMSO): δ (ppm) = 179.6 (C1), 162.4 (C9), 150.6 (C10), 146.8 (C2), 142.0 (C6), 141.3 (C3), 127.8 (C4 and C8), 127.5 (C5 and C7), 127.0 (C15), 126.2 (C12), 125.5 (C13), 120.4 (C14), 111.5 (C11), 14.3 (C16).

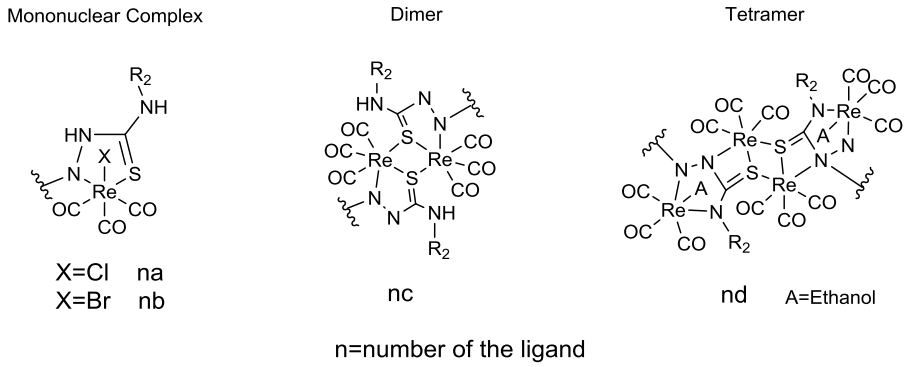
H_2L^8: Yield: 126 mg (91.9%). M.p.: 248°C (dec.). $C_{17}H_{16}N_4OS$ (324.11): found C, 62.79; H, 4.49; N, 15.38; S, 7.98; calcd. C, 62.94; H, 4.97; N, 17.27; S, 9.88. MS-ESI: m/z (%) = 325.11 (100) $[M]^+$. IR (KBr): ν (cm^{-1}) = 3376m, 3187w (NH), 1544vs, 1239s (C=N), 1115m (C-O), 840m, 764m (C-S). UV-Vis solid (λ_{max}, nm): 296 and 391. ^{1}H-NMR (400 MHz, DMSO): δ (ppm)= 10.14 (s, 1H, NH-2), 8.61 (s, 1H, NH-1), 8.22 (m, 4H, H4, H5, H7 and H8), 7.84 (m, 2H, H11 and H14), 7.46 (m, 2H, H12 and H13), 3.08 (d, 3H, J = 4.5 Hz, H17), 2.37 (s, 3H, H16). ^{13}C-NMR (100 MHz, DMSO): δ (ppm) = 179.2 (C1), 162.4 (C9), 150.8 (C10), 146.6 (C2), 142.0 (C6), 141.3 (C3), 127.8 (C4 and C8), 127.5 (C5 and C7), 127.0 (C15), 126.2 (C12), 125.5 (C13), 120.4 (C14), 111.5 (C11), 31.7 (C17), 14.4 (C16).

H_2L^9: Yield: 146 mg (89.4%). M.p.: 260°C (dec.). $C_{22}H_{18}N_4OS$ (386.11): found C, 68.52; H, 4.30; N, 13.63; S, 7.52; calcd. C, 68.37; H, 4.70; N, 14.51; S, 8.28. MS-ESI: m/z (%) = 387.13 (35.3) $[M]^+$. IR (KBr): ν (cm^{-1}) = 3300m, 3208w (NH), 1524vs, 1292w (C=N), 1189m (C-O), 847m, 748s (C-S). UV-Vis solid (λ_{max}, nm): 290 and 397. ^{1}H-NMR (400 MHz, DMSO): δ (ppm)= 10.74 (s, 1H, NH-2), 10.17 (s, 1H, NH-1), 8.28 (d, 2H, J = 8.6 Hz, H4 and H8), 8.21 (d, 2H, J = 8.6 Hz, H5 and H7), 7.83 (m, 3H, H11, H14 and H20), 7.56 (d, 2H, J = 7.7 Hz, H18 and H22), 7.42 (m, 3H, H12, H19 and H21), 7.24 (t, J = 7.4 Hz, 1H, H13), 2.44 (s, 3H, H16). ^{13}C-NMR (100 MHz, DMSO): δ (ppm) = 177.7 (C1), 162.4 (C9), 150.8 (C10), 148.0 (C2), 142.0 (C6), 141.1 (C3), 139.7 (C17), 128.6 (C4

and C8), 128.2 (C19 and C21), 127.5 (C5 and C7), 127.2 (C15), 126.6 (C18 and C22), 126.2 (C12), 126.0 (C20), 125.5 (C13), 120.4 (C14), 111.5 (C11), 14.8 (C16).

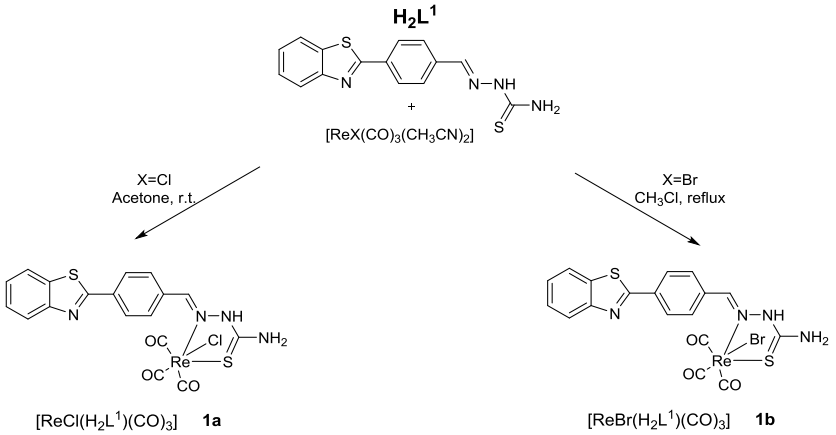
Synthesis of the complexes

The synthesis of the complexes with bidentate thiosemicarbazone ligands were performed using in different synthetic strategies where we could obtain different products like mononuclear species, dinuclear (dimers) or rarely tetranuclear. In the case of dimers the ligands are monodeprotonated while in the case of the tetramer, the ligand is bideprotonated. Moreover the complexes are poorly soluble in conventional solvents (chloroform, acetone…) and they are only soluble in dimethylsulfoxide. However in this solvent the ligands are labilizated, for this reason we didn´t do its characterization by NMR. A general scheme of these structures and their label is shown in Scheme S4.



Scheme S4. The complexes with bidentate thiosemicarbazone obtained in this work.

Complexes of H_2L^1



Scheme S5. Synthesis of the complexes with H_2L^1.

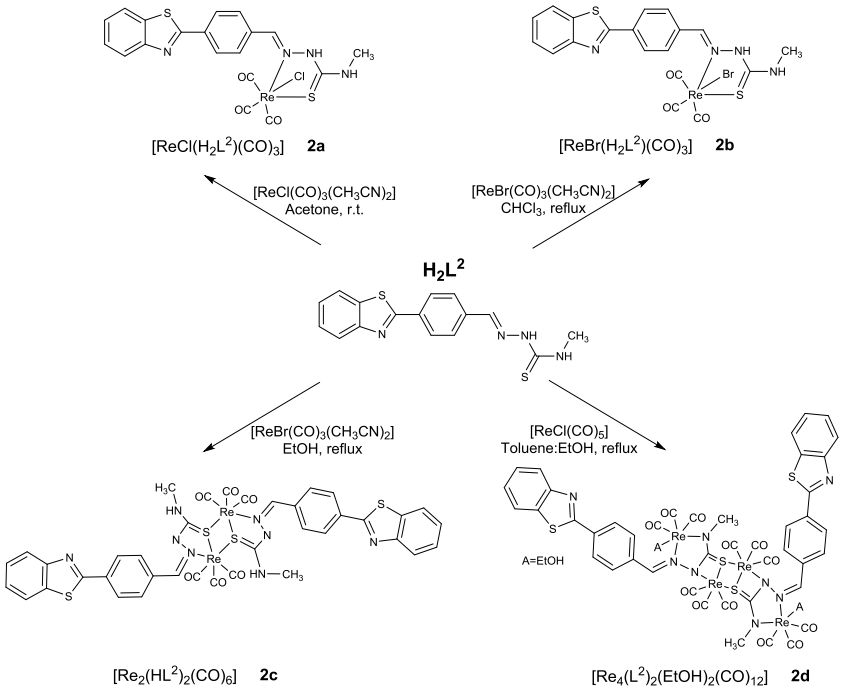
[$ReCl(H_2L^1)(CO)_3$] (**1a**): A solution of [$ReCl(CO)_3(CH_3CN)_2$] (102 mg, 0.26 mmol) in dry acetone (10 mL) was added dropwise to the ligand (82 mg, 0.26 mmol) in 20 mL of acetone and the resulting yellow solution was stirred for 48 h. Then the solvent was evaporated under reduced pressure and the orange solid was vacuum dried over $CaCl_2$/KOH.

Yield: 60 mg (37.1%). M.p.: 225°C (dec.). $C_{18}H_{12}ClO_3N_4S_2Re$ (618.10): found C, 35.74; H, 2.34; N, 8.98; S, 10.00; calcd. C, 34.98; H, 1.96; N, 9.06; S, 10.38. MS-ESI: m/z (%) = 582.99 (27.48%) $[Re(CO)_3(H_2L^1)]^+$, 624.02 (100%) $|[Re(CO)_3(H_2L^1)] + CH_3CN|^+$. IR (KBr): ν ($cm^{-1}$) = 3386m, 3261m, 3177m (NH), 2022vs, 1932s, 1911vs (C-O), 1619m (C=N), 813w, 754m (C-S). UV-Vis solid (λ_{max}, nm): 261, 320 and 445.

[$ReBr(H_2L^1)(CO)_3$] (**1b**): A mixture of the free ligand (73 mg, 0.23 mmol) with the corresponding equimolar amount of [$ReBr(CO)_3(CH_3CN)_2$] (102 mg, 0.23 mmol) in dry chloroform (15 mL) was heated at reflux for 3 h. The dark yellow solid formed was filtered off and vacuum dried over $CaCl_2$/KOH.

Yield: 129 mg (82.7%). M.p.: 240°C (dec.). $C_{18}H_{12}BrO_3N_4S_2Re$ (660.55): found C, 32.16; H, 1.89; N, 9.08; S, 9.80; calcd. C, 32.63; H, 1.83; N, 8.46; S, 9.66. MS-ESI: m/z (%) = 582.99 (2.46%) $[Re(CO)_3(H_2L^1)]^+$, 624.02 (100%) $|[Re(CO)_3(H_2L^1)] + CH_3CN|^+$, 661.01 (2.67%) $[ReBr(CO)_3(H_2L^1)]+$. IR (KBr): ν (cm^{-1}) = 3452m, 3263m, 3187m (NH), 2021vs, 1987s (C-O), 1613m (C=N), 829w, 756m (C-S). UV-Vis solid (λ_{max}, nm): 251, 339 and 441.

Complexes of H_2L^2



Scheme S6. Synthesis of the complexes of H_2L^2.

$[ReCl(H_2L^2)(CO)_3]$ (**2a**): A solution of $[ReCl(CO)_3(CH_3CN)_2]$ (103 mg, 0.26 mmol) in dry acetone (10 mL) was added dropwise to the ligand (85 mg, 0.26 mmol) in 20 mL of acetone and the resulting orange solution was stirred for 48 h. Then the solvent was evaporated under reduced pressure and the orange solid was dried over $CaCl_2$/KOH.

Yield: 31 mg (20.1%). M.p.: 208°C (dec.). $C_{19}H_{14}ClO_3N_4S_2Re$ (633.13): found C, 36.21; H, 2.32; N, 8.81; S, 9.96; calcd. C, 36.08; H, 2.23; N, 8.86; S, 10.12. MS-ESI: m/z (%) = 597.01 (55.84%) $[Re(CO)_3(H_2L^2)]^+$, 638.03 (100%) $|[Re(CO)_3(H_2L^2)] + CH_3CN|^+$. IR (KBr): ν ($cm^{-1}$) = 3393m, 3180m (NH), 2022vs, 1933s, 1913vs (C-O), 1571m (C=N), 833w, 762m (C-S). UV-Vis solid (λ_{max}, nm): 261, 311 and 429.

$[ReBr(H_2L^2)(CO)_3]$ (**2b**): A mixture of the free ligand (76 mg, 0.23 mmol) with the corresponding equimolar amount of $[ReBr(CO)_3(CH_3CN)_2]$ (100 mg, 0.23 mmol) in dry chloroform (15 mL) was heated at reflux for 3 h. Then the solvent was evaporated under reduced pressure and the brown solid were vacuum dried over $CaCl_2$/KOH.

Yield: 57 mg (36.3 %). M.p.: 195°C (dec.). $C_{19}H_{14}BrO_3N_4S_2Re$ (677.58): found C, 33.40; H, 2.28; N, 8.48; S, 10.15; calcd. C, 33.73; H, 2.09; N, 8.29; S, 9.48. MS-ESI: m/z (%) = 597.01 (8.04%) $[Re(CO)_3(H_2L^2)]^+$, 638.03 (100%) $|[Re(CO)_3(H_2L^2)] + CH_3CN|^+$, 679.06 (3.04%) $[ReBr(CO)_3(H_2L^2)]^+$. IR (KBr): ν (cm^{-1}) = 3428m, 3235m (NH), 2022vs, 1920vs, 1896vs (C-O), 1588m (C=N), 833w, 760m (C-S). UV-Vis solid (λ_{max}, nm): 258, 318 and 474.

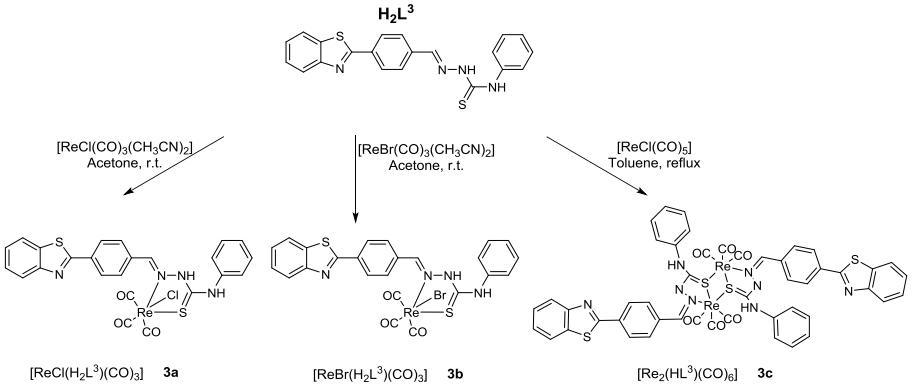
$[Re_2(HL^2)_2(CO)_6]$ (**2c**): For the synthesis of the dimeric complex we use two different synthetic strategies. In the first, the mixture of 77 mg (0.23 mmol) of ligand and 102 mg (0.23mmol) of $[ReBr(CO)_3(CH_3CN)_2]$ in ethanol (15 mL) was heated at reflux for 4 h. The orange solid obtained was vacuum dried over $CaCl_2$/KOH. The IR and NMR spectra shown signals corresponding a mixture of products which corresponded to mononuclear and dimeric complexes. Single crystals of the dimer 2c were obtained after slow evaporation of the mother liquor. For these reason, other strategy synthetic was tried to obtain the dimeric complex pure. In this reaction the mixture of 91 mg (0.28 mmol) of free ligand and 102 mg (0.28 mmol) of $[ReCl(CO)_5]$ in toluene (15 mL) was heated at reflux for 8 h. A brown solid was filtered off, washed with ethanol and vacuum dried over $CaCl_2$/KOH.

Yield: 63 mg (38.3 %). M.p.: 305°C (dec.). $C_{38}H_{26}O_6N_8S_4Re_2$ (1191.99): found C, 38.15; H, 2.21; N, 9.14; S, 10.53; calcd. C, 38.25; H, 2.30; N, 9.39; S, 10.73. MS-ESI: m/z (%) = 597.01 (55.84%) $[Re(CO)_3(HL^2)]^+$, 638.03 (100%) $|[Re(CO)_3(HL^2)] + CH_3CN|^+$, 1190.99 (2.36%) $[Re_2(HL^2)_2(CO)_6]^+$. IR (KBr): ν (cm^{-1}) = 3448w, 3421m (NH), 2034vs, 2017s, 1935s, 1984vs (C-O), 1575m (C=N), 841w, 763m (C-S). UV-Vis solid (λ_{max}, nm): 253, 336 and 421.

$[Re_4(L^2)_2(EtOH)_2(CO)_{12}]$ (**2d**): Formation of the tetramer **2d** was confirmed by X-ray studies of some single crystals isolated from the ethanol solution resulted of washing **2c**.

M.p.: 180°C (dec.). $C_{48}H_{36}O_{14}N_8S_4Re_4$ (1916.03): found C, 33.78; H, 2.57; N, 6.38; S, 8.02; calcd. C, 31.58; H, 1.99; N, 6.14; S, 7.01. IR (KBr): ν (cm^{-1}) = 2010s, 1890vs (C-O), 1542s (C=N), 818w, 755m (C-S).

Complexes of H_2L^3



Scheme S7. Synthesis of the complexes of H_2L^3.

$[ReX(H_2L^3)(CO)_3]$ (X=Cl, Br; **3a** and **3b**): A solution of $[ReX(CO)_3(CH_3CN)_2]$ in dry acetone (10 mL) was added dropwise to a suspension of the corresponding ligand in 20 mL of acetone and the resulting solution was stirred for 24 h (see table bellow).

In the case of $[ReBr(H_2L^3)(CO)_3]$ the solvent was evaporated under reduced pressure and the orange solid was dried over $CaCl_2$/KOH.

In the case of $[ReCl(H_2L^3)(CO)_3]$ the orange precipitate was isolated and dried over $CaCl_2$/KOH. Single crystals were obtained after slow evaporation of the mother liquor.

Amount used in the synthesis of the complexes.

Complex	X	Ligand mg (mmol)	Rhenium Precursor mg (mmol)
3a	Cl	100 (0.26)	103 (0.27)
3b	Br	89 (0.23)	101 (0.23)

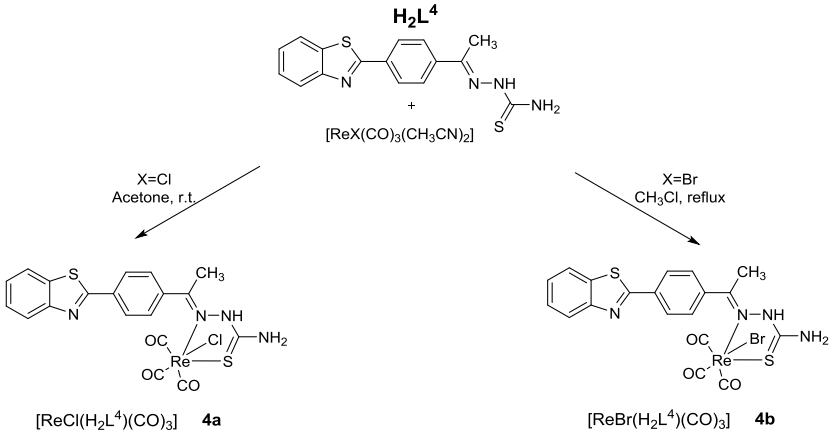
3a: Yield: 54 mg (28.6%). M.p.: 253°C (dec.). $C_{24}H_{16}ClO_3N_4S_2Re$ (693.99): found C, 42.56; H, 2.50; N, 8.22; S, 10.02; calcd. C, 41.52; H, 2.32; N, 8.07; S, 9.24. MS-ESI: m/z (%) = 659.02 (12.44%) $[Re(CO)_3(H_2L^3)]^+$, 700.05 (100%) $|[Re(CO)_3(H_2L^3)] + CH_3CN|^+$, 737.04 (2.34%) $|[ReCl(CO)_3(H_2L^3)] + CH_3CN|^+$. IR (KBr): ν ($cm^{-1}$) = 3283w, 3265w (NH), 2029s, 1946vs, 1911vs (C-O), 1582m (C=N), 827w, 762m (C-S). UV-Vis solid (λ_{max}, nm): 253, 340 and 394.

3b: Yield: 67 mg (39.6%). M.p.: 247°C (dec.). $C_{24}H_{16}BrO_3N_4S_2Re$ (737.94): found C, 39.75; H, 2.24; N, 7.65; S, 9.00; calcd. C, 41.49; H, 2.32; N, 8.07; S, 9.21. MS-ESI: m/z (%) = 659.02 (61.07%) $[Re(CO)_3(H_2L^3)]^+$, 700.05 (100%) $|[Re(CO)_3(H_2L^3)] + CH_3CN|^+$. IR (KBr): ν ($cm^{-1}$) = 3257m, 3272m (NH), 2029vs, 1945s, 1912vs (C-O), 1576m (C=N), 826w, 761m (C-S). UV-Vis solid (λmax, nm): 250, 340 and 395.

$[Re_2(HL^3)_2(CO)_6]$ (**3c**): The mixture of 94 mg (0.28 mmol) of free ligand and 100 mg (0.28 mmol) of $[ReCl(CO)_5]$ in toluene (10 mL) was heated at reflux for 8 h. The brown solid obtained was filtered off and dried over $CaCl_2$/KOH.

Yield: 28 mg (15.4%). M.p.: 262°C (dec.). $C_{48}H_{30}O_6N_8S_4Re_2$ (1316.03): found C, 43.55; H, 2.29; N, 8.34; S, 8.85; calcd. C, 43.83; H, 2.30; N, 8.52; S, 9.75. MS-ESI: m/z (%) = 659.02 (95.36%) $[Re(CO)_3(HL^3)]^+$, 700.05 (100%) $|[Re(CO)_3(HL^3)] + CH_3CN|^+$, 1317.04 (36.85%) $[Re_2(CO)_6(HL^3)_2]^+$. IR (KBr): ν (cm^{-1}) = 3376m (NH), 2035s, 2014s, 1907vs, 1880vs, 1896vs (C-O), 1597m (C=N), 833w, 754m (C-S). UV-Vis solid (λ_{max}, nm): 255, 340 and 448.

Complexes of H_2L^4



Scheme S8. Synthesis of the complexes with H_2L^4.

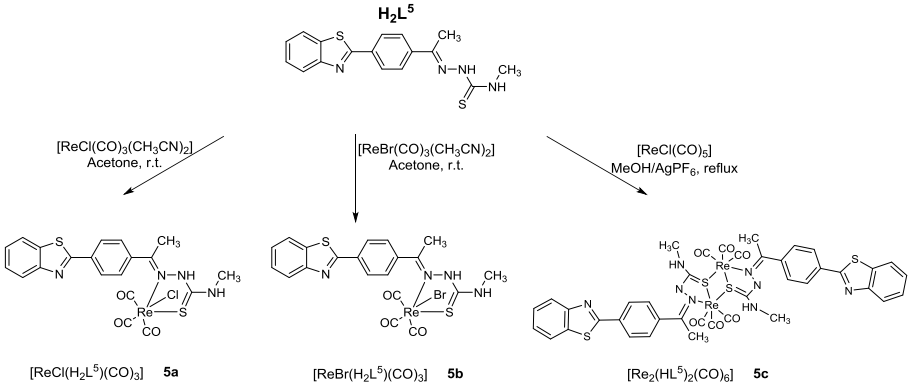
$[ReCl(H_2L^4)(CO)_3]$ (**4a**): A solution of $[ReCl(CO)_3(CH_3CN)_2]$ (103 mg, 0.26 mmol) in dry acetone (10 mL) was added dropwise to a suspension of ligand (83 mg, 0.26 mmol) in 20 mL of acetone and the resulting yellow solution was stirred for 72 h. The resulting yellow solid was filtered off and dried over $CaCl_2$/KOH. Single crystals were obtained after slow evaporation of the mother liquor.

Yield: 30 mg (18.6%). M.p.: 264°C (dec.). $C_{19}H_{14}ClO_3N_4S_2Re$ (631.97): found C, 36.87; H, 2.39; N, 8.95; S, 10.12; calcd. C, 36.08; H, 2.23; N, 8.86; S, 10.12. MS-ESI: m/z (%) = 597.01 (100%) $[Re(CO)_3(H_2L^4)]^+$, 638.03 (20.6%) $|[Re(CO)_3(H_2L^4)] + CH_3CN|^+$. IR (KBr): ν ($cm^{-1}$) = 3402w, 3299w, 3159w (NH), 2024s, 1919vs, 1901vs (C-O), 1586m (C=N), 832w, 754m (C-S). UV-Vis solid (λ_{max}, nm): 257, 328 and 417.

$[ReBr(H_2L^4)(CO)_3]$ (**4b**): A mixture of the free ligand (80 mg, 0.23 mmol) with the corresponding equimolar amount of $[ReBr(CO)_3(CH_3CN)_2]$ (100 mg, 0.23 mmol) in dry chloroform (15 mL) was heated at reflux for 3 h. The yellow solid formed was filtered off and vacuum dried over $CaCl_2$/KOH. Single crystal were obtained after slow evaporation of the mother liquor.

Yield: 134 mg (80.8%). M.p.: 247°C (dec.). $C_{19}H_{14}BrO_3N_4S_2Re$ (675.92): found C, 34.22; H, 2.19; N, 8.94; S, 10.10; calcd. C, 33.73; H, 2.08; N, 8.29; S, 9.46. MS-ESI: m/z (%) = 597.01 (100%) $[Re(CO)_3(H_2L^4)]^+$, 638.03 (4.5%) $|[Re(CO)_3(H_2L^4)] + CH_3CN|^+$. IR (KBr): ν ($cm^{-1}$) = 3439m, 3272m, 3182m (NH), 2015vs, 1887s (C-O), 1616m (C=N), 845w, 760m (C-S). UV-Vis solid (λ_{max}, nm): 255, 324 and 421.

Complexes of H_2L^5



Scheme S9. Synthesis of the complexes with H_2L^5.

$[ReCl(H_2L^5)(CO)_3]$ (**5a**): A solution of $[ReCl(CO)_3(CH_3CN)_2]$ (101 mg, 0.26 mmol) in dry acetone (10 mL) was added dropwise to a suspension of ligand (88 mg, 0.26 mmol) in 20 mL of acetone and the resulting yellow solution was stirred for 24 h. The resulting pale yellow solid resulting was isolated off and dried over $CaCl_2$/KOH.

Yield: 100 mg (59.6%). M.p.: 254°C (dec.). $C_{20}H_{16}ClO_3N_4S_2Re$ (645.99): found C, 37.50; H, 2.66; N, 8.94; S, 10.08; calcd. C, 37.18; H, 2.50; N, 8.67; S, 9.92. MS-ESI: m/z (%) = 611.02 (12.7%) $[Re(CO)_3(H_2L^5)]^+$, 652.05 (100%) $|[Re(CO)_3(H_2L^5)] + CH_3CN|^+$. IR (KBr): ν ($cm^{-1}$) = 3234m, 3047w (NH), 2022s, 1919vs, 1885vs (C-O), 1579s (C=N), 843w, 764m (C-S). UV-Vis solid (λ_{max}, nm): 251, 340 and 386.

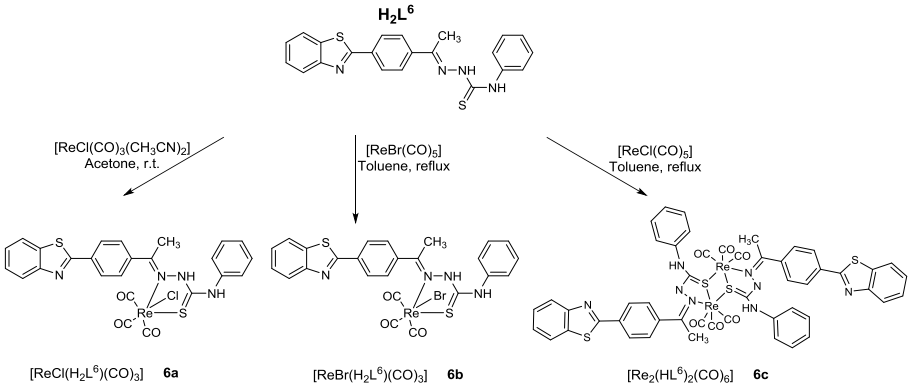
$[ReBr(H_2L^5)(CO)_3]$ (**5b**): A mixture of the free ligand (79 mg, 0.23 mmol) with the corresponding equimolar amount of $[ReBr(CO)_3(CH_3CN)_2]$ (101 mg, 0.23 mmol) in dry chloroform (15 mL) was heated at reflux for 2 h. The yellow solid formed was filtered off and vacuum dried over $CaCl_2$/KOH.

Yield: 85 mg (53.1%). M.p.: 236°C (dec.). $C_{20}H_{16}BrO_3N_4S_2Re$ (689.94): found C, 34.86; H, 2.29; N, 8.01; S, 8.76; calcd. C, 34.78; H, 2.33; N, 8.11; S, 9.26. MS-ESI: m/z (%) = 611.02 (27.4%) $[Re(CO)_3(H_2L^5)]^+$, 652.05 (100%) $|[Re(CO)_3(H_2L^5)] + CH_3CN|^+$, 690.04 (1.7%) $[ReBr(CO)_3(H_2L^5)]^+$. IR (KBr): ν (cm^{-1}) = 3219m, 3042m (NH), 2038vs, 1939s, 1903vs (C-O), 1585m (C=N), 840w, 754w (C-S). UV-Vis solid (λ_{max}, nm): 250, 340 and 384.

$[Re_2(HL^5)_2(CO)_6]$ (**5c**): A solution of $(NEt_4)_2[ReBr_3(CO)_3]$ (77 mg, 0.10 mmol) and silver hexafluorophosphate (78 mg, 0.30 mmol) in methanol (10 mL) was stirred to room temperature for 2 h. The mixture was filtered and on the solution was added H_2L^5 (34 mg, 0.10 mmol) dissolved in methanol (2 mL). Then the resulting mixture was refluxed for 2 h. The yellow precipitate was filtered off and vacuum dried over $CaCl_2$/KOH. Single crystal were obtained after slow evaporation of the mother liquor.

Yield: 60 mg (98.4%). M.p.: 212°C (dec.). $C_{40}H_{30}O_6N_8S_4Re_2$ (1220.03): found C, 38.90; H, 2.87; N, 8.79; S, 10.10; calcd. C, 39.40; H, 2.48; N, 9.19; S, 10.52. MS-ESI: m/z (%) = 611.01 (10.7%) $[Re(CO)_3(HL^5)]^+$, 652.05 (10.4%) $|[Re(CO)_3(HL^5)] + CH_3CN|^+$, 789.05 (100%), 1235.01 (1.71%) $|[Re_2(CO)_6(HL^5)_2] + H_2O|^+$. IR (KBr): ν ($cm^{-1}$)= 3377m (NH), 2013s, 1921vs, 1896vs (C-O), 1582s (C=N), 840s, 760s (C-S). UV-Vis solid (λ_{max}, nm): 253, 337 and 381.

Complexes of H_2L^6



Scheme S10. Synthesis of the complexes with H_2L^6.

$[ReCl(H_2L^6)(CO)_3]$ (**6a**): A solution of $[ReCl(CO)_3(CH_3CN)_2]$ (100 mg, 0.26 mmol) in dry acetone (10 mL) was added dropwise to a suspension of ligand (104 mg, 0.26 mmol) in 20 mL of acetone and the mixture was stirred for 24 h. The yellow solid resulting was filtered off and vacuum dried over $CaCl_2$/KOH. Single crystal were obtained after slow evaporation of the mother liquor.

Yield: 85 mg (46.4%). M.p.: 245°C (dec.). $C_{25}H_{18}ClO_3N_4S_2Re$ (708.00): found C, 44.37; H, 2.56; N, 7.91; S, 9.03; calcd. C, 44.45; H, 2.75; N, 8.05; S, 9.08. MS-ESI: m/z (%) = 673.04 (100%) $[Re(CO)_3(H_2L^6)]^+$, 714.06 (71.4%) $|[Re(CO)_3(H_2L^6)] + CH_3CN|^+$. IR (KBr): ν ($cm^{-1}$) = 3415m, 3058w (NH), 2022vs, 1922vs, 1886vs (C-O), 1547s (C=N), 846m, 765s (C-S). UV-Vis solid (λ_{max}, nm): 254, 339 and 393.

$[ReBr(H_2L^6)(CO)_3]$ (**6b**): The mixture of 100 mg (0.25 mmol) of free ligand and 101 mg (0.25 mmol) of $[ReBr(CO)_5]$ in toluene (15 mL) was heated at reflux for 8 h. The resulting dark yellow solid was filtered off and vacuum dried over $CaCl_2$/KOH. Single crystal were obtained after slow evaporation of the mother liquor.

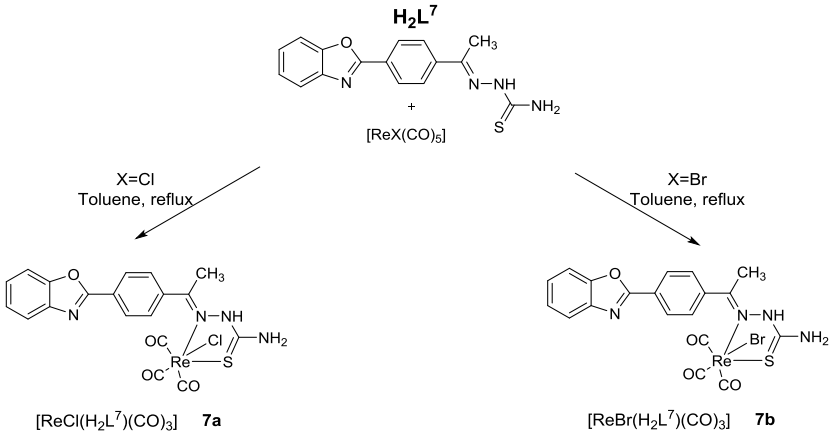
Yield: 103 mg (55.1%). M.p.: 236°C (dec.). $C_{25}H_{18}BrO_3N_4S_2Re$ (751.96): found C, 40.14; H, 2.55; N, 7.48; S, 8.84; calcd. C, 39.89; H, 2.41; N, 7.44; S, 8.52. MS-ESI: m/z (%) = 673.04 (24.3%)

$[Re(CO)_3(H_2L^6)]^+$, 714.06 (100%) $|[Re(CO)_3(H_2L^6)] + CH_3CN|^+$. IR (KBr): ν ($cm^{-1}$) = 3228w, 3059w (NH), 2022vs, 1924s, 1896vs (C-O), 1558s (C=N), 842m, 757s (C-S). UV-Vis solid (λ_{max}, nm): 252, 364 and 420.

$[Re_2(HL^6)_2(CO)_6]$ (**6c**): A mixture of 112 mg (0.28 mmol) of free ligand and 102 mg (0.28 mmol) of $[ReCl(CO)_5]$ in toluene (15 mL) was heated at reflux for 8 h. The resulting pale brown solid obtained was filtered off and dried over $CaCl_2$/KOH. Single crystal were obtained after slow evaporation of the mother liquor.

Yield: 130 mg (69.4%). M.p.: 278°C (dec.). $C_{50}H_{36}O_6N_8S_4Re_2$ (1344.07): found C, 44.45; H, 2.70; N, 8.39; S, 9.63; calcd. C, 44.63; H, 2.70; N, 8.33; S, 9.53. MS-ESI: m/z (%) = 714.06 (100%) $|[Re(CO)_3(HL^6)] + CH_3CN|^+$, 1345.06 (41.5%) $[Re_2(CO)_6(HL^6)_2]^+$. IR (KBr): ν (cm^{-1}) = 3415m (NH), 2022vs, 1922vs, 1886vs (C-O), 1547s (C=N), 846m, 765s (C-S). UV-Vis solid (λ_{max}, nm): 252, 290 and 394.

Complexes of H_2L^7



Scheme S11. Synthesis of the complexes with H_2L^7.

$[ReX(H_2L^7)(CO)^3]$ (X=Cl, Br; 7a and 7b): A mixture of $[ReX(CO)_5]$ and the corresponding ligand in dry toluene (5 mL) was heated at reflux for 5 h (see table bellow). The yellow precipitates were isolated and vacuum dried over $CaCl_2$/KOH.

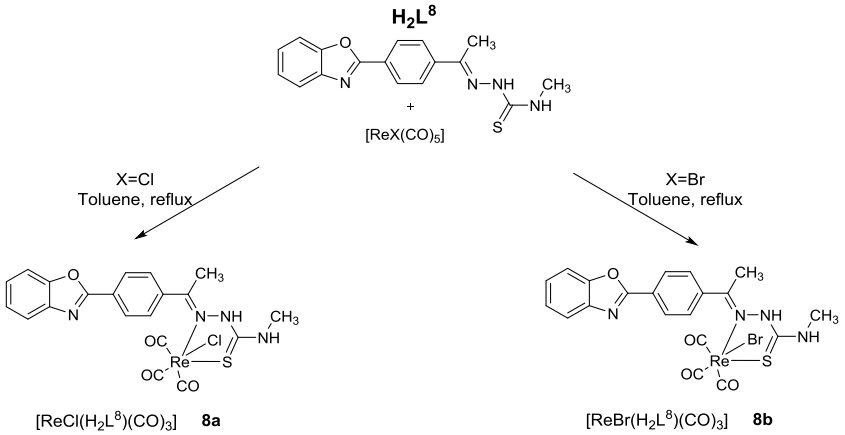
Amount used in the synthesis of the complexes.

Complex	X	Ligand mg (mmol)	Rhenium Precursor g (mmol)
7a	Cl	32 (0.10)	36 (0.10)
7b	Br	31 (0.10)	41 (0.10)

7a: Yield: 54 mg (85.2%). M.p.: 269°C (dec.). $C_{19}H_{14}ClO_4N_4SRe$ (615.99): found C, 39.58; H, 2.35; N, 9.29; S, 5.13; calcd. C, 37.01; H, 2.29; N, 9.09; S, 5.19. MS-ESI: m/z (%) = 581.03 (100%) $[Re(CO)_3(H_2L^7)]^+$, 622.05 (38.5%) $|[Re(CO)_3(H_2L^7)] + CH_3CN|^+$. IR (ATR): ν ($cm^{-1}$) = 3269w, 3142m (NH), 2001s, 1918m, 1898vs, 1062m (C-O), 1608m, 1561s (C=N), 847w, 742s (C-S). UV-Vis solid (λ_{max}, nm): 279 and 404.

7b: Yield: 37 mg (56.3%). M.p.: 260°C (dec.). $C_{19}H_{14}BrO_4N_4SRe$ (659.95): found C, 34.51; H, 2.25; N, 8.32; S, 4.96; calcd. C, 34.55; H, 2.14; N, 8.48; S, 4.85. MS-ESI: m/z (%) = 581.02 (100%) $[Re(CO)_3(H_2L^7)]^+$, 622.05 (1.28%) $|[Re(CO)_3(H_2L^7)] + CH_3CN|^+$, 659.03 (0.52%) $[ReBr(CO)_3(H_2L^7)]^+$. IR (ATR): ν (cm^{-1}) = 3266w, 3163w (NH), 2021vs, 1920s, 1902vs, 1062m (C-O), 1624m, 1557s (C=N), 846m, 741s (C-S). UV-Vis solid (λ_{max}, nm): 277 and 386.

Complexes of H_2L^8



Scheme S12. Synthesis of the complexes with H_2L^8.

$[ReX(H_2L^8)(CO)_3]$ (X=Cl, Br; **8a** and **8b**): A mixture of $[ReX(CO)_5]$ and the corresponding ligand in dry toluene (5 mL) was heated at reflux for 5 h (see table bellow). The yellow precipitates were isolated and vacuum dried over $CaCl_2$/KOH. Single crystals of 8b were obtained from the acetone solution.

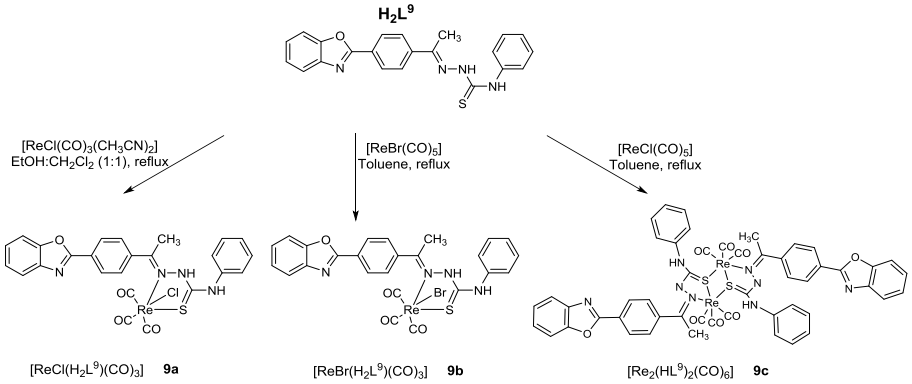
Amount used in the synthesis of the complexes.

Complex	X	Ligand mg (mmol)	Rhenium Precursor mg (mmol)
8a	Cl	33 (0.10)	36 (0.10)
8b	Br	33 (0.10)	45 (0.10)

8a: Yield: 22 mg (34.4%). M.p.: 253°C (dec.). $C_{20}H_{16}ClO_4N_4SRe$ (630.01): found C, 37.73; H, 2.51; N, 8.35; S, 4.90; calcd. C, 38.09; H, 2.56; N, 8.89; S, 5.07. MS-ESI: m/z (%) = 595.04 (82.3%) $[Re(CO)_3(H_2L^8)]$+, 636.07 (100%) $|[Re(CO)_3(H_2L^8)] + CH_3CN|^+$. IR (ATR): ν ($cm^{-1}$) = 3233m, 3048w (NH), 2001s, 1918s, 1885vs, 1041w (C-O), 1578s (C=N), 846m, 747s (C-S). UV-Vis solid (λ_{max}, nm): 385.

8b: Yield: 36 mg (52.6%). M.p.: 229°C (dec.). $C_{20}H_{16}BrO_4N_4SRe$ (673.96): found C, 35.05; H, 2.43; N, 8.08; S, 4.68; calcd. C, 35.61; H, 2.39; N, 8.31; S, 4.74. MS-ESI: m/z (%) = 595.05 (77.3%) $[Re(CO)_3(H_2L^8)]^+$, 636.07 (100%) $|[Re(CO)_3(H_2L^8)] + CH_3CN|$+. IR (ATR): ν ($cm^{-1}$) = 3221m, 3055w (NH), 2018vs, 1911s, 1888vs, 1044m (C-O), 1577s (C=N), 847m, 751s (C-S). UV-Vis solid (λ_{max}, nm): 389.

Complexes of H_2L^9



Scheme S13. Synthesis of the complexes with H_2L^9.

$[ReCl(H_2L^9)(CO)_3]$ (**9a**): The mixture of $[ReCl(CO)_3(CH_3CN)_2]$ (39 mg, 0.10 mmol) and free ligand (38 mg, 0.10 mmol) in 5 mL of a ethanol:dichloromethane (1:1) mixture was refluxed for 4 h. The yellow precipitate was filtered off and vacuum dried over $CaCl_2$/KOH.

Yield: 24 mg (35.3%). M.p.: 264°C (dec.). $C_{25}H_{18}ClO_4N_4SRe$ (692.07): found C, 42.49; H, 2.44; N, 7.91; S, 4.46; calcd. C, 43.35; H, 2.62; N, 8.09; S, 4.62. MS-ESI: m/z (%) = 657.06 (100%) $[Re(CO)_3(H_2L^9)]^+$, 698.09 (91.7%) $|[Re(CO)_3(H_2L^9)] + CH_3CN|^+$. IR (ATR): ν ($cm^{-1}$) = 3276m, 3109w (NH), 2018vs, 1920vs, 1888s, 1159w (C-O), 1566m (C=N), 847s, 754s (C-S). UV-Vis solid (λ_{max}, nm): 301 and 415.

$[ReBr(H_2L^9)(CO)_3]$ (**9b**): A mixture of $[ReBr(CO)_5]$ (41 mg, 0.10 mmol) and ligand (39 mg, 0.10 mmol) in dry toluene (5 mL) was heated at reflux for 5 h. The yellow precipitate was filtered off and vacuum dried over $CaCl_2$/KOH.

Yield: 36 mg (52.6%). M.p.: 229°C (dec.). $C_{25}H_{18}BrO_4N_4SRe$ (735.98): found C, 41.25; H, 2.41; N, 7.71; S, 4.28; calcd. C, 40.76; H, 2.46; N, 7.61; S, 4.34. MS-ESI: m/z (%) = 657.06 (100%) $[Re(CO)_3(H_2L^9)]^+$, 698.09 (86.3%) $|[Re(CO)_3(H_2L^9)] + CH_3CN|^+$. IR (ATR): ν ($cm^{-1}$) = 3268w, 3029m (NH), 2019vs, 1922s, 1892vs, 1184m (C-O), 1566s (C=N), 846m, 743m (C-S). UV-Vis solid (λ_{max}, nm): 306 and 414.

$[Re_2(HL^9)_2(CO)_6]$ (**9c**): A mixture of $[ReCl(CO)_5]$ (36 mg, 0.10 mmol) and the ligand (37 mg, 0.10 mmol) in dry toluene (5 mL) was heated at reflux for 4 h. The yellow precipitate was filtered off and vacuum dried over $CaCl_2$/KOH. Single crystals were obtained after slow evaporation of the mother liquor.

Yield: 43 mg (68.6%). M.p.: 264°C (dec.). $C_{50}H_{34}O_8N_8S_2Re_2$ (1312.11): found C, 45.28; H, 2.62; N, 8.29; S, 4.68; calcd. C, 45.72; H, 2.61; N, 8.54; S, 4.87. MS-ESI: m/z (%) = 657.06 (100%) $[Re(CO)_3(HL^9)]^+$, 698.09 (32.2%) $|[Re(CO)_3(HL^9)] + CH_3CN|^+$. IR (ATR): ν ($cm^{-1}$) = 3401m (NH), 2012vs, 1940m, 1902vs, 1131m (C-O), 1568s (C=N), 845m, 739s (C-S). UV-Vis solid (λ_{max}, nm): 389.

Table S1. Crystal data and structure refinement for the ligands H_2L^n

Compound	**H_2L^1**.DMSO	**H_2L^2**	**H_2L^4**	**H_2L^5**	**H_2L^7**.DMSO	**H_2L^8**.DMSO
Formula	$C_{17}H_{18}N_4OS_3$	$C_{16}H_{14}N_4S_2$	$C_{16}H_{14}N_4S_2$	$C_{17}H_{16}N_4S_2$	$C_{18}H_{20}N_4O_2S_2$	$C_{19}H_{22}N_4O_2S_2$
Formula weight	390.53	326.43	326.43	340.46	388.50	402.52
CCDC ref.	1828601	1828602	1828603	1828604	1828605	1828606
Temperature (K)	296(2)	100(2)	293(2)	296(2)	296(2)	296(2)
Wavelength (Å)	1.54178	1.54178	1.54178	1.54178	1.54178	1.54178
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*$P2_1/c$*	*C2/c*	*$P2_1/n$*	*C2/c*	*P -1*	*$P2_1/c$*
a (Å)	21.5521(8)	13.2120(12)	8.4909(2)	24.5508(5)	7.0286(3)	7.0142(10)
b (Å)	7.4568(3)	8.2301(8)	10.4575(2)	4.84793(9)	7.2375(3)	10.5822(15)
c (Å)	11.8391(5)	28.449(2)	17.7945(4)	31.3250(6)	21.0132(9)	26.777(4)
α (°)	90	90	90	90	93.789(3)	90
β (°)	97.832(2)	95.856(6)	100.2890(10)	106.7736(9)	96.875(2)	92.457(8)
γ (°)	90	90	90	90	116.450(3)	90
Volume ($Å^3$)	1884.91(13)	3077.2(5)	1554.63(6)	3569.68(12)	941.55(7)	1985.9(5)
Z	4	8	4	8	2	4
ρc (Mg/m^3)	1.376	1.409	1.395	1.267	1.370	1.346
μ (mm^{-1})	3.702	3.140	3.108	2.728	2.734	2.611
F(000)	816	1360	680	1424	408	848
θ (°) range collection	2.069 - 67.680	3.123 - 67.563	4.926 - 67.894	2.947 - 68.231	2.137 - 68.399	3.304 - 68.614
h;k;l ranges	-25,24; 0,8; 0,3	-15,13; -8,8, -33,33	-9,9; -12,12; -21,20	-28,29; -5,5; -36,36	-8,8; -8,8; -25,25	-8,8; -12,12; -32,32
Reflections collected	5271	6408	35134	16193	9804	23439
Independent reflections (Rint)	5271 (--)	2298 (0.0500)	2730 (0.0308)	3189 (0.0329)	3346 (0.1129)	3649 (0.1274)
Max./min. transmission	0.7530/0.5494	0.7530/0.5781	0.8893/0.7805	--	0.7531/0.4814	0.7531/0.3538
Data / restraints / parameters	5271 / 83 / 254	6379 / 30 / 218	2730 / 0 / 200	3189/ 0/ 210	3346 / 0 / 237	3649 / 1 / 251
Goodness-of-fit on F^2	1.043	1.039	1.035	0.617	1.016	1.072
R1/wR2 indices [I>2sigma(I)]	0.0525/ 0.1455	0.0966/ 0.2433	0.0357/ 0.0937	0.0376/ 0.1276	0.0622/ 0.1508	0.0768/ 0.2154
R1/wR2 indices (all data)	0.0564/ 0.1492	0.1091/ 0.2531	0.0393/ 0.0961	0.0419/ 0.1417	0.11587 0.1850	0.0982/ 0.2405

Table S2. Crystal data and structure refinement for the complexes fac-[ReX(CO)$_3$(H$_2$L^n)].

Compound	**4a**	**4b**	**6a**	**6b**.C_7H_8	**8b**.H_2O
Formula	$C_{19}H_{14}ClN_4O_3ReS_2$	$C_{19}H_{14}BrN_4O_3ReS_2$	$C_{25}H_{18}ClN_4O_3ReS_2$	$C_{32}H_{26}BrN_4O_3ReS_2$	$C_{20}H_{16}BrN_4O_5ReS$
Formula weight	632.11	676.57	708.20	844.80	690.54
CCDC ref.	1828607	1828608	1828609	1828610	1828611
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Wavelength (Å)	1.54178	1.54178	1.54178	1.54178	1.54178
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	*P -1*	*P -1*	*P 2$_1$/c*	*P -1*	*P -1*
a (Å)	7.658(3)	6.7644(5)	13.6740(3)	11.1685(11)	8.6134(3)
b (Å)	8.649(3)	7.2881(5)	10.4643(2)	11.8169(12)	11.6521(5)
c (Å)	16.281(11)	21.7998(15)	19.2746(4)	14.2696(15)	12.9674(5)
α (°)	90.16(3)	92.975(3)	90	67.082(4)	65.0899(12)
β (°)	97.44(4)	93.114(2)	110.4060(10)	69.126(3)	83.9903(15)
γ (°)	99.22(2)	101.098(3)	90	83.278(4)	89.3394(18)
Volume (Å^3)	1055.1(9)	1050.93(13)	2584.90(9)	1620.2(3)	1173.14(8)
Z	2	2	4	2	2
ρc (Mg/m^3)	1.990	2.138	1.820	1.732	1.955
μ (mm^{-1})	14.539	15.655	11.953	10.299	13.296
F(000)	608	644	1376	824	660
θ (°) range collection	2.738 - 68.438	2.034 - 66.505	3.448 - 66.560	3.575 - 66.799	3.781 - 68.747
h;k;l ranges	-8,8; -10,10; -19,19	-8,7; -8,7; -25,25	-15,15; -11,12; -22,22	-13,13; -14,13; -16,16	-10,10; -14,13; -15,15
Reflections collected	16299	26007	26578	49437	18464
Independent reflections (Rint)	3714 (0.0315)	3573 (0.0582)	4371 (0.0428)	5531 (0.0488)	4074 (0.0451)
Max./min. transmission	0.7530 / 0.5105	0.7528 / 0.4658	0.5842 / 0.3384	0.7468 / 0.6257	0.7530 / 0.4231
Data / restraints / parameters	3714 / 12 / 272	3573 / 109 / 290	4371 / 0 / 334	5531 / 0 / 390	4074 / 0 / 291
Goodness-of-fit on F^2	1.061	1.054	1.002	1.082	1.146
R1/wR2 indices [I>2sigma(I)]	0.0211/0.0534	0.0288/0.0717	0.0285/0.0775	0.0263/0.0665	0.0344/0.1029
R1/wR2 indices (all data)	0.0229/0.0546	0.0325/0.0739	0.0303/0.0800	0.0296/0.0688	0.0353/0.1047

Table S3. Crystal data and structure refinement for the complexes $[Re_2(HL^n)_2(CO)_6]$ and $[Re_4(L^2)_2(CO)_{12}(EtOH)_2]$.

Compound	**2c**	**3c**.C_3H_6O	**5c**	**6c**.C_7H_8	**9c**.C_2H_5OH	**2d**. 2 C_2H_5OH
Formula	$C_{38}H_{26}N_8O_6Re_2S_4$	$C_{96}H_{60}N_{16}O_{12}Re_4S_8$	$C_{40}H_{30}N_8O_6Re_2S_4$	$C_{64}H_{50}N_8O_6Re_2S_4$	$C_{50}H_{34}N_8O_8Re_2S_2$	$C_{26}H_{24}N_4O_8Re_2S_2$
Formula weight	1191.31	2630.88	1219.36	1527.76	1311.37	957.01
CCDC ref.	1828612	1828613	1828614	1828615	1828616	1828617
Temperature (K)	296(2)	296(2)	293(2)	296(2)	100(2)	296(2)
Wavelength (Å)	1.54178	1.54178	0.71073	1.54178	0.71073	1.54178
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*$P2_1/n$*	*P -1*	*$P2_1/a$*	*P -1*	*$P2_1/n$*	*$P2_1/c$*
a (Å)	10.3658(15)	15.0539(10)	10.2951(8)	7.6843(2)	9.8797(9)	10.5694(7)
b (Å)	10.1221(15)	17.4102(12)	16.0225(16)	12.5075(3)	15.0510(13)	14.1822(10)
c (Å)	38.934(5)	20.9041(14)	13.4259(11)	16.6105(4)	18.0200(17)	20.5737(14)
α (°)	90	74.153(4)	90	72.8951(7)	90	90
β (°)	94.518(6)	73.586(4)	104.251(6)	82.2567(8)	96.779(3)	98.892(3)
γ (°)	90	88.641(4)	90	83.5158(10)	90	90
Volume ($Å^3$)	4072.4(10)	5047.3(6)	2146.5(3)	1507.39(6)	2660.8(4)	3046.9(4)
Z	4	4	2	1	2	4
ρc (Mg/m^3)	1.943	1.769	1.887	1.683	1.637	2.086
μ (mm^{-1})	13.842	11.262	5.885	9.505	4.681	17.043
F(000)	2288	2544	1176	752	1272	1816
θ (°) range collection	2.277 - 68.173	2.294 - 69.434	3.380 - 29.334	2.799 - 68.197	2.247 - 28.429	3.800 - 68.114
h;k;l ranges	-11,11; -11,12; -46,43	-17,17; -20,19; -25,23	-14,13; -21,21; -18,18	-9,9; -14,14; -19,19	-13,13; -20,20; -23,24	-12,12; -16,16; -24,24
Reflections collected	43968	64217	17510	33023	83846	40059
Independent reflections (Rint)	7023 (0.0432)	16715 (0.1189)	5780 (0.0960)	5190 (0.0593)	6640 (0.0598)	5426 (0.0415)
Max./min. transmission	0.7530 / 0.4166	0.7530 / 0.3725	0.7530 / 0.4166	0.7531 / 0.5190	0.7457 / 0.4314	0.7530 / 0.4194
Data / restraints / parameters	7023 / 36 / 561	16742 / 5 / 1213	5780 / 0 / 273	5190 / 132 / 381	6640 / 0 / 318	5426 / 116 / 383
Goodness-of-fit on F^2	1.002	1.074	0.907	1.078	1.212	1.062
R1/wR2 indices [I>2sigma(I)]	0.0336/0.0948	0.1087/0.2820	0.0461/0.0922	0.0293/0.0732	0.0461/0.0827	0.0394/0.1091
R1/wR2 indices (all data)	0.0374/0.0979	0.1513/0.3034	0.0903/0.1031	0.0330/0.0750	0.0569/0.0852	0.0435/0.1146

Table S4. Bond lengths [Å] and angles [°] for H_2L^1.(DMSO)**.**

S(11S)-O(1S)	1.484(12)	C(4)-C(3)-C(8)	117.9(3)
S(11S)-C(2S)	1.731(16)	C(4)-C(3)-C(2)	123.3(3)
S(11S)-C(3S)	1.737(16)	C(8)-C(3)-C(2)	118.8(3)
S(1S)-O(1S)	1.510(3)	N(4B)-C(9)-N(4A)	106.9(6)
S(1S)-C(3S)	1.732(8)	N(4B)-C(9)-C(6)	128.7(6)
S(1S)-C(2S)	1.760(7)	N(4A)-C(9)-C(6)	124.4(4)
S(1)-C(1)	1.679(5)	N(4B)-C(9)-S(2A)	9.8(5)
N(4B)-C(9)	1.195(10)	N(4A)-C(9)-S(2A)	116.6(3)
N(4B)-C(10)	1.569(11)	C(6)-C(9)-S(2A)	118.9(3)
N(3)-C(2)	1.272(5)	N(4B)-C(9)-S(2B)	115.9(6)
N(3)-N(2)	1.375(5)	N(4A)-C(9)-S(2B)	9.2(3)
N(2)-C(1)	1.339(6)	C(6)-C(9)-S(2B)	115.3(3)
C(3)-C(4)	1.394(6)	S(2A)-C(9)-S(2B)	125.7(3)
C(3)-C(8)	1.397(5)	C(15)-S(2B)-C(9)	79.8(3)
C(3)-C(2)	1.450(5)	C(5)-C(6)-C(7)	118.0(4)
C(9)-N(4A)	1.316(7)	C(5)-C(6)-C(9)	121.4(3)
C(9)-C(6)	1.463(5)	C(7)-C(6)-C(9)	120.6(3)
C(9)-S(2A)	1.788(4)	N(3)-C(2)-C(3)	122.8(3)
C(9)-S(2B)	1.879(5)	C(7)-C(8)-C(3)	121.2(3)
S(2B)-C(15)	1.657(6)	C(4)-C(5)-C(6)	120.8(4)
C(6)-C(5)	1.400(6)	C(5)-C(4)-C(3)	121.4(4)
C(6)-C(7)	1.401(5)	C(8)-C(7)-C(6)	120.7(3)
C(8)-C(7)	1.367(5)	C(15)-C(10)-C(11)	119.4(5)
C(5)-C(4)	1.364(7)	C(15)-C(10)-N(4B)	95.4(5)
C(10)-C(15)	1.372(6)	C(11)-C(10)-N(4B)	145.2(6)
C(10)-C(11)	1.414(8)	C(15)-C(10)-S(2A)	117.7(4)
C(10)-S(2A)	1.701(5)	C(11)-C(10)-S(2A)	122.9(4)
C(15)-C(14)	1.367(6)	N(4B)-C(10)-S(2A)	22.2(3)
C(15)-N(4A)	1.452(6)	C(14)-C(15)-C(10)	121.2(4)
C(1)-N(1)	1.310(6)	C(14)-C(15)-N(4A)	129.2(5)
C(12)-C(11)	1.372(10)	C(10)-C(15)-N(4A)	109.6(4)
C(12)-C(13)	1.383(10)	C(14)-C(15)-S(2B)	107.6(4)
C(14)-C(13)	1.306(8)	C(10)-C(15)-S(2B)	131.2(4)
		N(4A)-C(15)-S(2B)	21.6(2)
O(1S)-S(11S)-C(2S)	108.7(11)	N(1)-C(1)-N(2)	117.0(4)
O(1S)-S(11S)-C(3S)	108.6(7)	N(1)-C(1)-S(1)	123.0(4)
C(2S)-S(11S)-C(3S)	97.7(8)	N(2)-C(1)-S(1)	119.9(4)
O(1S)-S(1S)-C(3S)	107.7(3)	C(11)-C(12)-C(13)	120.7(5)
O(1S)-S(1S)-C(2S)	106.1(3)	C(12)-C(11)-C(10)	117.2(5)
C(3S)-S(1S)-C(2S)	96.9(4)	C(13)-C(14)-C(15)	119.7(5)
C(9)-N(4B)-C(10)	117.6(7)	C(14)-C(13)-C(12)	121.8(5)
C(2)-N(3)-N(2)	115.6(3)	C(9)-N(4A)-C(15)	110.4(5)
C(1)-N(2)-N(3)	120.6(4)	C(10)-S(2A)-C(9)	85.6(2)

Table S5. Hydrogen bonds for H_2L^1.(DMSO) **[Å and °].**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1B)...O(1S)#1	0.86	2.11	2.952(5)	164.9
N(1)-H(1B)...S(11S)#1	0.86	2.97	3.704(12)	144.1
C(2)-H(2A)...O(1S)#2	0.93	2.54	3.339(5)	144.5
N(2)-H(2)...O(1S)#2	0.86	2.06	2.902(4)	167.0
N(2)-H(2)...S(1S)#2	0.86	2.98	3.819(3)	164.1
C(3S)-H(3S2)...S(1S)#3	0.96	2.99	3.795(7)	141.9
N(1)-H(1B)...O(1S)#1	0.86	2.11	2.952(5)	164.9
N(1)-H(1B)...S(11S)#1	0.86	2.97	3.704(12)	144.1
C(2)-H(2A)...O(1S)#2	0.93	2.54	3.339(5)	144.5
N(2)-H(2)...O(1S)#2	0.86	2.06	2.902(4)	167.0
N(2)-H(2)...S(1S)#2	0.86	2.98	3.819(3)	164.1
C(3S)-H(3S2)...S(1S)#3	0.96	2.99	3.795(7)	141.9
C(2S)-H(2S5)...S(1)#4	0.96	3.12	3.790(7)	127.9

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z+1 #2 x,-y+1/2,z+1/2 #3 -x+2,-y+1,-z+1

#4 -x+2,-y+1,-z+2

Table S6. Bond lengths [Å] and angles [°] for H_2L^2.

S(2A)-C(15)	1.737(8)	N(1)-C(1)-N(2)	116.9(5)
S(2A)-C(9)	1.779(6)	N(1)-C(1)-S(1)	124.3(4)
N(4A)-C(9)	1.297(9)	N(2)-C(1)-S(1)	118.8(5)
N(4A)-C(10)	1.383(11)	N(3)-C(2)-C(3)	120.5(6)
N(4B)-C(9)	1.386(17)	C(4)-C(3)-C(8)	119.3(6)
N(4B)-C(15)	1.391(19)	C(4)-C(3)-C(2)	122.6(5)
S(2B)-C(10)	1.63(3)	C(8)-C(3)-C(2)	118.1(6)
S(2B)-C(9)	1.81(3)	C(5)-C(4)-C(3)	120.3(5)
S(1)-C(1)	1.711(7)	C(4)-C(5)-C(6)	120.4(6)
N(1)-C(1)	1.325(8)	C(7)-C(6)-C(5)	119.2(6)
N(1)-C(16)	1.437(7)	C(7)-C(6)-C(9)	122.2(6)
N(2)-C(1)	1.355(7)	C(5)-C(6)-C(9)	118.5(6)
N(2)-N(3)	1.378(7)	C(8)-C(7)-C(6)	120.7(6)
N(3)-C(2)	1.279(7)	C(7)-C(8)-C(3)	120.1(6)
C(2)-C(3)	1.480(9)	N(4A)-C(9)-C(6)	124.9(6)
C(3)-C(4)	1.390(9)	N(4B)-C(9)-C(6)	137.5(11)
C(3)-C(8)	1.392(8)	N(4A)-C(9)-S(2A)	114.6(5)
C(4)-C(5)	1.379(9)	C(6)-C(9)-S(2A)	120.4(5)
C(5)-C(6)	1.390(9)	N(4B)-C(9)-S(2B)	108.6(14)
C(6)-C(7)	1.382(10)	C(6)-C(9)-S(2B)	113.8(11)
C(6)-C(9)	1.481(9)	N(4A)-C(10)-C(11)	125.4(6)
C(7)-C(8)	1.379(10)	N(4A)-C(10)-C(15)	114.6(7)
C(10)-C(11)	1.388(11)	C(11)-C(10)-C(15)	119.8(7)
C(10)-C(15)	1.392(9)	C(11)-C(10)-S(2B)	105.4(13)
C(11)-C(12)	1.360(11)	C(15)-C(10)-S(2B)	134.8(13)
C(12)-C(13)	1.371(11)	C(12)-C(11)-C(10)	119.2(7)
C(13)-C(14)	1.385(11)	C(11)-C(12)-C(13)	121.6(8)
C(14)-C(15)	1.402(10)	C(12)-C(13)-C(14)	121.0(7)
		C(13)-C(14)-C(15)	117.6(7)
C(15)-S(2A)-C(9)	88.2(3)	N(4B)-C(15)-C(10)	92.0(11)
C(9)-N(4A)-C(10)	112.0(6)	N(4B)-C(15)-C(14)	146.9(11)
C(9)-N(4B)-C(15)	123.7(18)	C(10)-C(15)-C(14)	120.7(7)
C(10)-S(2B)-C(9)	80.1(10)	C(10)-C(15)-S(2A)	110.5(5)
C(1)-N(1)-C(16)	124.6(5)	C(14)-C(15)-S(2A)	128.8(6)
C(1)-N(2)-N(3)	119.4(5)		
C(2)-N(3)-N(2)	116.0(5)		

Table S7. Hydrogen bonds for H_2L^2 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...S(1)#1	0.88	2.59	3.319(6)	141.1
N(2)-H(2)...S(1)#2	0.88	2.42	3.294(6)	172.2
C(2)-H(2A)...S(1)#2	0.95	3.01	3.816(7)	142.9
C(11)-H(11)...N(4)#3	0.95	2.64	3.479(11)	147.2

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,y-1/2,-z+1/2 #2 -x+1,y,-z+1/2 #3 -x+3/2,-y+1/2,-z

Table S8. Bond lengths [Å] and angles [°] for H_2L^4.

S(1)-C(15)	1.6845(18)	C(2)-C(1)-C(6)	117.9(2)
S(2)-C(6)	1.728(2)	C(1)-C(2)-C(3)	121.1(2)
S(2)-C(7)	1.7475(19)	C(2)-C(3)-C(4)	121.7(2)
N(1)-C(7)	1.301(2)	C(3)-C(4)-C(5)	117.9(2)
N(1)-C(5)	1.391(2)	C(6)-C(5)-N(1)	115.19(17)
N(2)-C(14)	1.287(2)	C(6)-C(5)-C(4)	119.86(18)
N(2)-N(3)	1.382(2)	N(1)-C(5)-C(4)	124.94(18)
N(3)-C(15)	1.351(2)	C(5)-C(6)-C(1)	121.46(19)
C(1)-C(2)	1.371(3)	C(5)-C(6)-S(2)	109.77(14)
C(1)-C(6)	1.395(3)	C(1)-C(6)-S(2)	128.77(17)
C(2)-C(3)	1.375(3)	N(1)-C(7)-C(8)	124.49(17)
C(3)-C(4)	1.384(3)	N(1)-C(7)-S(2)	115.61(13)
C(4)-C(5)	1.396(3)	C(8)-C(7)-S(2)	119.90(14)
C(5)-C(6)	1.388(3)	C(13)-C(8)-C(9)	119.09(17)
C(7)-C(8)	1.474(2)	C(13)-C(8)-C(7)	120.76(17)
C(8)-C(13)	1.386(3)	C(9)-C(8)-C(7)	120.15(17)
C(8)-C(9)	1.391(3)	C(10)-C(9)-C(8)	120.38(17)
C(9)-C(10)	1.379(3)	C(9)-C(10)-C(11)	120.92(18)
C(10)-C(11)	1.394(3)	C(10)-C(11)-C(12)	118.42(17)
C(11)-C(12)	1.394(3)	C(10)-C(11)-C(14)	120.97(17)
C(11)-C(14)	1.485(2)	C(12)-C(11)-C(14)	120.60(17)
C(12)-C(13)	1.385(3)	C(13)-C(12)-C(11)	120.62(18)
C(14)-C(16)	1.497(3)	C(12)-C(13)-C(8)	120.50(18)
C(15)-N(4)	1.319(2)	N(2)-C(14)-C(11)	115.84(16)
		N(2)-C(14)-C(16)	124.86(17)
C(6)-S(2)-C(7)	88.99(9)	C(11)-C(14)-C(16)	119.30(16)
C(7)-N(1)-C(5)	110.43(16)	N(4)-C(15)-N(3)	117.89(16)
C(14)-N(2)-N(3)	117.75(15)	N(4)-C(15)-S(1)	123.05(14)
C(15)-N(3)-N(2)	119.32(14)	N(3)-C(15)-S(1)	119.05(13)

Table S9. Hydrogen bonds for H_2L^4 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3)...S(1)#1	0.86	2.78	3.6109(15)	164.1
C(16)-H(16C)...S(1)#1	0.96	2.85	3.431(2)	120.2
N(4)-H(4A)...N(1)#2	0.86	2.42	3.200(2)	150.3
N(4)-H(4B)...S(1)#3	0.86	2.68	3.5174(16)	165.6

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z+2 #2 -x+1/2,y+1/2,-z+3/2 #3 -x+1,-y+2,-z+2

Table S10. Bond lengths [Å] and angles [°] for H_2L^5.

S(2)-C(10)	1.7305(18)	C(5)-C(6)-C(7)	118.51(16)
S(2)-C(9)	1.7491(17)	C(5)-C(6)-C(9)	121.39(16)
S(1)-C(1)	1.6770(19)	C(7)-C(6)-C(9)	120.09(17)
N(2)-C(1)	1.360(3)	C(9)-N(4)-C(11)	110.48(15)
N(2)-N(3)	1.373(2)	N(4)-C(9)-C(6)	124.20(16)
N(3)-C(2)	1.284(2)	N(4)-C(9)-S(2)	115.54(13)
C(8)-C(7)	1.381(3)	C(6)-C(9)-S(2)	120.26(13)
C(8)-C(3)	1.398(3)	C(4)-C(3)-C(8)	117.59(16)
C(6)-C(5)	1.388(3)	C(4)-C(3)-C(2)	121.64(16)
C(6)-C(7)	1.391(3)	C(8)-C(3)-C(2)	120.76(16)
C(6)-C(9)	1.470(2)	C(8)-C(7)-C(6)	120.50(18)
N(4)-C(9)	1.292(2)	N(4)-C(11)-C(10)	115.69(16)
N(4)-C(11)	1.391(2)	N(4)-C(11)-C(12)	124.88(17)
C(3)-C(4)	1.391(3)	C(10)-C(11)-C(12)	119.41(17)
C(3)-C(2)	1.482(2)	C(1)-N(1)-C(17)	124.09(19)
C(11)-C(10)	1.393(3)	N(3)-C(2)-C(3)	115.64(16)
C(11)-C(12)	1.399(3)	N(3)-C(2)-C(16)	123.74(16)
N(1)-C(1)	1.316(3)	C(3)-C(2)-C(16)	120.61(16)
N(1)-C(17)	1.451(3)	C(4)-C(5)-C(6)	120.83(17)
C(2)-C(16)	1.492(3)	C(15)-C(10)-C(11)	122.00(18)
C(5)-C(4)	1.388(3)	C(15)-C(10)-S(2)	129.11(16)
C(10)-C(15)	1.387(3)	C(11)-C(10)-S(2)	108.89(13)
C(13)-C(12)	1.376(3)	C(5)-C(4)-C(3)	121.04(18)
C(13)-C(14)	1.387(3)	N(1)-C(1)-N(2)	115.55(17)
C(14)-C(15)	1.375(3)	N(1)-C(1)-S(1)	124.10(15)
		N(2)-C(1)-S(1)	120.34(15)
C(10)-S(2)-C(9)	89.38(8)	C(12)-C(13)-C(14)	121.16(19)
C(1)-N(2)-N(3)	118.26(16)	C(13)-C(12)-C(11)	118.5(2)
C(2)-N(3)-N(2)	118.91(16)	C(15)-C(14)-C(13)	121.37(19)
C(7)-C(8)-C(3)	121.50(17)	C(14)-C(15)-C(10)	117.6(2)

Table S11. Hydrogen bonds for H_2L^5 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...S(1)#1	0.86	2.82	3.6741(17)	175.0
C(16)-H(16B)...S(2)#2	0.96	3.01	3.892(2)	153.7
C(16)-H(16C)...S(1)#1	0.96	2.91	3.442(2)	116.4

Symmetry transformations used to generate equivalent atoms:

#1 -x-1/2,-y+5/2,-z #2 -x,-y,-z

Table S12. Bond lengths [Å] and angles [°] for H_2L^7.(DMSO)**.**

C(1)-N(1)	1.319(5)	N(3)-C(2)-C(16)	125.9(4)
C(1)-N(2)	1.360(5)	C(3)-C(2)-C(16)	120.1(4)
C(1)-S(1)	1.671(4)	C(8)-C(3)-C(4)	116.7(4)
C(2)-N(3)	1.286(5)	C(8)-C(3)-C(2)	121.3(4)
C(2)-C(3)	1.483(6)	C(4)-C(3)-C(2)	122.0(4)
C(2)-C(16)	1.490(6)	C(5)-C(4)-C(3)	121.7(4)
C(3)-C(8)	1.384(6)	C(4)-C(5)-C(6)	120.6(4)
C(3)-C(4)	1.395(6)	C(5)-C(6)-C(7)	118.2(4)
C(4)-C(5)	1.376(6)	C(5)-C(6)-C(9)	121.3(4)
C(5)-C(6)	1.384(6)	C(7)-C(6)-C(9)	120.5(4)
C(6)-C(7)	1.398(6)	C(8)-C(7)-C(6)	120.4(4)
C(6)-C(9)	1.452(6)	C(7)-C(8)-C(3)	122.5(4)
C(7)-C(8)	1.363(6)	N(4)-C(9)-O(1)	114.7(4)
C(9)-N(4)	1.302(6)	N(4)-C(9)-C(6)	127.9(4)
C(9)-O(1)	1.365(5)	O(1)-C(9)-C(6)	117.4(4)
C(10)-C(15)	1.371(6)	C(15)-C(10)-C(11)	119.5(4)
C(10)-C(11)	1.386(6)	C(15)-C(10)-N(4)	109.4(4)
C(10)-N(4)	1.396(6)	C(11)-C(10)-N(4)	131.1(4)
C(11)-C(12)	1.360(7)	C(12)-C(11)-C(10)	117.9(5)
C(12)-C(13)	1.392(7)	C(11)-C(12)-C(13)	121.8(5)
C(13)-C(14)	1.388(7)	C(14)-C(13)-C(12)	121.6(5)
C(14)-C(15)	1.385(6)	C(15)-C(14)-C(13)	114.7(5)
C(15)-O(1)	1.382(5)	C(10)-C(15)-O(1)	107.4(4)
N(2)-N(3)	1.379(5)	C(10)-C(15)-C(14)	124.4(4)
C(1S)-S(1S)	1.764(6)	O(1)-C(15)-C(14)	128.2(4)
C(2S)-S(1S)	1.765(6)	C(1)-N(2)-N(3)	117.1(4)
O(1S)-S(1S)	1.498(3)	C(2)-N(3)-N(2)	120.1(4)
		C(9)-N(4)-C(10)	104.2(4)
N(1)-C(1)-N(2)	116.1(4)	C(9)-O(1)-C(15)	104.3(3)
N(1)-C(1)-S(1)	123.1(3)	O(1S)-S(1S)-C(1S)	106.9(3)
N(2)-C(1)-S(1)	120.7(3)	O(1S)-S(1S)-C(2S)	105.0(3)
N(3)-C(2)-C(3)	114.0(4)	C(1S)-S(1S)-C(2S)	97.3(3)

Table S13. Hydrogen bonds for H_2L^7.(DMSO) **[Å and °].**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(16)-H(16C)...O(1S)#1	0.96	2.31	3.268(6)	172.8
N(1)-H(1B)...O(1S)#2	0.86	2.19	2.885(5)	137.8
N(2)-H(2)...O(1S)#1	0.99(6)	1.94(6)	2.918(5)	168(5)
N(2)-H(2)...S(1S)#1	0.99(6)	2.98(6)	3.816(4)	142(4)
C(2S)-H(2S2)...S(1)#3	0.96	2.99	3.929(6)	166.4
C(2S)-H(2S3)...S(1)#4	0.96	2.99	3.914(7)	161.9

Symmetry transformations used to generate equivalent atoms: #1 x,y+1,z #2 x+1,y+1,z #3 -x+2,-y+2,-z+1 #4 x-1,y-1,z

Table 14. Bond lengths [Å] and angles [°] for H_2L^8.(DMSO)**.**

C(1)-N(1)	1.320(6)	N(3)-C(2)-C(16)	124.9(4)
C(1)-N(2)	1.357(5)	C(3)-C(2)-C(16)	120.3(3)
C(1)-S(1)	1.683(4)	C(8)-C(3)-C(4)	117.2(3)
C(1S)-S(1S)	1.758(7)	C(8)-C(3)-C(2)	121.0(3)
C(2)-N(3)	1.291(5)	C(4)-C(3)-C(2)	121.8(3)
C(2)-C(3)	1.481(5)	C(5)-C(4)-C(3)	121.2(4)
C(2)-C(16)	1.491(5)	C(4)-C(5)-C(6)	121.2(4)
C(2S)-S(1S)	1.775(6)	C(5)-C(6)-C(7)	118.0(4)
C(3)-C(8)	1.394(6)	C(5)-C(6)-C(9)	122.2(4)
C(3)-C(4)	1.400(5)	C(7)-C(6)-C(9)	119.8(4)
C(4)-C(5)	1.377(6)	C(8)-C(7)-C(6)	121.1(4)
C(5)-C(6)	1.377(6)	C(7)-C(8)-C(3)	121.3(4)
C(6)-C(7)	1.398(5)	O(1)-C(9)-N(4)	114.6(3)
C(6)-C(9)	1.447(6)	O(1)-C(9)-C(6)	123.8(4)
C(7)-C(8)	1.371(6)	N(4)-C(9)-C(6)	121.5(4)
C(9)-O(1)	1.320(5)	C(11)-C(10)-C(15)	121.8(4)
C(9)-N(4)	1.338(6)	C(11)-C(10)-O(1)	130.5(4)
C(10)-C(11)	1.374(6)	C(15)-C(10)-O(1)	107.6(3)
C(10)-C(15)	1.381(6)	C(10)-C(11)-C(12)	115.6(4)
C(10)-O(1)	1.399(5)	C(13)-C(12)-C(11)	122.4(4)
C(11)-C(12)	1.395(7)	C(14)-C(13)-C(12)	121.7(4)
C(12)-C(13)	1.377(7)	C(13)-C(14)-C(15)	116.1(4)
C(13)-C(14)	1.375(6)	C(10)-C(15)-C(14)	122.4(4)
C(14)-C(15)	1.382(6)	C(10)-C(15)-N(4)	108.1(3)
C(15)-N(4)	1.391(5)	C(14)-C(15)-N(4)	129.4(4)
C(17)-N(1)	1.451(6)	C(1)-N(1)-C(17)	125.1(4)
N(2)-N(3)	1.369(4)	C(1)-N(2)-N(3)	118.1(3)
O(1S)-S(1S)	1.505(3)	C(2)-N(3)-N(2)	119.3(3)
		C(9)-N(4)-C(15)	104.6(3)
N(1)-C(1)-N(2)	116.4(4)	C(9)-O(1)-C(10)	105.0(3)
N(1)-C(1)-S(1)	124.4(3)	O(1S)-S(1S)-C(1S)	105.6(3)
N(2)-C(1)-S(1)	119.2(3)	O(1S)-S(1S)-C(2S)	105.3(2)
N(3)-C(2)-C(3)	114.8(3)	C(1S)-S(1S)-C(2S)	98.1(4)

Table S15. Hydrogen bonds for H_2L^8.(DMSO) **[Å and °].**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(16)-H(16A)...O(1S)	0.96	2.32	3.231(5)	158.4
C(16)-H(16B)...S(1)#1	0.96	2.86	3.728(5)	150.6
C(17)-H(17A)...S(1S)#2	0.96	2.94	3.678(5)	134.2
N(2)-H(2)...O(1S)	0.86	2.21	2.944(5)	143.9

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y-1/2,-z+1/2 #2 x+1,y,z

Table S16. Bond lengths [Å] and angles [°] for 4a.

Re(1)-C(22)	1.907(4)	C(22)-Re(1)-Cl(1)	176.70(11)
Re(1)-C(21)	1.912(4)	C(21)-Re(1)-Cl(1)	91.06(12)
Re(1)-C(20)	1.950(4)	C(20)-Re(1)-Cl(1)	91.60(11)
Re(1)-N(3)	2.239(3)	N(3)-Re(1)-Cl(1)	82.00(8)
Re(1)-S(1)	2.4543(13)	S(1)-Re(1)-Cl(1)	86.87(5)
Re(1)-Cl(1)	2.5075(18)	C(1)-S(1)-Re(1)	98.72(12)
S(1)-C(1)	1.696(4)	C(2)-N(3)-N(2)	115.8(3)
N(3)-C(2)	1.291(4)	C(2)-N(3)-Re(1)	130.0(2)
N(3)-N(2)	1.399(4)	N(2)-N(3)-Re(1)	113.81(19)
O(20)-C(20)	1.132(5)	C(1)-N(2)-N(3)	122.0(3)
N(2)-C(1)	1.343(4)	O(20)-C(20)-Re(1)	174.5(3)
O(21)-C(21)	1.133(5)	N(3)-C(2)-C(3)	118.6(3)
C(2)-C(3)	1.483(5)	N(3)-C(2)-C(16)	125.0(3)
C(2)-C(16)	1.492(5)	C(3)-C(2)-C(16)	116.4(3)
C(3)-C(4)	1.385(5)	O(21)-C(21)-Re(1)	177.5(4)
C(3)-C(8)	1.393(5)	C(4)-C(3)-C(8)	119.1(3)
C(1)-N(1)	1.321(5)	C(4)-C(3)-C(2)	120.3(3)
C(5)-C(4)	1.378(5)	C(8)-C(3)-C(2)	120.5(3)
C(5)-C(6)	1.399(5)	N(1)-C(1)-N(2)	117.0(3)
C(6)-C(7)	1.384(5)	N(1)-C(1)-S(1)	121.0(3)
C(6)-C(9)	1.470(5)	N(2)-C(1)-S(1)	122.0(3)
S(2)-C(15)	1.734(5)	C(4)-C(5)-C(6)	120.5(3)
S(2)-C(9)	1.741(4)	C(7)-C(6)-C(5)	119.1(3)
O(22)-C(22)	1.138(5)	C(7)-C(6)-C(9)	119.3(3)
N(4)-C(9)	1.301(5)	C(5)-C(6)-C(9)	121.6(3)
N(4)-C(10)	1.395(5)	C(5)-C(4)-C(3)	120.5(3)
C(7)-C(8)	1.383(5)	C(15)-S(2)-C(9)	89.3(2)
C(10)-C(15)	1.388(7)	C(9)-N(4)-C(10)	110.1(4)
C(10)-C(11)	1.405(7)	C(8)-C(7)-C(6)	120.2(3)
C(15)-C(14)	1.397(7)	O(22)-C(22)-Re(1)	179.1(4)
C(11)-C(12)	1.383(9)	C(7)-C(8)-C(3)	120.6(3)
C(13)-C(14)	1.363(9)	C(15)-C(10)-N(4)	115.6(4)
C(13)-C(12)	1.382(10)	C(15)-C(10)-C(11)	119.0(5)
		N(4)-C(10)-C(11)	125.4(5)
C(22)-Re(1)-C(21)	90.98(16)	N(4)-C(9)-C(6)	124.1(4)
C(22)-Re(1)-C(20)	91.16(16)	N(4)-C(9)-S(2)	115.8(3)
C(21)-Re(1)-C(20)	85.03(15)	C(6)-C(9)-S(2)	120.1(3)
C(22)-Re(1)-N(3)	95.71(14)	C(10)-C(15)-C(14)	122.5(5)
C(21)-Re(1)-N(3)	170.96(13)	C(10)-C(15)-S(2)	109.2(3)
C(20)-Re(1)-N(3)	100.87(13)	C(14)-C(15)-S(2)	128.3(5)
C(22)-Re(1)-S(1)	90.38(12)	C(12)-C(11)-C(10)	118.0(6)
C(21)-Re(1)-S(1)	94.81(12)	C(14)-C(13)-C(12)	121.7(5)
C(20)-Re(1)-S(1)	178.46(10)	C(13)-C(12)-C(11)	121.5(6)
N(3)-Re(1)-S(1)	79.11(8)	C(13)-C(14)-C(15)	117.2(6)

Table S17. Hydrogen bonds for 4a [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...Cl(1)#1	0.86	2.43	3.246(3)	158.0
C(16)-H(16C)...Cl(1)#1	0.96	3.07	3.604(4)	116.3
N(1)-H(1A)...Cl(1)#2	0.86	2.78	3.338(3)	123.7
N(1)-H(1A)...Cl(1)#1	0.86	2.55	3.336(4)	151.4
N(1)-H(1B)...S(1)#3	0.86	3.02	3.799(4)	151.8

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z #2 x-1,y,z #3 -x,-y+3,-z

Table S18. Bond lengths [Å] and angles [°] for 4b.

N(4A)-C(9)	1.180(16)	C(20)-Re(1)-Br(1)	92.40(17)
N(4A)-C(10)	1.461(15)	C(21)-Re(1)-Br(1)	89.67(17)
S(2A)-C(11)	1.663(9)	N(3)-Re(1)-Br(1)	82.74(11)
S(2A)-C(9)	1.824(11)	S(1)-Re(1)-Br(1)	85.84(4)
S(2B)-C(10)	1.700(9)	C(1)-S(1)-Re(1)	99.32(17)
S(2B)-C(9)	1.837(8)	C(2)-N(3)-N(2)	115.4(4)
N(4B)-C(9)	1.283(17)	C(2)-N(3)-Re(1)	127.7(3)
N(4B)-C(11)	1.424(15)	N(2)-N(3)-Re(1)	114.4(3)
C(12)-C(11)	1.367(13)	C(1)-N(2)-N(3)	121.4(4)
C(12)-C(13)	1.375(14)	N(3)-C(2)-C(3)	118.9(4)
Re(1)-C(22)	1.891(7)	N(3)-C(2)-C(16)	123.3(4)
Re(1)-C(20)	1.899(6)	C(3)-C(2)-C(16)	117.7(4)
Re(1)-C(21)	1.936(6)	O(20)-C(20)-Re(1)	178.4(6)
Re(1)-N(3)	2.237(4)	N(1)-C(1)-N(2)	116.5(5)
Re(1)-S(1)	2.4527(13)	N(1)-C(1)-S(1)	121.2(4)
Re(1)-Br(1)	2.6619(7)	N(2)-C(1)-S(1)	122.3(4)
S(1)-C(1)	1.691(5)	C(4)-C(3)-C(8)	119.1(5)
N(3)-C(2)	1.303(6)	C(4)-C(3)-C(2)	122.6(5)
N(3)-N(2)	1.398(5)	C(8)-C(3)-C(2)	118.0(5)
N(2)-C(1)	1.347(6)	C(5)-C(6)-C(7)	119.4(5)
C(2)-C(3)	1.483(7)	C(5)-C(6)-C(9)	122.8(6)
C(2)-C(16)	1.496(7)	C(7)-C(6)-C(9)	117.7(6)
C(20)-O(20)	1.150(6)	N(4A)-C(9)-N(4B)	98.9(12)
N(1)-C(1)	1.322(6)	N(4A)-C(9)-C(6)	129.9(10)
C(3)-C(4)	1.374(8)	N(4B)-C(9)-C(6)	131.2(9)
C(3)-C(8)	1.405(8)	N(4A)-C(9)-S(2A)	111.4(8)
C(6)-C(5)	1.372(9)	N(4B)-C(9)-S(2A)	12.8(9)
C(6)-C(7)	1.402(9)	C(6)-C(9)-S(2A)	118.7(5)
C(6)-C(9)	1.483(9)	N(4A)-C(9)-S(2B)	14.6(7)
C(8)-C(7)	1.387(7)	N(4B)-C(9)-S(2B)	113.4(10)
C(5)-C(4)	1.379(8)	C(6)-C(9)-S(2B)	115.4(6)
C(21)-O(21)	1.139(7)	S(2A)-C(9)-S(2B)	125.9(4)
C(11)-C(10)	1.359(11)	C(7)-C(8)-C(3)	119.9(5)
C(10)-C(15)	1.388(11)	C(6)-C(5)-C(4)	120.6(6)
C(15)-C(14)	1.348(13)	C(3)-C(4)-C(5)	121.0(6)
O(22)-C(22)	1.124(7)	C(8)-C(7)-C(6)	119.9(6)
C(13)-C(14)	1.334(15)	O(21)-C(21)-Re(1)	176.8(5)
		C(10)-C(11)-C(12)	122.5(8)
C(9)-N(4A)-C(10)	122.9(11)	C(10)-C(11)-N(4B)	102.7(11)
C(11)-S(2A)-C(9)	83.1(5)	C(12)-C(11)-N(4B)	134.8(13)
C(10)-S(2B)-C(9)	82.1(4)	C(10)-C(11)-S(2A)	124.7(7)
C(9)-N(4B)-C(11)	117.6(15)	C(12)-C(11)-S(2A)	112.8(9)
C(11)-C(12)-C(13)	117.3(11)	N(4B)-C(11)-S(2A)	22.2(8)
C(22)-Re(1)-C(20)	89.4(2)	C(11)-C(10)-C(15)	118.9(8)
C(22)-Re(1)-C(21)	89.7(3)	C(11)-C(10)-N(4A)	97.9(8)
C(20)-Re(1)-C(21)	87.3(2)	C(15)-C(10)-N(4A)	143.2(10)
C(22)-Re(1)-N(3)	95.6(2)	C(11)-C(10)-S(2B)	124.1(6)
C(20)-Re(1)-N(3)	172.23(18)	C(15)-C(10)-S(2B)	117.0(8)
C(21)-Re(1)-N(3)	98.68(19)	N(4A)-C(10)-S(2B)	26.3(5)
C(22)-Re(1)-S(1)	94.7(2)	C(14)-C(15)-C(10)	117.8(9)
C(20)-Re(1)-S(1)	94.29(17)	O(22)-C(22)-Re(1)	176.8(6)
C(21)-Re(1)-S(1)	175.28(17)	C(14)-C(13)-C(12)	120.2(11)
N(3)-Re(1)-S(1)	79.35(10)	C(13)-C(14)-C(15)	123.3(10)
C(22)-Re(1)-Br(1)	178.08(17)		

Table S19. Hydrogen bonds for 4b [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...Br(1)#1	0.86	2.78	3.436(4)	134.5
N(1)-H(1A)...Br(1)#1	0.86	2.83	3.540(5)	141.4
N(1)-H(1A)...Br(1)#2	0.86	3.00	3.574(4)	125.7
N(1)-H(1B)...O(20)#3	0.86	2.53	3.338(6)	156.4
C(16)-H(16A)...O(20)#4	0.96	2.36	3.218(7)	149.2
C(16)-H(16C)...Br(1)#1	0.96	3.00	3.753(6)	136.1

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x,-y,-z+1 #3 -x+1,-y+1,-z+1

#4 x-1,y-1,z

Table S20. Bond lengths [Å] and angles [°] for 6a.

Re(1)-C(23)	1.902(6)	C(24)-Re(1)-Cl(1)	90.09(17)
Re(1)-C(24)	1.926(5)	C(25)-Re(1)-Cl(1)	177.35(16)
Re(1)-C(25)	1.936(6)	N(3)-Re(1)-Cl(1)	80.58(9)
Re(1)-N(3)	2.247(3)	S(1)-Re(1)-Cl(1)	85.84(4)
Re(1)-S(1)	2.4424(11)	C(1)-N(1)-C(17)	129.2(4)
Re(1)-Cl(1)	2.5204(12)	C(1)-N(2)-N(3)	122.7(4)
O(23)-C(23)	1.153(7)	C(2)-N(3)-N(2)	115.0(3)
O(24)-C(24)	1.146(6)	C(2)-N(3)-Re(1)	129.8(3)
O(25)-C(25)	1.090(7)	N(2)-N(3)-Re(1)	112.8(2)
N(1)-C(1)	1.337(5)	C(9)-N(4)-C(10)	110.7(4)
N(1)-C(17)	1.420(5)	C(1)-S(1)-Re(1)	98.38(14)
N(2)-C(1)	1.349(5)	C(15)-S(2)-C(9)	89.0(2)
N(2)-N(3)	1.375(5)	N(1)-C(1)-N(2)	114.3(4)
N(3)-C(2)	1.301(5)	N(1)-C(1)-S(1)	123.6(3)
N(4)-C(9)	1.287(6)	N(2)-C(1)-S(1)	122.1(3)
N(4)-C(10)	1.400(6)	N(3)-C(2)-C(3)	120.0(4)
S(1)-C(1)	1.688(4)	N(3)-C(2)-C(16)	122.6(4)
S(2)-C(15)	1.734(5)	C(3)-C(2)-C(16)	117.3(4)
S(2)-C(9)	1.760(5)	C(4)-C(3)-C(8)	119.1(4)
C(2)-C(3)	1.486(6)	C(4)-C(3)-C(2)	121.0(4)
C(2)-C(16)	1.499(6)	C(8)-C(3)-C(2)	119.7(4)
C(3)-C(4)	1.383(6)	C(3)-C(4)-C(5)	120.6(4)
C(3)-C(8)	1.393(6)	C(4)-C(5)-C(6)	120.3(4)
C(4)-C(5)	1.386(6)	C(7)-C(6)-C(5)	119.2(4)
C(5)-C(6)	1.388(7)	C(7)-C(6)-C(9)	121.6(4)
C(6)-C(7)	1.384(6)	C(5)-C(6)-C(9)	119.2(4)
C(6)-C(9)	1.476(6)	C(6)-C(7)-C(8)	120.4(4)
C(7)-C(8)	1.388(6)	C(7)-C(8)-C(3)	120.3(4)
C(10)-C(15)	1.385(7)	N(4)-C(9)-C(6)	123.0(4)
C(10)-C(11)	1.392(7)	N(4)-C(9)-S(2)	115.5(3)
C(11)-C(12)	1.372(8)	C(6)-C(9)-S(2)	121.5(4)
C(12)-C(13)	1.380(9)	C(15)-C(10)-C(11)	119.7(5)
C(13)-C(14)	1.375(8)	C(15)-C(10)-N(4)	115.4(4)
C(14)-C(15)	1.389(7)	C(11)-C(10)-N(4)	124.8(5)
C(17)-C(22)	1.375(6)	C(12)-C(11)-C(10)	118.8(6)
C(17)-C(18)	1.380(7)	C(11)-C(12)-C(13)	120.8(5)
C(18)-C(19)	1.374(8)	C(14)-C(13)-C(12)	121.5(5)
C(19)-C(20)	1.378(9)	C(13)-C(14)-C(15)	117.6(6)
C(20)-C(21)	1.361(9)	C(10)-C(15)-C(14)	121.5(5)
C(21)-C(22)	1.372(7)	C(10)-C(15)-S(2)	109.4(4)
		C(14)-C(15)-S(2)	129.1(4)
C(23)-Re(1)-C(24)	89.50(19)	C(22)-C(17)-C(18)	120.0(4)
C(23)-Re(1)-C(25)	88.06(19)	C(22)-C(17)-N(1)	124.5(4)
C(24)-Re(1)-C(25)	91.8(3)	C(18)-C(17)-N(1)	115.5(4)
C(23)-Re(1)-N(3)	170.39(16)	C(19)-C(18)-C(17)	119.9(5)
C(24)-Re(1)-N(3)	98.26(16)	C(18)-C(19)-C(20)	120.1(6)
C(25)-Re(1)-N(3)	97.31(16)	C(21)-C(20)-C(19)	119.5(5)
C(23)-Re(1)-S(1)	92.30(14)	C(20)-C(21)-C(22)	121.3(5)
C(24)-Re(1)-S(1)	175.64(17)	C(21)-C(22)-C(17)	119.3(5)
C(25)-Re(1)-S(1)	92.22(19)	O(23)-C(23)-Re(1)	178.5(5)
N(3)-Re(1)-S(1)	79.58(9)	O(24)-C(24)-Re(1)	178.3(4)
C(23)-Re(1)-Cl(1)	93.80(14)	O(25)-C(25)-Re(1)	176.3(6)

Table S21. Hydrogen bonds for 6a [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(14)-H(14)...Cl(1)#1	0.93	2.86	3.684(6)	148.6
C(16)-H(16A)...S(1)#2	0.96	3.03	3.862(6)	146.0
C(22)-H(22)...S(1)	0.93	2.68	3.179(5)	114.7
N(2)-H(2)...Cl(1)#2	0.76(5)	2.75(5)	3.402(4)	146(4)
N(1)-H(1)...Cl(1)#2	0.76(5)	2.44(5)	3.193(4)	172(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z #2 -x+2,y+1/2,-z+1/2

Table S22. Bond lengths [Å] and angles [°] for 6b.(C_7H_8).

C(22)-C(14)	1.494(5)	C(23)-Re(1)-N(2)	99.15(14)
Re(1)-C(24)	1.889(4)	C(24)-Re(1)-S(2)	92.44(13)
Re(1)-C(25)	1.908(4)	C(25)-Re(1)-S(2)	94.65(12)
Re(1)-C(23)	1.936(4)	C(23)-Re(1)-S(2)	175.65(13)
Re(1)-N(2)	2.233(3)	N(2)-Re(1)-S(2)	79.14(8)
Re(1)-S(2)	2.4558(10)	C(24)-Re(1)-Br(1)	179.06(13)
Re(1)-Br(1)	2.6546(5)	C(25)-Re(1)-Br(1)	91.24(13)
S(1)-C(6)	1.738(4)	C(23)-Re(1)-Br(1)	88.31(13)
S(1)-C(7)	1.743(4)	N(2)-Re(1)-Br(1)	84.82(7)
S(2)-C(15)	1.681(3)	S(2)-Re(1)-Br(1)	87.56(3)
N(1)-C(7)	1.295(5)	C(6)-S(1)-C(7)	89.1(2)
N(1)-C(5)	1.387(5)	C(15)-S(2)-Re(1)	99.27(12)
N(2)-C(14)	1.293(4)	C(7)-N(1)-C(5)	110.4(4)
N(2)-N(3)	1.392(4)	C(14)-N(2)-N(3)	115.0(3)
N(3)-C(15)	1.360(4)	C(14)-N(2)-Re(1)	130.9(2)
N(4)-C(15)	1.337(4)	N(3)-N(2)-Re(1)	113.72(19)
N(4)-C(16)	1.427(4)	C(15)-N(3)-N(2)	121.9(3)
C(1)-C(2)	1.356(7)	C(15)-N(4)-C(16)	131.2(3)
C(1)-C(6)	1.372(6)	C(2)-C(1)-C(6)	118.5(5)
C(2)-C(3)	1.367(7)	C(1)-C(2)-C(3)	121.3(5)
C(3)-C(4)	1.374(7)	C(2)-C(3)-C(4)	121.0(5)
C(4)-C(5)	1.401(6)	C(3)-C(4)-C(5)	118.0(5)
C(5)-C(6)	1.370(6)	C(6)-C(5)-N(1)	116.1(4)
C(7)-C(8)	1.472(5)	C(6)-C(5)-C(4)	119.5(4)
C(8)-C(9)	1.381(6)	N(1)-C(5)-C(4)	124.3(4)
C(8)-C(13)	1.382(6)	C(5)-C(6)-C(1)	121.7(4)
C(9)-C(10)	1.384(6)	C(5)-C(6)-S(1)	109.0(3)
C(10)-C(11)	1.380(5)	C(1)-C(6)-S(1)	129.4(4)
C(11)-C(12)	1.377(5)	N(1)-C(7)-C(8)	123.8(4)
C(11)-C(14)	1.487(5)	N(1)-C(7)-S(1)	115.3(3)
C(12)-C(13)	1.383(6)	C(8)-C(7)-S(1)	120.9(3)
C(16)-C(21)	1.379(5)	C(9)-C(8)-C(13)	119.1(4)
C(16)-C(17)	1.382(5)	C(9)-C(8)-C(7)	118.7(4)
C(17)-C(18)	1.382(6)	C(13)-C(8)-C(7)	122.1(4)
C(18)-C(19)	1.360(7)	C(8)-C(9)-C(10)	120.3(4)
C(19)-C(20)	1.369(6)	C(11)-C(10)-C(9)	120.6(4)
C(20)-C(21)	1.373(6)	C(12)-C(11)-C(10)	118.8(4)
C(25)-O(25)	1.136(5)	C(12)-C(11)-C(14)	121.5(3)
C(23)-O(23)	1.119(5)	C(10)-C(11)-C(14)	119.6(3)
C(24)-O(24)	1.129(5)	C(11)-C(12)-C(13)	120.8(4)
C(7S)-C(2S)	1.491(13)	C(8)-C(13)-C(12)	120.1(4)
C(1S)-C(6S)	1.356(12)	N(2)-C(14)-C(11)	119.1(3)
C(1S)-C(2S)	1.384(12)	N(2)-C(14)-C(22)	124.5(3)
C(2S)-C(3S)	1.358(12)	C(11)-C(14)-C(22)	116.3(3)
C(3S)-C(4S)	1.396(16)	N(4)-C(15)-N(3)	113.4(3)
C(4S)-C(5S)	1.370(17)	N(4)-C(15)-S(2)	125.1(3)
C(5S)-C(6S)	1.415(14)	N(3)-C(15)-S(2)	121.6(3)
		C(21)-C(16)-C(17)	119.5(4)
C(24)-Re(1)-C(25)	87.82(18)	C(21)-C(16)-N(4)	125.3(3)
C(24)-Re(1)-C(23)	91.72(19)	C(17)-C(16)-N(4)	115.2(3)
C(25)-Re(1)-C(23)	86.78(17)	C(16)-C(17)-C(18)	119.7(4)
C(24)-Re(1)-N(2)	96.10(14)	C(19)-C(18)-C(17)	121.0(4)
C(25)-Re(1)-N(2)	172.76(14)	C(18)-C(19)-C(20)	118.9(4)

C(19)-C(20)-C(21)	121.6(4)	C(3S)-C(2S)-C(7S)	117.6(14)
C(20)-C(21)-C(16)	119.3(4)	C(1S)-C(2S)-C(7S)	122.8(11)
O(25)-C(25)-Re(1)	178.5(4)	C(2S)-C(3S)-C(4S)	120.0(13)
O(23)-C(23)-Re(1)	176.9(4)	C(5S)-C(4S)-C(3S)	119.3(13)
O(24)-C(24)-Re(1)	177.7(4)	C(4S)-C(5S)-C(6S)	121.5(14)
C(6S)-C(1S)-C(2S)	122.9(11)	C(1S)-C(6S)-C(5S)	116.7(12)
C(3S)-C(2S)-C(1S)	119.6(11)		

Table S23. Hydrogen bonds for 6b.(C_7H_8) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(22)-H(22B)...S(1)#1	0.96	3.00	3.668(4)	127.5
C(22)-H(22C)...Br(1)#2	0.96	3.13	3.811(4)	129.0
N(3)-H(3)...Br(1)#2	0.86	2.70	3.487(3)	153.4
N(4)-H(4)...Br(1)#2	0.86	2.46	3.307(3)	170.3
C(17)-H(17)...O(25)#3	0.93	2.52	3.319(5)	143.9
C(21)-H(21)...S(2)	0.93	2.62	3.206(4)	121.3

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1 #2 -x+1,-y+1,-z #3 x-1,y,z

Table S24. Bond lengths [Å] and angles [°] for 8b.(H_2O).

S(2)-C(1)	1.683(6)	N(3)-Re(1)-S(2)	78.72(13)
S(2)-Re(1)	2.4648(16)	C(31)-Re(1)-Br(1)	89.6(2)
Re(1)-C(31)	1.897(7)	C(32)-Re(1)-Br(1)	177.3(2)
Re(1)-C(32)	1.931(8)	C(30)-Re(1)-Br(1)	87.7(2)
Re(1)-C(30)	1.940(7)	N(3)-Re(1)-Br(1)	83.93(13)
Re(1)-N(3)	2.256(5)	S(2)-Re(1)-Br(1)	87.70(5)
Re(1)-Br(1)	2.6361(8)	N(1)-C(1)-N(2)	114.8(6)
C(1)-N(1)	1.322(8)	N(1)-C(1)-S(2)	122.7(5)
C(1)-N(2)	1.353(8)	N(2)-C(1)-S(2)	122.5(4)
C(2)-N(3)	1.294(8)	N(3)-C(2)-C(17)	123.6(6)
C(2)-C(17)	1.491(9)	N(3)-C(2)-C(3)	118.9(5)
C(2)-C(3)	1.494(8)	C(17)-C(2)-C(3)	117.5(6)
C(3)-C(8)	1.385(10)	C(8)-C(3)-C(4)	120.0(6)
C(3)-C(4)	1.395(9)	C(8)-C(3)-C(2)	119.9(6)
C(4)-C(5)	1.390(9)	C(4)-C(3)-C(2)	119.9(6)
C(5)-C(6)	1.404(10)	C(5)-C(4)-C(3)	119.6(6)
C(6)-C(7)	1.392(10)	C(4)-C(5)-C(6)	119.9(6)
C(6)-C(9)	1.463(9)	C(7)-C(6)-C(5)	119.1(6)
C(7)-C(8)	1.373(10)	C(7)-C(6)-C(9)	120.8(6)
C(9)-N(5)	1.288(9)	C(5)-C(6)-C(9)	120.1(6)
C(9)-O(1)	1.367(8)	C(8)-C(7)-C(6)	120.6(6)
C(10)-C(11)	1.363(10)	C(7)-C(8)-C(3)	120.2(6)
C(10)-O(1)	1.366(9)	N(5)-C(9)-O(1)	115.2(6)
C(10)-C(15)	1.371(11)	N(5)-C(9)-C(6)	126.8(6)
C(11)-C(12)	1.401(13)	O(1)-C(9)-C(6)	117.9(6)
C(12)-C(13)	1.405(14)	C(11)-C(10)-O(1)	127.8(8)
C(13)-C(14)	1.375(13)	C(11)-C(10)-C(15)	124.8(8)
C(14)-C(15)	1.398(11)	O(1)-C(10)-C(15)	107.4(6)
C(15)-N(5)	1.416(9)	C(10)-C(11)-C(12)	115.5(9)
C(16)-N(1)	1.461(10)	C(11)-C(12)-C(13)	121.1(8)
C(30)-O(30)	1.132(9)	C(14)-C(13)-C(12)	121.3(8)
C(31)-O(31)	1.156(9)	C(13)-C(14)-C(15)	117.6(9)
C(32)-O(32)	1.114(9)	C(10)-C(15)-C(14)	119.7(7)
N(2)-N(3)	1.390(7)	C(10)-C(15)-N(5)	109.0(6)
		C(14)-C(15)-N(5)	131.2(8)
C(1)-S(2)-Re(1)	98.5(2)	O(30)-C(30)-Re(1)	177.3(6)
C(31)-Re(1)-C(32)	87.8(3)	O(31)-C(31)-Re(1)	179.0(7)
C(31)-Re(1)-C(30)	87.3(3)	O(32)-C(32)-Re(1)	179.3(8)
C(32)-Re(1)-C(30)	91.4(3)	C(1)-N(1)-C(16)	123.4(6)
C(31)-Re(1)-N(3)	171.0(2)	C(1)-N(2)-N(3)	121.7(5)
C(32)-Re(1)-N(3)	98.7(2)	C(2)-N(3)-N(2)	115.4(5)
C(30)-Re(1)-N(3)	98.6(2)	C(2)-N(3)-Re(1)	131.1(4)
C(31)-Re(1)-S(2)	94.8(2)	N(2)-N(3)-Re(1)	113.2(4)
C(32)-Re(1)-S(2)	93.3(2)	C(9)-N(5)-C(15)	103.6(6)
C(30)-Re(1)-S(2)	174.9(2)	C(10)-O(1)-C(9)	104.8(5)

Table S25. Hydrogen bonds for 8b.(H_2O) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(11)-H(11)...Br(1)#1	0.93	2.96	3.853(9)	160.4
C(16)-H(16B)...Br(1)#2	0.96	2.89	3.795(8)	156.7
N(1)-H(1)...O(1S)#3	0.86	2.11	2.903(9)	152.5
N(2)-H(2)...O(1S)#3	0.86	2.17	2.947(8)	149.3

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z+1 #2 -x,-y+1,-z #3 x-1,y,z

Table S26. Bond lengths [Å] and angles [°] for 2c.

S(21)-C(10)	1.722(9)	C(5A)-C(6A)	1.390(12)
S(21)-C(9)	1.826(11)	C(5)-C(6)	1.381(13)
N(41)-C(9)	1.197(15)	C(6A)-C(7A)	1.399(12)
N(41)-C(15)	1.419(14)	C(6A)-C(9A)	1.465(11)
S(22)-C(15)	1.722(18)	C(6)-C(7)	1.360(13)
S(22)-C(9)	1.967(16)	C(6)-C(9)	1.495(12)
N(42)-C(9)	1.21(4)	C(7)-C(8)	1.391(11)
N(42)-C(10)	1.58(3)	C(7A)-C(8A)	1.396(11)
S(2A1)-C(10A)	1.61(2)	C(10A)-C(15A)	1.339(15)
S(2A1)-C(9A)	1.812(14)	C(10A)-C(11A)	1.367(14)
N(4A1)-C(9A)	1.08(4)	C(10)-C(11)	1.394(16)
N(4A1)-C(15A)	1.69(3)	C(10)-C(15)	1.399(16)
N(4A2)-C(9A)	1.260(18)	C(11)-C(12)	1.356(17)
N(4A2)-C(10A)	1.45(2)	C(11A)-C(12A)	1.312(19)
S(2A2)-C(15A)	1.675(12)	C(12A)-C(13A)	1.30(2)
S(2A2)-C(9A)	1.794(10)	C(12)-C(13)	1.339(19)
Re(1)-C(21A)	1.919(9)	C(13A)-C(14A)	1.36(2)
Re(1)-C(20A)	1.928(8)	C(13)-C(14)	1.385(19)
Re(1)-C(22A)	1.932(9)	C(14A)-C(15A)	1.467(19)
Re(1)-N(3A)	2.209(5)	C(14)-C(15)	1.383(15)
Re(1)-S(1A)	2.4597(16)		
Re(1)-S(1)	2.5557(18)	C(10)-S(21)-C(9)	86.0(5)
Re(2)-C(20)	1.895(7)	C(9)-N(41)-C(15)	116.7(12)
Re(2)-C(21)	1.913(9)	C(15)-S(22)-C(9)	74.1(7)
Re(2)-C(22)	1.944(8)	C(9)-N(42)-C(10)	120(3)
Re(2)-N(3)	2.205(6)	C(10A)-S(2A1)-C(9A)	82.3(8)
Re(2)-S(1)	2.4581(17)	C(9A)-N(4A1)-C(15A)	118(2)
Re(2)-S(1A)	2.5407(16)	C(9A)-N(4A2)-C(10A)	112.4(15)
S(1)-C(1)	1.769(7)	C(15A)-S(2A2)-C(9A)	87.2(5)
S(1A)-C(1A)	1.776(6)	C(21A)-Re(1)-C(20A)	88.3(3)
N(1A)-C(1A)	1.347(9)	C(21A)-Re(1)-C(22A)	88.9(3)
N(1A)-C(16A)	1.446(9)	C(20A)-Re(1)-C(22A)	90.9(3)
N(1)-C(1)	1.357(9)	C(21A)-Re(1)-N(3A)	93.2(3)
N(1)-C(16)	1.436(10)	C(20A)-Re(1)-N(3A)	172.8(3)
N(2)-C(1)	1.297(8)	C(22A)-Re(1)-N(3A)	96.2(3)
N(2)-N(3)	1.388(8)	C(21A)-Re(1)-S(1A)	94.1(2)
N(2A)-C(1A)	1.301(8)	C(20A)-Re(1)-S(1A)	94.3(2)
N(2A)-N(3A)	1.393(8)	C(22A)-Re(1)-S(1A)	174.1(2)
N(3)-C(2)	1.287(9)	N(3A)-Re(1)-S(1A)	78.59(16)
N(3A)-C(2A)	1.286(9)	C(21A)-Re(1)-S(1)	173.7(2)
O(20)-C(20)	1.168(9)	C(20A)-Re(1)-S(1)	86.5(3)
O(20A)-C(20A)	1.134(10)	C(22A)-Re(1)-S(1)	94.8(3)
O(21)-C(21)	1.148(10)	N(3A)-Re(1)-S(1)	91.46(16)
O(21A)-C(21A)	1.143(10)	S(1A)-Re(1)-S(1)	82.69(5)
O(22)-C(22)	1.131(9)	C(20)-Re(2)-C(21)	87.7(3)
O(22A)-C(22A)	1.130(10)	C(20)-Re(2)-C(22)	91.9(3)
C(2A)-C(3A)	1.465(10)	C(21)-Re(2)-C(22)	92.0(3)
C(2)-C(3)	1.453(10)	C(20)-Re(2)-N(3)	172.8(3)
C(3)-C(4)	1.383(12)	C(21)-Re(2)-N(3)	91.9(3)
C(3)-C(8)	1.386(11)	C(22)-Re(2)-N(3)	95.3(3)
C(3A)-C(8A)	1.388(11)	C(20)-Re(2)-S(1)	94.5(3)
C(3A)-C(4A)	1.416(10)	C(21)-Re(2)-S(1)	95.5(2)
C(4A)-C(5A)	1.361(11)	C(22)-Re(2)-S(1)	170.2(2)
C(4)-C(5)	1.372(12)	N(3)-Re(2)-S(1)	78.38(16)

C(20)-Re(2)-S(1A)	88.0(2)	C(3A)-C(8A)-C(7A)	120.4(8)
C(21)-Re(2)-S(1A)	175.3(2)	N(4A1)-C(9A)-C(6A)	125.4(17)
C(22)-Re(2)-S(1A)	89.9(2)	N(4A2)-C(9A)-C(6A)	126.1(12)
N(3)-Re(2)-S(1A)	92.16(16)	N(4A2)-C(9A)-S(2A2)	114.1(12)
S(1)-Re(2)-S(1A)	83.03(5)	C(6A)-C(9A)-S(2A2)	119.8(7)
C(1)-S(1)-Re(2)	96.5(2)	N(4A1)-C(9A)-S(2A1)	116.8(17)
C(1)-S(1)-Re(1)	105.6(2)	C(6A)-C(9A)-S(2A1)	117.8(10)
Re(2)-S(1)-Re(1)	96.91(6)	N(41)-C(9)-C(6)	126.7(11)
C(1A)-S(1A)-Re(1)	96.6(2)	N(42)-C(9)-C(6)	130.2(16)
C(1A)-S(1A)-Re(2)	104.2(2)	N(41)-C(9)-S(21)	114.5(9)
Re(1)-S(1A)-Re(2)	97.27(6)	C(6)-C(9)-S(21)	118.8(7)
C(1A)-N(1A)-C(16A)	122.9(7)	N(42)-C(9)-S(22)	115.9(15)
C(1)-N(1)-C(16)	123.7(7)	C(6)-C(9)-S(22)	113.4(9)
C(1)-N(2)-N(3)	116.0(6)	C(15A)-C(10A)-C(11A)	120.7(11)
C(1A)-N(2A)-N(3A)	116.2(5)	C(15A)-C(10A)-N(4A2)	110.2(10)
C(2)-N(3)-N(2)	114.2(6)	C(11A)-C(10A)-N(4A2)	129.1(13)
C(2)-N(3)-Re(2)	125.3(5)	C(15A)-C(10A)-S(2A1)	131.5(9)
N(2)-N(3)-Re(2)	120.4(4)	C(11A)-C(10A)-S(2A1)	107.6(11)
C(2A)-N(3A)-N(2A)	115.1(5)	C(11)-C(10)-C(15)	121.3(9)
C(2A)-N(3A)-Re(1)	124.5(5)	C(11)-C(10)-N(42)	148.4(19)
N(2A)-N(3A)-Re(1)	120.5(4)	C(15)-C(10)-N(42)	89.8(17)
N(2)-C(1)-N(1)	118.4(6)	C(11)-C(10)-S(21)	124.5(10)
N(2)-C(1)-S(1)	126.0(6)	C(15)-C(10)-S(21)	114.0(8)
N(1)-C(1)-S(1)	115.5(5)	C(12)-C(11)-C(10)	116.9(12)
N(2A)-C(1A)-N(1A)	118.7(6)	C(12A)-C(11A)-C(10A)	120.4(15)
N(2A)-C(1A)-S(1A)	125.9(5)	C(13A)-C(12A)-C(11A)	122.1(15)
N(1A)-C(1A)-S(1A)	115.4(5)	C(13)-C(12)-C(11)	122.1(11)
N(3A)-C(2A)-C(3A)	130.8(7)	C(12A)-C(13A)-C(14A)	122.4(13)
N(3)-C(2)-C(3)	132.4(7)	C(12)-C(13)-C(14)	122.9(11)
C(4)-C(3)-C(8)	116.5(7)	C(13A)-C(14A)-C(15A)	116.3(13)
C(4)-C(3)-C(2)	126.6(7)	C(15)-C(14)-C(13)	116.7(13)
C(8)-C(3)-C(2)	116.9(8)	C(14)-C(15)-C(10)	119.9(10)
C(8A)-C(3A)-C(4A)	117.5(7)	C(14)-C(15)-N(41)	131.4(13)
C(8A)-C(3A)-C(2A)	126.8(7)	C(10)-C(15)-N(41)	108.7(10)
C(4A)-C(3A)-C(2A)	115.7(7)	C(14)-C(15)-S(22)	102.2(11)
C(5A)-C(4A)-C(3A)	121.8(7)	C(10)-C(15)-S(22)	137.9(9)
C(5)-C(4)-C(3)	121.5(8)	O(20)-C(20)-Re(2)	176.2(6)
C(4A)-C(5A)-C(6A)	121.1(8)	O(20A)-C(20A)-Re(1)	177.3(8)
C(4)-C(5)-C(6)	120.7(10)	O(21)-C(21)-Re(2)	176.6(8)
C(5A)-C(6A)-C(7A)	117.9(7)	O(21A)-C(21A)-Re(1)	177.0(7)
C(5A)-C(6A)-C(9A)	121.2(8)	O(22A)-C(22A)-Re(1)	179.9(9)
C(7A)-C(6A)-C(9A)	121.0(8)	O(22)-C(22)-Re(2)	175.2(7)
C(7)-C(6)-C(5)	119.5(8)	C(10A)-C(15A)-C(14A)	117.9(11)
C(7)-C(6)-C(9)	120.8(8)	C(10A)-C(15A)-S(2A2)	116.0(8)
C(5)-C(6)-C(9)	119.6(9)	C(14A)-C(15A)-S(2A2)	126.1(10)
C(6)-C(7)-C(8)	119.2(8)	C(10A)-C(15A)-N(4A1)	90.9(14)
C(8A)-C(7A)-C(6A)	121.4(8)	C(14A)-C(15A)-N(4A1)	150.9(17)
C(3)-C(8)-C(7)	122.6(9)		

Table S27. Hydrogen bonds for 2c [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1A)-H(1A)...O(20A)#1	0.86	2.28	3.099(8)	157.9
N(1)-H(1)...O(22A)#2	0.86	2.46	3.146(9)	137.1
C(11A)-H(11A)...S(22)#3	0.93	2.58	3.50(2)	168.8

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z #2 -x+2,-y+1,-z #3 -x+5/2,y-1/2,-z+1/2

Table S28. Bond lengths [Å] and angles [°] for 3c.(C_3H_6O).

Re(1)-C(23A)	1.84(2)	N(4B)-C(9B)	1.57(2)
Re(1)-C(22A)	1.84(3)	C(2B)-C(3B)	1.41(2)
Re(1)-C(24A)	1.902(18)	C(3B)-C(8B)	1.40(2)
Re(1)-N(3A)	2.187(14)	C(3B)-C(4B)	1.43(2)
Re(1)-S(1B)	2.464(4)	C(4B)-C(5B)	1.37(2)
Re(1)-S(1A)	2.559(4)	C(5B)-C(6B)	1.40(2)
Re(2)-C(23B)	1.83(2)	C(6B)-C(7B)	1.36(2)
Re(2)-C(22B)	1.84(2)	C(6B)-C(9B)	1.47(2)
Re(2)-C(24B)	1.908(15)	C(7B)-C(8B)	1.34(2)
Re(2)-N(3B)	2.190(15)	C(10B)-C(15B)	1.41(2)
Re(2)-S(1A)	2.448(4)	C(10B)-C(11B)	1.49(3)
Re(2)-S(1B)	2.549(4)	C(11B)-C(12B)	1.47(4)
S(1A)-C(1B)	1.745(19)	C(12B)-C(13B)	1.36(4)
S(2A)-C(15A)	1.684(18)	C(13B)-C(14B)	1.22(4)
S(2A)-C(9A)	1.750(19)	C(14B)-C(15B)	1.40(3)
N(1A)-C(1A)	1.34(2)	C(16B)-C(17B)	1.35(3)
N(1A)-C(16A)	1.40(2)	C(16B)-C(21B)	1.41(2)
N(2A)-C(1A)	1.329(18)	C(17B)-C(18B)	1.34(3)
N(2A)-N(3A)	1.401(18)	C(18B)-C(19B)	1.39(3)
N(3A)-C(2A)	1.321(18)	C(19B)-C(20B)	1.39(3)
N(4A)-C(10A)	1.43(2)	C(20B)-C(21B)	1.38(3)
N(4A)-C(9A)	1.47(2)	O(22B)-C(22B)	1.22(2)
C(1A)-S(1B)	1.766(17)	O(23B)-C(23B)	1.25(2)
C(2A)-C(3A)	1.48(2)	O(24B)-C(24B)	1.143(19)
C(3A)-C(4A)	1.36(2)	Re(3)-C(22C)	1.76(3)
C(3A)-C(8A)	1.39(2)	Re(3)-C(24C)	1.84(5)
C(4A)-C(5A)	1.31(2)	Re(3)-C(23C)	1.863(19)
C(5A)-C(6A)	1.46(2)	Re(3)-N(3C)	2.212(16)
C(6A)-C(7A)	1.39(2)	Re(3)-S(1C)	2.444(5)
C(6A)-C(9A)	1.46(2)	Re(3)-S(1D)	2.557(5)
C(7A)-C(8A)	1.36(2)	Re(4)-C(23D)	1.72(3)
C(10A)-C(11A)	1.41(3)	Re(4)-C(22D)	1.89(3)
C(10A)-C(15A)	1.42(3)	Re(4)-C(24D)	1.97(3)
C(11A)-C(12A)	1.30(4)	Re(4)-N(3D)	2.176(19)
C(12A)-C(13A)	1.39(4)	Re(4)-S(1D)	2.454(5)
C(13A)-C(14A)	1.43(4)	Re(4)-S(1C)	2.577(6)
C(14A)-C(15A)	1.41(3)	S(1C)-C(1C)	1.79(2)
C(16A)-C(17A)	1.37(2)	S(2C)-C(10C)	1.693(19)
C(16A)-C(21A)	1.42(2)	S(2C)-C(9C)	1.759(18)
C(17A)-C(18A)	1.36(3)	N(1C)-C(1C)	1.35(2)
C(18A)-C(19A)	1.36(3)	N(1C)-C(16C)	1.38(2)
C(19A)-C(20A)	1.40(3)	N(2C)-C(1C)	1.29(2)
C(20A)-C(21A)	1.38(3)	N(2C)-N(3C)	1.36(2)
O(22A)-C(22A)	1.26(3)	N(3C)-C(2C)	1.31(2)
O(23A)-C(23A)	1.19(2)	N(4C)-C(15C)	1.40(2)
O(24A)-C(24A)	1.18(2)	N(4C)-C(9C)	1.59(2)
S(2B)-C(10B)	1.61(2)	C(2C)-C(3C)	1.45(3)
S(2B)-C(9B)	1.730(18)	C(3C)-C(8C)	1.36(2)
N(1B)-C(1B)	1.36(2)	C(3C)-C(4C)	1.38(2)
N(1B)-C(16B)	1.41(2)	C(4C)-C(5C)	1.42(2)
N(2B)-C(1B)	1.33(2)	C(5C)-C(6C)	1.36(2)
N(2B)-N(3B)	1.404(18)	C(6C)-C(7C)	1.43(2)
N(3B)-C(2B)	1.33(2)	C(6C)-C(9C)	1.45(2)
N(4B)-C(15B)	1.47(2)	C(7C)-C(8C)	1.36(2)

C(10C)-C(11C)	1.41(3)
C(10C)-C(15C)	1.42(3)
C(11C)-C(12C)	1.44(4)
C(12C)-C(13C)	1.31(4)
C(13C)-C(14C)	1.37(4)
C(14C)-C(15C)	1.40(4)
C(16C)-C(17C)	1.40(2)
C(16C)-C(21C)	1.42(3)
C(17C)-C(18C)	1.32(2)
C(18C)-C(19C)	1.38(3)
C(19C)-C(20C)	1.36(3)
C(20C)-C(21C)	1.30(3)
O(22C)-C(22C)	1.33(3)
O(23C)-C(23C)	1.17(2)
O(24C)-C(24C)	1.19(4)
S(1D)-C(1D)	1.82(2)
S(2D)-C(10D)	1.656(16)
S(2D)-C(9D)	1.772(18)
N(1D)-C(1D)	1.32(3)
N(1D)-C(16D)	1.42(3)
N(2D)-C(1D)	1.34(3)
N(2D)-N(3D)	1.45(2)
N(3D)-C(2D)	1.35(2)
N(4D)-C(9D)	1.45(2)
N(4D)-C(15D)	1.479(18)
C(2D)-C(3D)	1.46(3)
C(3D)-C(8D)	1.37(3)
C(3D)-C(4D)	1.37(2)
C(4D)-C(5D)	1.44(3)
C(5D)-C(6D)	1.43(3)
C(6D)-C(9D)	1.41(3)
C(6D)-C(7D)	1.45(2)
C(7D)-C(8D)	1.35(3)
C(10D)-C(11D)	1.3900
C(10D)-C(15D)	1.3900
C(11D)-C(12D)	1.3900
C(12D)-C(13D)	1.3900
C(13D)-C(14D)	1.3900
C(14D)-C(15D)	1.3900
C(16D)-C(17D)	1.36(3)
C(16D)-C(21D)	1.43(3)
C(17D)-C(18D)	1.43(3)
C(18D)-C(19D)	1.35(3)
C(19D)-C(20D)	1.38(3)
C(20D)-C(21D)	1.35(4)
O(22D)-C(22D)	1.11(3)
O(23D)-C(23D)	1.33(3)
O(24D)-C(24D)	1.10(3)

C(23A)-Re(1)-C(22A)	90.9(8)
C(23A)-Re(1)-C(24A)	89.0(9)
C(22A)-Re(1)-C(24A)	88.2(8)
C(23A)-Re(1)-N(3A)	87.4(7)
C(22A)-Re(1)-N(3A)	173.2(6)
C(24A)-Re(1)-N(3A)	98.3(7)
C(23A)-Re(1)-S(1B)	96.5(7)
C(22A)-Re(1)-S(1B)	95.7(5)
C(24A)-Re(1)-S(1B)	173.1(6)
N(3A)-Re(1)-S(1B)	78.0(4)
C(23A)-Re(1)-S(1A)	177.9(6)
C(22A)-Re(1)-S(1A)	88.5(5)
C(24A)-Re(1)-S(1A)	93.0(6)
N(3A)-Re(1)-S(1A)	93.0(3)
S(1B)-Re(1)-S(1A)	81.47(13)
C(23B)-Re(2)-C(22B)	88.0(9)
C(23B)-Re(2)-C(24B)	86.3(9)
C(22B)-Re(2)-C(24B)	92.0(8)
C(23B)-Re(2)-N(3B)	91.4(8)
C(22B)-Re(2)-N(3B)	171.7(7)
C(24B)-Re(2)-N(3B)	96.3(7)
C(23B)-Re(2)-S(1A)	97.5(8)
C(22B)-Re(2)-S(1A)	93.9(6)
C(24B)-Re(2)-S(1A)	173.1(6)
N(3B)-Re(2)-S(1A)	78.0(4)
C(23B)-Re(2)-S(1B)	177.7(8)
C(22B)-Re(2)-S(1B)	89.8(5)
C(24B)-Re(2)-S(1B)	94.4(5)
N(3B)-Re(2)-S(1B)	90.7(4)
S(1A)-Re(2)-S(1B)	81.98(13)
C(1B)-S(1A)-Re(2)	97.9(6)
C(1B)-S(1A)-Re(1)	103.3(6)
Re(2)-S(1A)-Re(1)	98.29(14)
C(15A)-S(2A)-C(9A)	89.4(9)
C(1A)-N(1A)-C(16A)	130.6(14)
C(1A)-N(2A)-N(3A)	114.6(13)
C(2A)-N(3A)-N(2A)	112.7(13)
C(2A)-N(3A)-Re(1)	124.3(12)
N(2A)-N(3A)-Re(1)	122.9(9)
C(10A)-N(4A)-C(9A)	99.7(15)
N(2A)-C(1A)-N(1A)	120.3(15)
N(2A)-C(1A)-S(1B)	125.2(14)
N(1A)-C(1A)-S(1B)	114.5(11)
N(3A)-C(2A)-C(3A)	132.4(16)
C(4A)-C(3A)-C(8A)	118.6(15)
C(4A)-C(3A)-C(2A)	125.3(13)
C(8A)-C(3A)-C(2A)	116.1(15)
C(5A)-C(4A)-C(3A)	121.4(15)
C(4A)-C(5A)-C(6A)	122.4(17)
C(7A)-C(6A)-C(5A)	115.5(16)
C(7A)-C(6A)-C(9A)	122.3(14)
C(5A)-C(6A)-C(9A)	122.1(17)
C(8A)-C(7A)-C(6A)	120.6(14)
C(7A)-C(8A)-C(3A)	121.4(16)
C(6A)-C(9A)-N(4A)	120.6(15)
C(6A)-C(9A)-S(2A)	120.4(12)
N(4A)-C(9A)-S(2A)	118.9(12)
C(11A)-C(10A)-C(15A)	117(2)
C(11A)-C(10A)-N(4A)	123(2)
C(15A)-C(10A)-N(4A)	120.8(16)
C(12A)-C(11A)-C(10A)	123(3)
C(11A)-C(12A)-C(13A)	121(3)
C(12A)-C(13A)-C(14A)	122(2)
C(15A)-C(14A)-C(13A)	114(2)
C(14A)-C(15A)-C(10A)	123.1(19)

C(14A)-C(15A)-S(2A)	125.8(17)	C(20B)-C(21B)-C(16B)	119.5(19)
C(10A)-C(15A)-S(2A)	111.1(14)	O(22B)-C(22B)-Re(2)	173.7(15)
C(17A)-C(16A)-N(1A)	117.5(16)	O(23B)-C(23B)-Re(2)	177(2)
C(17A)-C(16A)-C(21A)	118.6(17)	O(24B)-C(24B)-Re(2)	176.5(17)
N(1A)-C(16A)-C(21A)	123.8(16)	C(22C)-Re(3)-C(24C)	89.8(12)
C(18A)-C(17A)-C(16A)	119.9(17)	C(22C)-Re(3)-C(23C)	88.5(11)
C(17A)-C(18A)-C(19A)	123(2)	C(24C)-Re(3)-C(23C)	92.7(12)
C(18A)-C(19A)-C(20A)	118.8(19)	C(22C)-Re(3)-N(3C)	174.0(9)
C(21A)-C(20A)-C(19A)	119(2)	C(24C)-Re(3)-N(3C)	89.5(9)
C(20A)-C(21A)-C(16A)	120.3(18)	C(23C)-Re(3)-N(3C)	97.5(9)
O(22A)-C(22A)-Re(1)	178.2(15)	C(22C)-Re(3)-S(1C)	96.3(9)
O(23A)-C(23A)-Re(1)	178.6(18)	C(24C)-Re(3)-S(1C)	93.3(8)
O(24A)-C(24A)-Re(1)	174(2)	C(23C)-Re(3)-S(1C)	172.3(9)
C(1A)-S(1B)-Re(1)	97.5(6)	N(3C)-Re(3)-S(1C)	77.8(4)
C(1A)-S(1B)-Re(2)	105.4(5)	C(22C)-Re(3)-S(1D)	88.5(9)
Re(1)-S(1B)-Re(2)	98.16(13)	C(24C)-Re(3)-S(1D)	175.3(9)
C(10B)-S(2B)-C(9B)	89.1(9)	C(23C)-Re(3)-S(1D)	91.7(9)
C(1B)-N(1B)-C(16B)	128.4(16)	N(3C)-Re(3)-S(1D)	91.8(4)
C(1B)-N(2B)-N(3B)	114.3(14)	S(1C)-Re(3)-S(1D)	82.48(18)
C(2B)-N(3B)-N(2B)	112.8(14)	C(23D)-Re(4)-C(22D)	88.6(10)
C(2B)-N(3B)-Re(2)	125.3(11)	C(23D)-Re(4)-C(24D)	94.0(12)
N(2B)-N(3B)-Re(2)	121.8(11)	C(22D)-Re(4)-C(24D)	90.6(12)
C(15B)-N(4B)-C(9B)	94.2(11)	C(23D)-Re(4)-N(3D)	170.8(10)
N(2B)-C(1B)-N(1B)	119.5(16)	C(22D)-Re(4)-N(3D)	91.5(8)
N(2B)-C(1B)-S(1A)	125.6(13)	C(24D)-Re(4)-N(3D)	95.2(9)
N(1B)-C(1B)-S(1A)	114.6(14)	C(23D)-Re(4)-S(1D)	92.0(9)
N(3B)-C(2B)-C(3B)	132.2(16)	C(22D)-Re(4)-S(1D)	96.5(7)
C(8B)-C(3B)-C(2B)	127.1(16)	C(24D)-Re(4)-S(1D)	170.8(7)
C(8B)-C(3B)-C(4B)	118.4(15)	N(3D)-Re(4)-S(1D)	78.9(5)
C(2B)-C(3B)-C(4B)	114.5(14)	C(23D)-Re(4)-S(1C)	87.8(8)
C(5B)-C(4B)-C(3B)	119.1(14)	C(22D)-Re(4)-S(1C)	176.0(6)
C(4B)-C(5B)-C(6B)	121.9(15)	C(24D)-Re(4)-S(1C)	91.4(10)
C(7B)-C(6B)-C(5B)	116.7(15)	N(3D)-Re(4)-S(1C)	91.7(4)
C(7B)-C(6B)-C(9B)	121.6(14)	S(1D)-Re(4)-S(1C)	81.87(17)
C(5B)-C(6B)-C(9B)	121.6(15)	C(1C)-S(1C)-Re(3)	97.7(7)
C(8B)-C(7B)-C(6B)	125.0(16)	C(1C)-S(1C)-Re(4)	102.9(7)
C(7B)-C(8B)-C(3B)	118.8(17)	Re(3)-S(1C)-Re(4)	97.67(19)
C(6B)-C(9B)-N(4B)	120.4(13)	C(10C)-S(2C)-C(9C)	87.6(9)
C(6B)-C(9B)-S(2B)	119.3(12)	C(1C)-N(1C)-C(16C)	131.3(17)
N(4B)-C(9B)-S(2B)	120.4(11)	C(1C)-N(2C)-N(3C)	117.9(15)
C(15B)-C(10B)-C(11B)	119(2)	C(2C)-N(3C)-N(2C)	115.2(16)
C(15B)-C(10B)-S(2B)	115.1(15)	C(2C)-N(3C)-Re(3)	123.4(13)
C(11B)-C(10B)-S(2B)	125.5(18)	N(2C)-N(3C)-Re(3)	121.4(12)
C(12B)-C(11B)-C(10B)	112(2)	C(15C)-N(4C)-C(9C)	96.8(14)
C(13B)-C(12B)-C(11B)	124(2)	N(2C)-C(1C)-N(1C)	122.0(18)
C(14B)-C(13B)-C(12B)	121(3)	N(2C)-C(1C)-S(1C)	123.6(14)
C(13B)-C(14B)-C(15B)	125(3)	N(1C)-C(1C)-S(1C)	114.3(16)
C(14B)-C(15B)-C(10B)	119(2)	N(3C)-C(2C)-C(3C)	133.3(18)
C(14B)-C(15B)-N(4B)	119.8(19)	C(8C)-C(3C)-C(4C)	118.8(16)
C(10B)-C(15B)-N(4B)	121.1(15)	C(8C)-C(3C)-C(2C)	124.0(17)
C(17B)-C(16B)-C(21B)	116.9(16)	C(4C)-C(3C)-C(2C)	117.2(17)
C(17B)-C(16B)-N(1B)	126.6(16)	C(3C)-C(4C)-C(5C)	119.3(16)
C(21B)-C(16B)-N(1B)	116.3(17)	C(6C)-C(5C)-C(4C)	121.4(16)
C(18B)-C(17B)-C(16B)	125(2)	C(5C)-C(6C)-C(7C)	118.1(16)
C(17B)-C(18B)-C(19B)	119(2)	C(5C)-C(6C)-C(9C)	121.9(15)
C(20B)-C(19B)-C(18B)	118(2)	C(7C)-C(6C)-C(9C)	119.8(15)
C(21B)-C(20B)-C(19B)	121(2)	C(8C)-C(7C)-C(6C)	119.0(16)

C(7C)-C(8C)-C(3C)	123.2(17)	N(2D)-C(1D)-S(1D)	124(2)
C(6C)-C(9C)-N(4C)	121.4(13)	N(3D)-C(2D)-C(3D)	130(2)
C(6C)-C(9C)-S(2C)	119.6(13)	C(8D)-C(3D)-C(4D)	120.8(19)
N(4C)-C(9C)-S(2C)	118.8(12)	C(8D)-C(3D)-C(2D)	127.9(19)
C(11C)-C(10C)-C(15C)	121.3(19)	C(4D)-C(3D)-C(2D)	111.3(18)
C(11C)-C(10C)-S(2C)	124.9(16)	C(3D)-C(4D)-C(5D)	119.7(17)
C(15C)-C(10C)-S(2C)	113.8(14)	C(6D)-C(5D)-C(4D)	120.3(16)
C(10C)-C(11C)-C(12C)	117(2)	C(9D)-C(6D)-C(5D)	122.9(16)
C(13C)-C(12C)-C(11C)	122(3)	C(9D)-C(6D)-C(7D)	122.1(18)
C(12C)-C(13C)-C(14C)	121(3)	C(5D)-C(6D)-C(7D)	114.9(19)
C(13C)-C(14C)-C(15C)	123(3)	C(8D)-C(7D)-C(6D)	123(2)
C(14C)-C(15C)-N(4C)	121(2)	C(7D)-C(8D)-C(3D)	121.3(19)
C(14C)-C(15C)-C(10C)	116(2)	C(6D)-C(9D)-N(4D)	123.1(15)
N(4C)-C(15C)-C(10C)	122.9(19)	C(6D)-C(9D)-S(2D)	118.2(13)
N(1C)-C(16C)-C(17C)	125.2(17)	N(4D)-C(9D)-S(2D)	118.7(13)
N(1C)-C(16C)-C(21C)	119.5(17)	C(11D)-C(10D)-C(15D)	120.0
C(17C)-C(16C)-C(21C)	115.3(17)	C(11D)-C(10D)-S(2D)	126.6(11)
C(18C)-C(17C)-C(16C)	124.1(19)	C(15D)-C(10D)-S(2D)	113.4(11)
C(17C)-C(18C)-C(19C)	119(2)	C(12D)-C(11D)-C(10D)	120.0
C(20C)-C(19C)-C(18C)	118(2)	C(11D)-C(12D)-C(13D)	120.0
C(21C)-C(20C)-C(19C)	124(2)	C(14D)-C(13D)-C(12D)	120.0
C(20C)-C(21C)-C(16C)	119(2)	C(13D)-C(14D)-C(15D)	120.0
O(22C)-C(22C)-Re(3)	174(2)	C(14D)-C(15D)-C(10D)	120.0
O(23C)-C(23C)-Re(3)	174(3)	C(14D)-C(15D)-N(4D)	120.8(13)
O(24C)-C(24C)-Re(3)	177(2)	C(10D)-C(15D)-N(4D)	119.2(13)
C(1D)-S(1D)-Re(4)	97.9(10)	C(17D)-C(16D)-N(1D)	122.7(19)
C(1D)-S(1D)-Re(3)	104.9(7)	C(17D)-C(16D)-C(21D)	120(2)
Re(4)-S(1D)-Re(3)	97.94(19)	N(1D)-C(16D)-C(21D)	117(2)
C(10D)-S(2D)-C(9D)	89.1(8)	C(16D)-C(17D)-C(18D)	117(2)
C(1D)-N(1D)-C(16D)	127.2(19)	C(19D)-C(18D)-C(17D)	125(3)
C(1D)-N(2D)-N(3D)	114(2)	C(18D)-C(19D)-C(20D)	114(2)
C(2D)-N(3D)-N(2D)	112(2)	C(21D)-C(20D)-C(19D)	125(2)
C(2D)-N(3D)-Re(4)	124.2(16)	C(20D)-C(21D)-C(16D)	119(3)
N(2D)-N(3D)-Re(4)	122.9(14)	O(22D)-C(22D)-Re(4)	170(2)
C(9D)-N(4D)-C(15D)	99.5(14)	O(23D)-C(23D)-Re(4)	173(2)
N(1D)-C(1D)-N(2D)	123(2)	O(24D)-C(24D)-Re(4)	174(3))
N(1D)-C(1D)-S(1D)	113.2(19)		

Table S29. Hydrogen bonds for 3c.(C_3H_6O) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1A)-H(1A)...O(22A)#1	0.86	2.29	3.15(2)	174.1
N(1B)-H(1B)...O(1S)	0.86	2.15	2.98(3)	162.6
C(17B)-H(17B)...N(2B)	0.93	2.47	2.95(3)	112.0
C(21A)-H(21A)...N(2A)	0.93	2.32	2.88(3)	118.6
C(17C)-H(17C)...N(2C)	0.93	2.38	2.95(3)	119.1
C(17D)-H(17D)...N(2D)	0.93	2.47	2.95(3)	112.1

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2

Table S30. Bond lengths [Å] and angles [°] for 5c.

Re(1)-C(22)	1.905(8)	C(20)-Re(1)-S(1)#1	176.9(2)
Re(1)-C(20)	1.926(9)	C(21)-Re(1)-S(1)#1	91.1(2)
Re(1)-C(21)	1.927(8)	N(3)-Re(1)-S(1)#1	84.49(15)
Re(1)-N(3)	2.209(5)	S(1)-Re(1)-S(1)#1	82.00(6)
Re(1)-S(1)	2.4676(18)	C(1)-S(1)-Re(1)	96.2(2)
Re(1)-S(1)#1	2.5640(18)	C(1)-S(1)-Re(1)#1	97.9(2)
S(1)-C(1)	1.780(7)	Re(1)-S(1)-Re(1)#1	98.00(6)
S(1)-Re(1)#1	2.5641(18)	C(2)-N(3)-N(2)	110.9(6)
N(3)-C(2)	1.306(9)	C(2)-N(3)-Re(1)	129.7(5)
N(3)-N(2)	1.419(8)	N(2)-N(3)-Re(1)	119.4(4)
N(2)-C(1)	1.289(9)	C(1)-N(2)-N(3)	116.2(6)
O(22)-C(22)	1.151(9)	N(2)-C(1)-N(1)	118.8(6)
O(20)-C(20)	1.134(10)	N(2)-C(1)-S(1)	126.0(6)
C(1)-N(1)	1.337(9)	N(1)-C(1)-S(1)	115.1(5)
C(21)-O(21)	1.150(9)	O(20)-C(20)-Re(1)	177.6(7)
N(1)-C(17)	1.451(10)	O(21)-C(21)-Re(1)	175.0(7)
C(8)-C(7)	1.372(11)	C(1)-N(1)-C(17)	121.0(7)
C(8)-C(3)	1.384(11)	O(22)-C(22)-Re(1)	179.0(7)
C(2)-C(16)	1.494(10)	C(7)-C(8)-C(3)	120.5(7)
C(2)-C(3)	1.491(10)	N(3)-C(2)-C(16)	122.0(7)
C(3)-C(4)	1.392(10)	N(3)-C(2)-C(3)	120.1(6)
C(6)-C(7)	1.390(11)	C(16)-C(2)-C(3)	117.7(6)
C(6)-C(5)	1.391(11)	C(8)-C(3)-C(4)	119.4(7)
C(6)-C(9)	1.458(10)	C(8)-C(3)-C(2)	119.3(6)
C(5)-C(4)	1.388(11)	C(4)-C(3)-C(2)	120.6(7)
C(9)-N(4)	1.301(9)	C(7)-C(6)-C(5)	118.2(7)
C(9)-S(2)	1.770(8)	C(7)-C(6)-C(9)	122.2(7)
S(2)-C(15)	1.740(9)	C(5)-C(6)-C(9)	119.6(7)
N(4)-C(10)	1.380(10)	C(4)-C(5)-C(6)	121.0(7)
C(10)-C(15)	1.399(12)	C(3)-C(4)-C(5)	119.7(8)
C(10)-C(11)	1.401(12)	C(8)-C(7)-C(6)	121.1(8)
C(15)-C(14)	1.393(13)	N(4)-C(9)-C(6)	125.6(7)
C(11)-C(12)	1.352(13)	N(4)-C(9)-S(2)	114.2(6)
C(12)-C(13)	1.408(15)	C(6)-C(9)-S(2)	120.1(6)
C(14)-C(13)	1.371(15)	C(15)-S(2)-C(9)	89.7(4)
		C(9)-N(4)-C(10)	111.6(7)
C(22)-Re(1)-C(20)	87.5(3)	N(4)-C(10)-C(15)	116.1(7)
C(22)-Re(1)-C(21)	86.5(3)	N(4)-C(10)-C(11)	126.0(8)
C(20)-Re(1)-C(21)	91.1(3)	C(15)-C(10)-C(11)	117.8(8)
C(22)-Re(1)-N(3)	171.9(3)	C(14)-C(15)-C(10)	123.1(9)
C(20)-Re(1)-N(3)	93.0(3)	C(14)-C(15)-S(2)	128.4(8)
C(21)-Re(1)-N(3)	101.5(3)	C(10)-C(15)-S(2)	108.4(6)
C(22)-Re(1)-S(1)	93.4(3)	C(12)-C(11)-C(10)	119.9(10)
C(20)-Re(1)-S(1)	95.8(2)	C(11)-C(12)-C(13)	121.3(10)
C(21)-Re(1)-S(1)	173.1(2)	C(13)-C(14)-C(15)	117.0(10)
N(3)-Re(1)-S(1)	78.51(15)	C(14)-C(13)-C(12)	121.0(9)
C(22)-Re(1)-S(1)#1	94.8(2)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z

Table S31. Hydrogen bonds for 5c [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...N(4)#2	0.86	2.14	2.970(9)	161.2

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z #2 -x+3/2,y+1/2,-z

Table S32. Bond lengths [Å] and angles [°] for 6c.(C_7H_8).

Re(1)-C(23)	1.892(5)	C(25)-Re(1)-N(3)	172.69(15)
Re(1)-C(25)	1.905(5)	C(24)-Re(1)-N(3)	100.14(15)
Re(1)-C(24)	1.930(5)	C(23)-Re(1)-S(1)	95.53(14)
Re(1)-N(3)	2.233(3)	C(25)-Re(1)-S(1)	94.49(15)
Re(1)-S(1)	2.4654(9)	C(24)-Re(1)-S(1)	176.88(16)
Re(1)-S(1)#1	2.5557(10)	N(3)-Re(1)-S(1)	78.66(8)
S(1)-C(1)	1.783(4)	C(23)-Re(1)-S(1)#1	175.37(14)
S(1)-Re(1)#1	2.5556(10)	C(25)-Re(1)-S(1)#1	94.23(15)
S(2)-C(15)	1.721(4)	C(24)-Re(1)-S(1)#1	96.73(16)
S(2)-C(9)	1.752(4)	N(3)-Re(1)-S(1)#1	87.16(8)
N(1)-C(1)	1.359(5)	S(1)-Re(1)-S(1)#1	80.37(3)
N(1)-C(17)	1.416(5)	C(1)-S(1)-Re(1)	95.92(12)
N(2)-C(1)	1.282(5)	C(1)-S(1)-Re(1)#1	100.91(14)
N(2)-N(3)	1.411(4)	Re(1)-S(1)-Re(1)#1	99.63(3)
N(3)-C(2)	1.295(5)	C(15)-S(2)-C(9)	88.9(2)
N(4)-C(9)	1.303(5)	C(1)-N(1)-C(17)	128.6(3)
N(4)-C(10)	1.391(5)	C(1)-N(2)-N(3)	116.7(3)
O(23)-C(23)	1.161(6)	C(2)-N(3)-N(2)	110.7(3)
O(24)-C(24)	1.142(5)	C(2)-N(3)-Re(1)	130.1(2)
O(25)-C(25)	1.157(5)	N(2)-N(3)-Re(1)	118.2(2)
C(1S)-C(2S)	1.27(2)	C(9)-N(4)-C(10)	110.3(4)
C(1S)-C(6S)	1.56(2)	N(2)-C(1)-N(1)	119.9(3)
C(2)-C(3)	1.489(5)	N(2)-C(1)-S(1)	126.5(3)
C(2)-C(16)	1.498(5)	N(1)-C(1)-S(1)	113.5(3)
C(2S)-C(3S)	1.286(15)	C(2S)-C(1S)-C(6S)	106.8(12)
C(3)-C(4)	1.377(6)	N(3)-C(2)-C(3)	121.5(3)
C(3)-C(8)	1.390(6)	N(3)-C(2)-C(16)	122.1(3)
C(3S)-C(4S)	1.332(10)	C(3)-C(2)-C(16)	116.4(3)
C(4)-C(5)	1.383(5)	C(1S)-C(2S)-C(3S)	137(2)
C(4S)-C(5S)	1.361(11)	C(4)-C(3)-C(8)	118.7(3)
C(4S)-C(7S)	1.371(11)	C(4)-C(3)-C(2)	121.6(3)
C(5)-C(6)	1.394(5)	C(8)-C(3)-C(2)	119.2(4)
C(5S)-C(6S)	1.328(15)	C(2S)-C(3S)-C(4S)	111.8(11)
C(6)-C(7)	1.385(6)	C(3)-C(4)-C(5)	120.7(4)
C(6)-C(9)	1.474(5)	C(3S)-C(4S)-C(5S)	126.2(9)
C(7)-C(8)	1.379(6)	C(3S)-C(4S)-C(7S)	118.4(10)
C(10)-C(11)	1.382(7)	C(5S)-C(4S)-C(7S)	115.4(11)
C(10)-C(15)	1.398(6)	C(4)-C(5)-C(6)	120.6(4)
C(11)-C(12)	1.381(7)	C(6S)-C(5S)-C(4S)	116.4(11)
C(12)-C(13)	1.381(8)	C(7)-C(6)-C(5)	118.4(3)
C(13)-C(14)	1.365(8)	C(7)-C(6)-C(9)	122.0(3)
C(14)-C(15)	1.403(6)	C(5)-C(6)-C(9)	119.5(4)
C(17)-C(22)	1.377(6)	C(5S)-C(6S)-C(1S)	120.9(13)
C(17)-C(18)	1.381(6)	C(8)-C(7)-C(6)	120.6(4)
C(18)-C(19)	1.380(7)	C(7)-C(8)-C(3)	120.8(4)
C(19)-C(20)	1.372(8)	N(4)-C(9)-C(6)	123.3(4)
C(20)-C(21)	1.362(7)	N(4)-C(9)-S(2)	115.9(3)
C(21)-C(22)	1.374(7)	C(6)-C(9)-S(2)	120.8(3)
		C(11)-C(10)-N(4)	124.7(4)
C(23)-Re(1)-C(25)	88.2(2)	C(11)-C(10)-C(15)	120.5(4)
C(23)-Re(1)-C(24)	87.3(2)	N(4)-C(10)-C(15)	114.9(4)
C(25)-Re(1)-C(24)	86.83(19)	C(12)-C(11)-C(10)	117.9(5)
C(23)-Re(1)-N(3)	89.93(16)	C(13)-C(12)-C(11)	121.9(5)

C(14)-C(13)-C(12)	121.1(5)	C(19)-C(18)-C(17)	118.9(5)
C(13)-C(14)-C(15)	117.9(5)	C(20)-C(19)-C(18)	120.9(5)
C(10)-C(15)-C(14)	120.7(4)	C(21)-C(20)-C(19)	120.1(5)
C(10)-C(15)-S(2)	110.1(3)	C(20)-C(21)-C(22)	119.7(5)
C(14)-C(15)-S(2)	129.2(4)	C(21)-C(22)-C(17)	120.7(4)
C(22)-C(17)-C(18)	119.7(4)	O(23)-C(23)-Re(1)	178.7(5)
C(22)-C(17)-N(1)	117.3(4)	O(24)-C(24)-Re(1)	174.8(4)
C(18)-C(17)-N(1)	122.9(4)	O(25)-C(25)-Re(1)	177.6(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+1

TableS 33. Hydrogen bonds for 6c.(C_7H_8) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(18)-H(18)...N(2)	0.93	2.49	2.947(5)	110.5

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+1

Table S34. Bond lengths [Å] and angles [°] for 9c.(EtOH).

S-C(1)	1.797(6)	C(31)-Re(1)-S	177.35(18)
S-Re(1)	2.4670(14)	N(3)-Re(1)-S	77.02(12)
S-Re(1)#1	2.5332(13)	C(32)-Re(1)-S#1	173.79(18)
Re(1)-C(32)	1.914(6)	C(30)-Re(1)-S#1	93.88(17)
Re(1)-C(30)	1.916(6)	C(31)-Re(1)-S#1	95.73(18)
Re(1)-C(31)	1.922(6)	N(3)-Re(1)-S#1	83.09(12)
Re(1)-N(3)	2.226(5)	S-Re(1)-S#1	82.27(5)
Re(1)-S#1	2.5332(13)	N(2)-C(1)-N(1)	121.8(5)
C(1)-N(2)	1.287(7)	N(2)-C(1)-S	125.1(4)
C(1)-N(1)	1.358(8)	N(1)-C(1)-S	113.0(4)
C(2)-N(3)	1.290(8)	N(3)-C(2)-C(16)	122.5(5)
C(2)-C(16)	1.497(9)	N(3)-C(2)-C(3)	122.3(5)
C(2)-C(3)	1.505(8)	C(16)-C(2)-C(3)	115.2(5)
C(3)-C(8)	1.370(10)	C(8)-C(3)-C(4)	119.3(6)
C(3)-C(4)	1.376(9)	C(8)-C(3)-C(2)	120.1(6)
C(4)-C(5)	1.385(9)	C(4)-C(3)-C(2)	120.5(6)
C(5)-C(6)	1.393(9)	C(3)-C(4)-C(5)	120.7(6)
C(6)-C(7)	1.379(9)	C(4)-C(5)-C(6)	120.2(6)
C(6)-C(9)	1.450(8)	C(7)-C(6)-C(5)	118.5(6)
C(7)-C(8)	1.388(10)	C(7)-C(6)-C(9)	120.9(6)
C(9)-N(4)	1.310(8)	C(5)-C(6)-C(9)	120.6(6)
C(9)-O(1)	1.359(8)	C(6)-C(7)-C(8)	120.8(7)
C(10)-C(15)	1.371(10)	C(3)-C(8)-C(7)	120.5(6)
C(10)-C(11)	1.401(10)	N(4)-C(9)-O(1)	114.4(5)
C(10)-N(4)	1.403(8)	N(4)-C(9)-C(6)	127.5(6)
C(11)-C(12)	1.385(11)	O(1)-C(9)-C(6)	118.0(6)
C(12)-C(13)	1.375(13)	C(15)-C(10)-C(11)	120.3(7)
C(13)-C(14)	1.392(11)	C(15)-C(10)-N(4)	109.1(6)
C(14)-C(15)	1.388(10)	C(11)-C(10)-N(4)	130.6(7)
C(15)-O(1)	1.382(8)	C(12)-C(11)-C(10)	116.7(8)
C(17)-C(18)	1.388(12)	C(13)-C(12)-C(11)	122.3(7)
C(17)-C(22)	1.391(11)	C(12)-C(13)-C(14)	121.5(7)
C(17)-N(1)	1.418(8)	C(15)-C(14)-C(13)	115.8(8)
C(18)-C(19)	1.391(11)	C(10)-C(15)-O(1)	107.3(6)
C(19)-C(20)	1.372(16)	C(10)-C(15)-C(14)	123.3(7)
C(20)-C(21)	1.364(16)	O(1)-C(15)-C(14)	129.3(7)
C(21)-C(22)	1.390(12)	C(18)-C(17)-C(22)	119.6(7)
C(30)-O(30)	1.156(7)	C(18)-C(17)-N(1)	122.2(7)
C(31)-O(31)	1.146(7)	C(22)-C(17)-N(1)	118.2(8)
C(32)-O(32)	1.150(7)	C(17)-C(18)-C(19)	119.2(9)
N(2)-N(3)	1.418(6)	C(20)-C(19)-C(18)	120.8(11)
O(1S)-C(1S)	1.311(12)	C(21)-C(20)-C(19)	120.3(9)
C(2S)-C(1S)	1.496(15)	C(20)-C(21)-C(22)	120.1(10)
		C(21)-C(22)-C(17)	120.1(10)
C(1)-S-Re(1)	95.10(19)	O(30)-C(30)-Re(1)	179.0(5)
C(1)-S-Re(1)#1	105.34(18)	O(31)-C(31)-Re(1)	176.9(6)
Re(1)-S-Re(1)#1	97.73(5)	O(32)-C(32)-Re(1)	179.6(6)
C(32)-Re(1)-C(30)	90.0(2)	C(1)-N(1)-C(17)	126.3(6)
C(32)-Re(1)-C(31)	89.3(3)	C(1)-N(2)-N(3)	115.0(5)
C(30)-Re(1)-C(31)	87.3(2)	C(2)-N(3)-N(2)	112.4(5)
C(32)-Re(1)-N(3)	92.4(2)	C(2)-N(3)-Re(1)	130.2(4)
C(30)-Re(1)-N(3)	171.3(2)	N(2)-N(3)-Re(1)	117.3(3)
C(31)-Re(1)-N(3)	101.0(2)	C(9)-N(4)-C(10)	104.2(6)
C(32)-Re(1)-S	92.59(19)	C(9)-O(1)-C(15)	104.9(5)
C(30)-Re(1)-S	94.54(18)	O(1S)-C(1S)-C(2S)	116.8(10)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+2

Table S35. Hydrogen bonds for 9c.(EtOH) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(16)-H(16A)...S#1	0.98	2.85	3.596(7)	133.5
N(1)-H(1)...O(1S)	0.88	2.03	2.819(8)	148.2
O(1S)-H(1S)...N(4)#2	0.84	2.06	2.834(8)	152.4
C(2S)-H(2S1)...S	0.98	2.98	3.828(11)	145.9

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+2 #2 -x+1/2,y+1/2,-z+3/2

Table S36. Bond lengths [Å] and angles [°] 2d.2(EtOH).

C(3S)-C(4S)	1.428(17)	C(21)-Re(1)-N(2)	106.6(2)
C(3S)-O(1S)	1.440(12)	C(20)-Re(1)-N(2)	162.8(2)
O(21)-C(21)	1.131(7)	C(22)-Re(1)-S(1)	98.4(2)
Re(1)-C(22)	1.910(6)	C(21)-Re(1)-S(1)	169.43(18)
Re(1)-C(21)	1.918(6)	C(20)-Re(1)-S(1)	98.05(18)
Re(1)-C(20)	1.919(6)	N(2)-Re(1)-S(1)	65.03(11)
Re(1)-N(2)	2.242(4)	C(22)-Re(1)-S(1)#1	178.9(2)
Re(1)-S(1)	2.5153(12)	C(21)-Re(1)-S(1)#1	92.9(2)
Re(1)-S(1)#1	2.5543(13)	C(20)-Re(1)-S(1)#1	92.35(19)
Re(2)-C(25)	1.902(8)	N(2)-Re(1)-S(1)#1	87.91(11)
Re(2)-C(24)	1.928(7)	S(1)-Re(1)-S(1)#1	80.71(4)
Re(2)-C(23)	1.935(7)	C(25)-Re(2)-C(24)	88.1(3)
Re(2)-N(1)	2.123(4)	C(25)-Re(2)-C(23)	90.5(4)
Re(2)-N(3)	2.173(4)	C(24)-Re(2)-C(23)	88.5(3)
Re(2)-O(1)	2.191(5)	C(25)-Re(2)-N(1)	94.7(3)
S(1)-C(1)	1.781(5)	C(24)-Re(2)-N(1)	98.1(3)
S(1)-Re(1)#1	2.5542(13)	C(23)-Re(2)-N(1)	171.7(3)
N(2)-C(1)	1.358(6)	C(25)-Re(2)-N(3)	92.4(2)
N(2)-N(3)	1.393(6)	C(24)-Re(2)-N(3)	172.8(3)
C(1)-N(1)	1.287(7)	C(23)-Re(2)-N(3)	98.7(2)
N(1)-C(16)	1.465(7)	N(1)-Re(2)-N(3)	74.70(16)
N(3)-C(2)	1.288(7)	C(25)-Re(2)-O(1)	173.0(2)
O(20)-C(20)	1.132(7)	C(24)-Re(2)-O(1)	98.2(3)
C(3)-C(8)	1.389(8)	C(23)-Re(2)-O(1)	92.9(3)
C(3)-C(4)	1.397(8)	N(1)-Re(2)-O(1)	81.28(18)
C(3)-C(2)	1.460(8)	N(3)-Re(2)-O(1)	81.04(18)
C(6)-C(5)	1.377(8)	C(1)-S(1)-Re(1)	81.05(16)
C(6)-C(7)	1.400(9)	C(1)-S(1)-Re(1)#1	102.88(17)
C(6)-C(9)	1.470(8)	Re(1)-S(1)-Re(1)#1	99.29(4)
C(8)-C(7)	1.373(9)	C(1)-N(2)-N(3)	111.3(4)
C(5)-C(4)	1.374(8)	C(1)-N(2)-Re(1)	101.7(3)
S(2)-C(10)	1.724(8)	N(3)-N(2)-Re(1)	137.6(3)
S(2)-C(9)	1.750(7)	N(1)-C(1)-N(2)	124.6(5)
O(1)-C(1S)	1.411(10)	N(1)-C(1)-S(1)	126.2(4)
O(22)-C(22)	1.131(8)	N(2)-C(1)-S(1)	109.0(4)
N(4)-C(9)	1.293(8)	C(1)-N(1)-C(16)	120.0(5)
N(4)-C(11)	1.387(9)	C(1)-N(1)-Re(2)	113.3(3)
O(24)-C(24)	1.144(8)	C(16)-N(1)-Re(2)	126.5(4)
C(25)-O(25)	1.137(9)	C(2)-N(3)-N(2)	120.2(5)
C(23)-O(23)	1.130(9)	C(2)-N(3)-Re(2)	124.8(4)
C(1S)-C(2S)	1.41(2)	N(2)-N(3)-Re(2)	114.7(3)
C(11)-C(10)	1.369(12)	C(8)-C(3)-C(4)	118.8(5)
C(11)-C(12)	1.385(11)	C(8)-C(3)-C(2)	119.2(5)
C(10)-C(15)	1.383(12)	C(4)-C(3)-C(2)	121.8(5)
C(12)-C(13)	1.371(12)	C(5)-C(6)-C(7)	118.8(5)
C(15)-C(14)	1.385(15)	C(5)-C(6)-C(9)	121.5(5)
C(13)-C(14)	1.337(15)	C(7)-C(6)-C(9)	119.7(5)
		C(7)-C(8)-C(3)	120.6(5)
C(4S)-C(3S)-O(1S)	112.6(12)	O(20)-C(20)-Re(1)	175.6(6)
C(22)-Re(1)-C(21)	87.9(3)	C(4)-C(5)-C(6)	121.1(5)
C(22)-Re(1)-C(20)	88.4(3)	N(3)-C(2)-C(3)	129.9(5)
C(21)-Re(1)-C(20)	90.6(2)	C(5)-C(4)-C(3)	120.0(5)
C(22)-Re(1)-N(2)	91.1(2)	C(10)-S(2)-C(9)	89.3(4)

C(1S)-O(1)-Re(2)	129.1(6)	C(10)-C(11)-C(12)	120.5(7)
C(9)-N(4)-C(11)	112.1(6)	C(10)-C(11)-N(4)	114.5(7)
N(4)-C(9)-C(6)	125.9(6)	C(12)-C(11)-N(4)	125.0(7)
N(4)-C(9)-S(2)	113.9(5)	O(24)-C(24)-Re(2)	178.5(8)
C(6)-C(9)-S(2)	120.2(5)	C(11)-C(10)-C(15)	121.1(9)
C(8)-C(7)-C(6)	120.2(5)	C(11)-C(10)-S(2)	110.1(6)
O(22)-C(22)-Re(1)	176.5(7)	C(15)-C(10)-S(2)	128.8(8)
O(25)-C(25)-Re(2)	178.0(7)	C(13)-C(12)-C(11)	118.5(9)
O(21)-C(21)-Re(1)	177.5(5)	C(10)-C(15)-C(14)	116.5(10)
O(23)-C(23)-Re(2)	179.4(8)	C(14)-C(13)-C(12)	120.4(9)
C(2S)-C(1S)-O(1)	117.9(11)	C(13)-C(14)-C(15)	123.0(9)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z

Table S37. Hydrogen bonds for 2d.2(EtOH) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(1S)	0.93	1.90	2.592(7)	129.0
O(1S)-H(1S)...N(4)#2	0.82	1.97	2.785(8)	172.8
C(16)-H(16A)...S(1)	0.96	2.56	3.097(6)	115.6

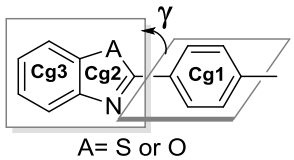
Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z #2 -x,y+1/2,-z+1/2

Table S38. Main distances (Å) and angles (°) describing the C–H…π and π-π interactions

Compound	Centroid-centroid distance[a]	Interplanar distance[b]	Closest interatomic contacts /distance[f]	γ(°)[e]
H_2L^1.DMSO	Cg(1)–Cg(2) = 3.617	3.442	C(3)–C(10) / 3.458	5.38
H_2L^2	Cg(1)–Cg(2) = 3.829	3.519	C(8)–C(10) / 3.450	16.14
H_2L^4	Cg(1)–Cg(2) = 4.429	-- [c]	C(5)–C(12) / 3.315	14.72
H_2L^5	Cg(1)–Cg(2) = 3.811	3.522 [d]	C(7)–C(11) / 3.527	16.08
H_2L^7.DMSO	Cg(1)–Cg(2) = 3.780	3.367	C(7)–C(9) / 3.416	2.91
H_2L^8.DMSO	Cg(1)–Cg(2) = 3.661	3.516	C(3)–C(15) / 3.550	2.04
4a	Cg(3)–Cg(3) = 3.665 2-x, 1-y, 1-z	3.503	C(10)–C(12) / 3.541	19.25
	Cg(1)-Cg(3) = 4.723 -1+x, y, z	-- [c]	C(5)–C(11) / 3.525	
4b	Cg(3)–Cg(2) = 4.045 1-x, 1-y, -z	3.337	C(12)–Cg(2) / 3.541	4.93
	Cg(1)–Cg(3) = 4.214 -x,-y,-z		C(5)–C(10) / 3.535 C(5)–C(15) / 3.542	
6a	---	--	C(21)–H(21)…N(4) / 2.593 C(20)–H(20)…O(24) / 2.432 1-x, 1-y, -z	15.33
6b.C_7H_8	--	--	C(12)–H(12)…Cg(4)[g] / 2.687 1-x, 1-y, -z C(1)–H(1)…O(23) / 2.733 2-x, -y, 1-z C(21)–H(21)…C(4) / 2.992 C(20)–H(20)…N(1) / 2.707 x, 1+y, -1+z C(22)–H(22A)…C(3S) / 2.970 C(22)–H(22A)…C(4S) / 3.004 C(22)–H(22A)…$Cg_{(solvent)}$ / 2.903	9.72
8b.H_2O	4.420		C(6)–O(1) / 3.49	16.98
2c	4.611–5.824		C(8)–N(4) / 3.61	
3c 1/2C_2H_6O	3.803–3.938		N(4)–C(6) / 3.532	
5c	4.780		C(15)–C(5) / 4.12	
6c C_7H_8	5.18–5.646		S(2)–C(7) / 3.70	
9c 2EtOH	5.607		O(1)–C(7) / 3.63	
2d.2EtOH	3.828		S(2)–C(7) / 3.677	

a) Defined as the distance between centroid Cg2 and Cg1 (see scheme) of the closest neighbor molecule. The symmetry operation (if included) is applied to the second centroid.



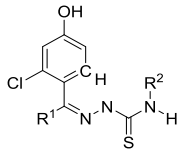
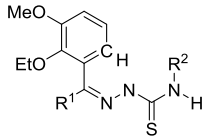
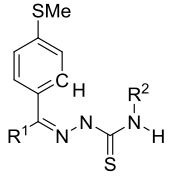
b) Distance between the best planes defined by the benzothiazole or benzoxazole fragment of two closed-packed molecules. c) The plane defined by the rings is not parallel. d) The benzothiazole groups are packed in the same direction. e) γ as defined in the scheme included in footnote a. f) Symmetry operation (if included) should be applied on the acceptor group. g) Centroid defined for the phenyl group at N(1) atom (R^2 = Ph)

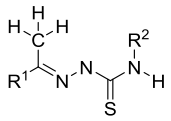
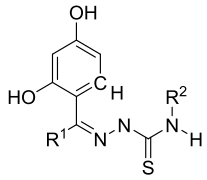
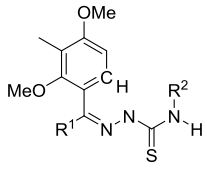
Table S39. Intramolecular interactions in $[Re_2(HL)_2(CO)_6]$ in this paper.

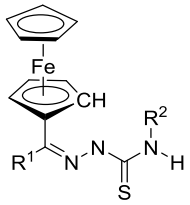
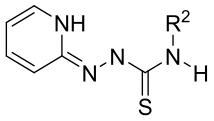
D-H…A	d(D-H)	D(H…A)	D(D…A)	<(DHA)
2c				
C(4)-H(4)…N(2)	0.93	2.25	2.831(8)	120.1
C(8A)-H(8A)…N(2A)	0.93	2.27	2.836(8)	118.7
3c				
C(4A)-H(4A)…N(2A)	0.93	2.31	2.86(2)	117.6
C(8B)-H(8B)…N(2B)	0.93	2.41	2.89(3)	112.2 .
C(8C)-H(8C)…N(2C)	0.93	2.31	2.86(3)	117.7
C(8D)-H(8D)…N(2D)	0.93	2.34	2.86(4)	114.6
C(21A)-H(21A)…N(2A)	0.93	2.32	2.88(3)	118.5
C(17B)-H(17B)…N(2B)	0.93	2.48	2.96(3)	111.9
C(17C)-H(17C)…N(2C)	0.93	2.37	2.94(3)	119.4
C(17D)-H(17D)…N(2D)	0.93	2.47	2.94(4)	112.0
6c				
C(18)-H(18)…N(2)	0.93	2.49	2.948(5)	110.4
9c				
C(18)-H(18)…N(2)	0.95	2.53	2.940(14)	106.0

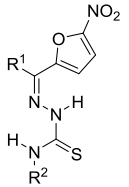
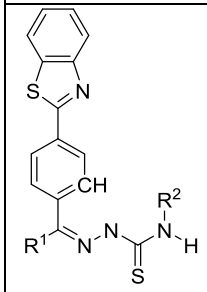
Table S40. Selected structural parameters of published complexes $[Re_2(L)_2(CO)_6]$.

Reference [14]

TSC ligand	R^1	R^2	Symmetry	Config C2=N3	C(H)-N2	Re-N	Re-S	Re-S*	S-Re-S*	Re-S-Re*	Refcode CCDC	Reference
	H	H	2	Z	CHarom-N(2)= 2.951	2.162(13)	2.461(4)	2.554(4)	82.12(13) 81.99(13)	97.57(13) 97.49(19)	QUHGUW	15
	H	Me	2	Z	CHarom-N(2)= 2.789	2.210(5)	2.463(14)	2.5614(5)	80.79(5)	98.90(5)	QUHHAD	
	H	Me	-1	Z	CHarom-N(2)= 2.894 CHarom-N(2)= 2.922	2.191(9)	2.458(3)	2.549(3)	82.84(9)	96.95(3)	KOFYEK	16
	H	Ph	-1	Z	CHarom-N(2)= 2.907 CHPh-N(2)= 3.033	2.202(3)	2.4588(8)	2.5467(9)	82.02(3)	97.98(3)	KOFYIO	
	H	H	2	Z	CHarom-N(2)= 2.897	2.203(10)	2.461(3)	2.553(3)	81.95(8)		PAKZIN	17
	H	Me	2	Z	CHarom-N(2)= 2.836	2.203(6)	2.4650(18)	2.5507(19)	82.36(6)		PAKZEJ	
	H	Ph	2	Z	CHarom-N(2)= 2.890 CHPh-N(2)= 2.954	2.214(8)	2.451(3)	2.558(3)	82.14(10)	97.62(10)	PAKYUY PAKZAF	

TSC ligand	R^1	R^2	Symmetry	Config C2=N3	C(H)-N2	Re-N	Re-S	Re-S*	S-Re-S*	Re-S-Re*	Refcode CCDC	Reference
	Me	Me	-1	--	--	2.228(4)	2.4756(11)	2.5341(10)	82.02(4)	99.98(4)	LIRDOH	18
	Me	Me	-1	Z		2.231(9)	2.487(3)	2.544(3)	81.62(11)	98.38(11)	LIRDIB	18
	Me	Ph	-1	E	CHarom-N(2)= 2.905	2.226(3)	2.4588(12)	2.5451(13)	80.96(4)	99.04(14)	LIRDUN LIRFAV	
	H	Me	2	Z		2.193(4)	2.4696(11)	2.5522(11)	82.48(4)	96.53(4)	HOLDUJ	19
	H	Ph	-1	Z	CHarom-N(2)= 2.954 CHPh-N(2)= 2.928	2.185(7)	2.457(3)	2.539(3)	82.63(9)	97.37(9)	HOLFAR	

TSC ligand	R^1	R^2	Symmetry	Config C2=N3	C(H)-N2	Re-N	Re-S	Re-S*	S-Re-S*	Re-S-Re*	Refcode CCDC	Reference
	H	H	-1	E	--	2.210(9)	2.465(3)	2.537(4)	81.34(12)	98.66(12)	XUHDIN	20
	H	Me	-1	E	CHarom-N(2)= 3.019	2.213(5)	2.4760(18)	2.5409(18)	81.36(6)	98.64(6)	XUHDOT	
	H	Me	-1	Z	--	2.067(4)	2,4697(13)	2.6706(13)	85.39(5)	94.61(5)	XUHDUT	
	--	Ph	-1	Z	CHPh-N(2)= 2.991, 2.993	2.189 2.197	2.466 2.462	2.539 2.535	82.87 82.35	97.13 97.65	BIFMAF	21

TSC ligand	R^1	R^2	Symmetry	Config C2=N3	C(H)-N2	Re-N	Re-S	Re-S*	S-Re-S*	Re-S-Re*	Refcode CCDC	Reference
	H	Ph	2	Z	CHarom-N(2)= 2.972 CHPh-N(2)= 2.928	2.182	2.460	2.570	81.22	96.17	PULJUD	22
	H	Me	2	Z	CHarom-N(2)= 2.861, 2.888	2.146 2.188	2.445 2.455	2.560 2.546	83.08 83.18	96.36 95.75	PULKAK	
	H	Et	2	Z	CHarom-N(2)= 2.902, 2.928, 2.893, 2.954	2.187 2.169	2.459 2.457	2.549 2.553	83.32 83.44	95.99 95.94	PULKOY	
	H	Me	2	Z	CHarom-N(2)= 2.831(8), 2.836(8)	2.209(5)	2.4597(2)	2.5557(18)	82.69(5)	96.90(5)		This work
	H	Ph	2	Z	CHarom-N(2)= 2.86(2) – 2.86(4) CHPh-N(2)= 2.88(3) – 2.96(3)	2.198(16)	2.464(5)	2.560(5)	81.51(15)	98.23(16)		
	Me	Me	-1	E	--	2.209(5)	2.4676(18)	2.5640(18)	82.00(6)	98.00(6)		
	Me	Ph	-1	E	CHPh-N(2)= 2.948(5)	2.233(3)	2.4654(9)	2.5557(10)	80.37(3)	99.64(3)		

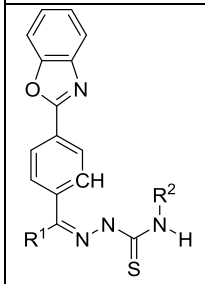
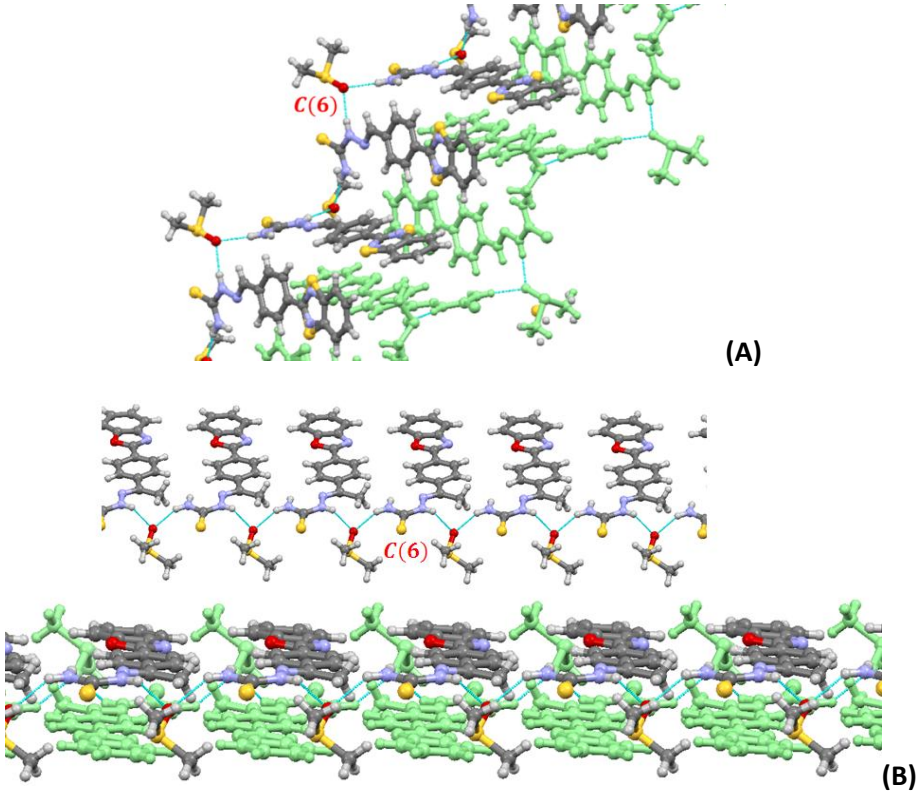
TSC ligand	R^1	R^2	Symmetry	Config C2=N3	C(H)-N2	Re-N	Re-S	Re-S*	S-Re-S*	Re-S-Re*	Refcode CCDC	Reference
	Me	Ph	-1	Z	CHPh-N(2)= 2.940(14)	2.226(5)	2.4670(14)	2.5332(13)	82.27(5)	97.72(4)		This work

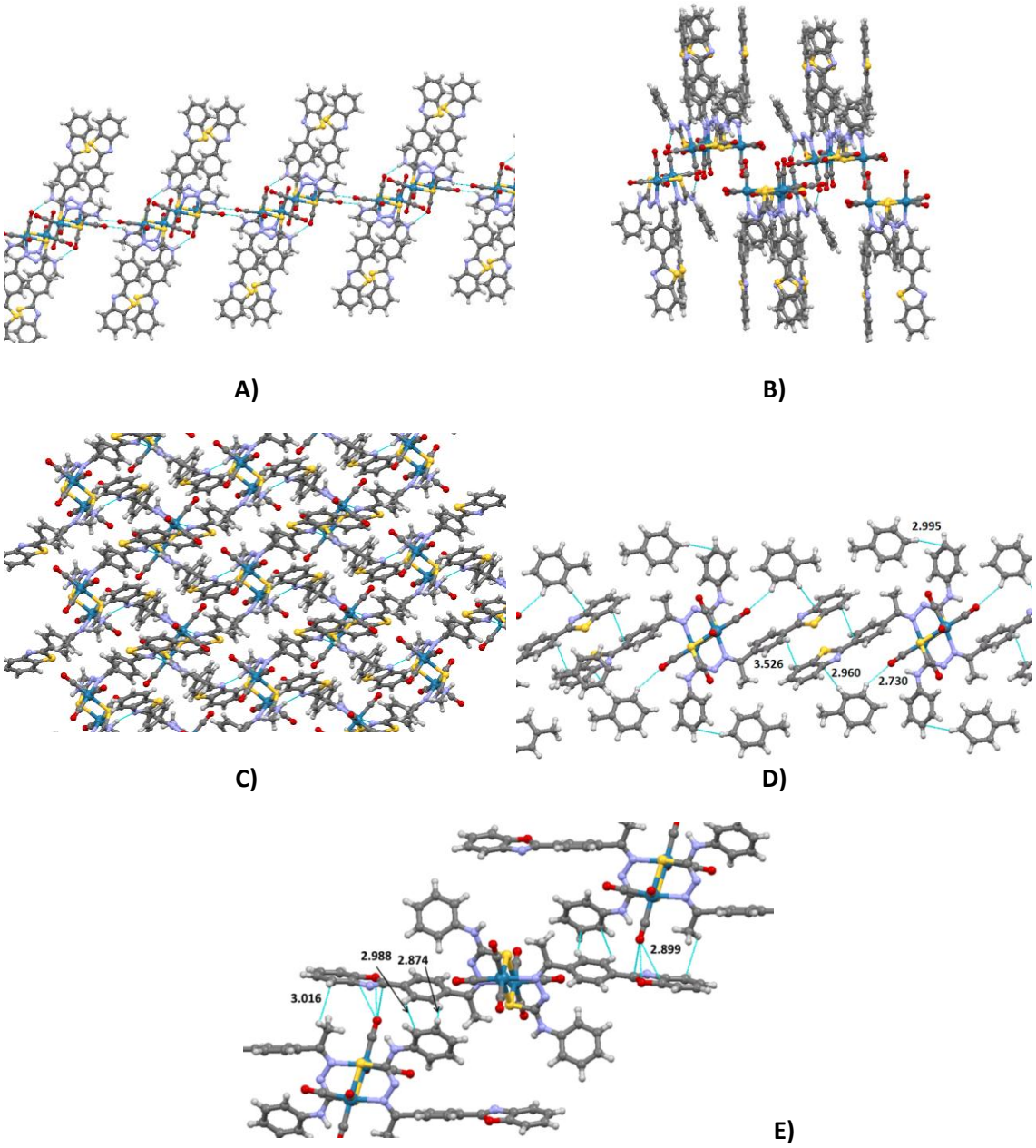
Figure S1. Molecular associations in the crystal structures of **H_2L^1.DMSO** (**A**), showing the disordered benzothiazole fragment, and **H_2L^7.DMSO** (B).



(A)

(B)

Figure S2. Molecular associations in the crystal structures of **2c** (**A**), **3c** (**B**), **5c** (**C**), **6c** (**D**) and **9c** (**E**).



References

[1] Farona, M. F.; Kraus, K. F. *Inorg. Chem.* **1970**, *9*, 1700 –1704 .
[2] Schmidt, P.; Trogler, W. C.; Basolo, F. *Inorg. Synth.* **1990**, *28*, 160 –165.
[3] Bruker (2015). APEX3, SAINT and SADABS. Bruker AXS Inc, Madison , Wisconsin, USA.
[4] Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3–8.
[5] Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112–122.
[6] Spek, A. L. *Acta Cryst.* **2009**, *D65*, 148–155.
[7] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, **2006**, *39*, 453-457.
[8] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09; Gaussian, Inc.: Wallingford, CT, 2009.
[9] Keith, T. A. IMAll (Version 16.10.31); TK Gristmill Software: Overland Park KS, USA, 2016; aim.tkgristmill.com.
[10] Pino-Cuevas, A.; Carballo, R.; Vázquez-López, E. M. *Acta Cryst.*, **2014**, *E70*, o926.
[11] Pino-Cuevas, A.; Carballo, R.; Vázquez-López, E. M. *Acta Cryst.*, **2014**, *E70*, o970.
[12] Jagst, A.; Sanchez, A.; Vázquez-López, E. M.; Abram, U. *Inorg. Chem.*, **2005**, *44*, 5738-5744.
[13] Zahran, M. A. H.; Essawy, F. A. A.; Yassin, S. M.; R. Salem, T. A.; Boshta, N. M. *Arch. Pharm. Chem.*, **2007**, *340*, 591.
[14] The Cambridge Structural Database, v. 2016 C. Groom, R.; Bruno, I. J.; Lightfoot M. P.; Ward, S. C. *Acta Cryst.* **2016**, *B72*, 171-179.
[15] Nuñez-Montenegro, A.; Carballo, R.; Vázquez López, E.M. *Polyhedron*, **2009**, *28*, 3915-3922.
[16] Núñez-Montenegro, A.; Carballo, R.; Vázquez López, E.M. *Polyhedron*, **2008**, *27*, 2867-2876.
[17] Núñez-Montenegro, A.; Carballo, R.; Hermida-Ramón, J.M.; Vázquez López, E.M. *Polyhedron*, **2011**, *30*, 2146-56.
[18] Nuñez-Montenegro, A.; Carballo, R.; Abram, U.; Vázquez-López, E.M. *Polyhedron*, **2013**, *65*, 221-228.
[19] Nuñez-Montenegro, A.; Carballo, R.; Vázquez-López, E.M. *J. Inorg. Biochem.* **2014**, *140*, 53-63.
[20] Carballo, R.; Casas, J.S.; García-Martínez, E.; Pereiras-Gabián, G.; Sánchez, A.; Sordo, J.; Vázquez-López, E.M.; Garcia-Monteagudo, J.C.; Abram., U. *J. Organomet. Chem.* **2002**, *656*, 1-10.
[21] Alberto, R.; Cowley, A. R.; Dilworth, J. R.; Donnelly, P. S.; Pratt, J. *Dalton Trans.* **2004**, 2610-2611.
[22] Nayak, D. K.; Baishya, R.; Natarajan, R.; Sen, T.; Debnath, M. C. *Dalton Trans.* **2015**, *44*, 16136-16148.