Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Non-covalent Sulfoxide···(Nitrosyl Group) Interactions Involving Coordinated Nitrosyl in a Ru(II) Nitrosyl Complex with *α*-Diimine Ligand: Structural, and Computational Studies

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Experimental (Methods and instrumentation)

All reagents were purchased from Aldrich and used as received. All solvents were reagent grade and purified by standard techniques where required. Infrared spectra in the region of 400-4000 cm^{-1} were recorded in KBr discs, solution phase and dropellet of solution on KBr disks with a Bruker IFD 25 FT-IR with a Perkin Elmer spectrum 100FT-IR spectrometer. The ^{1}H-NMR and $^{13}C\{^{1}H\}$ NMR spectra were recorded by Bruker Avance 500 MHz spectrometer. The elemental analyses were done by a LECO CHNO analyser.

Synthesis and crystallization of the title complex

An equimolar quantity of $[Ru(NO)Cl_3].\ 5H_2O$ (0.164 g, 0.5 mmol) and bis(2,6-diisopropylphenylimino)acenaphthequinone (0.250 g, 0.5 mmol) was heated under reflux condition in ethanol for 2 h. The dark-brown crystallites were filtered from the cooled solution, washed with cold ethanol and diethyl ether and dried in *vacuo*. Yield, 0.21 g (57%). For elemental analyses the crystallites from the synthesis were grinded and dried in *vacuo* at 80^0 C. Elemental analyses: *Calc*. (%): C, 58.58; H, 5.46; N, 5.69; O, 2.17 *Found*: C, 58.60; H, 5.43; N, 5.71; O, 2.15. ^{1}H-NMR (DMSO-d6, σ_{ppm}): 0.73 [6H, d, CH*(CH$_3$)$_2$*], 0.92 [6H, d, CH*(CH$_3$)$_2$*], 1.31 [6H, d, CH*(CH$_3$)$_2$*], 1.35 [6H, d, CH*(CH$_3$)$_2$*], 2.96 [2H, m, *CH*$(CH_3)_2$], 3.89 [2H, m, *CH*$(CH_3)_2$], 8.49 (d, 2H), 7.82 (2H, t), 7.65 (2H, dd), 7.55 (4H, ddd), 6.52 (2H, d). $^{13}C\{^{1}H\}$-NMR (DMSO-d6, σ_{ppm}): 24.04, 24.47, 24.63, 25.13, 28.54, 28.57, 124.26, 125.47, 125.68, 127.40, 129.34, 130.31, 130.83, 135.03, 139.05, 141.00, 142.03, 145.27, 179.48 (−C=N−). FT–IR (υ, cm^{-1}): 1856 (NO); 613 (Ru−NO).

Single-crystals suitable for X-ray analysis were grown by evaporation of the DMSO solution of the complex. The crystallographic data were deposited as CIF file with Deposition Number **2017460**.

1. **X-ray crystallography**

Single crystals of **1** suitable for X-ray diffraction analysis, were grown by slow vapor diffusion of *n*-hexane into dichloromethane solution of the complex. Details of the crystal data collection and refinement parameters, bond

lengths and angles, and hydrogen bonding parameters are summarized in Table S1-S2. X-ray intensity data were collected using the full sphere routine by φ and ω scans strategy on the Agilent *SuperNova* dual wavelength EoS *S*2 diffractometer with mirror monochromated Mo K*α* radiation (λ = 0.71073 Å). For all data collections the crystals were cooled to 150(2) K using an Oxford Diffraction Cryojet low-temperature attachment. The data reduction, including an empirical absorption correction using spherical harmonics, implemented in *SCALE3 ABSPACK* scaling algorithm [R. C. Clark, and J. S. Reid, *Acta Cryst*. 1995, A**64**, 887–897], was performed using the *CrysAlisPro* software package [SuperNova Eos S2 System: Empirical absorption correction, 2011, *CrysAlis*-Software package, Oxford Diffraction Ltd.]. The crystal structure was solved by direct methods using the online version of *AutoChem 2.0* in conjunction with *OLEX2* [O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, H., *J. Appl. Cryst*., 2009, 42, 339–341 and Agilent (2012). AutoChem 2.0, in conjunction with OLEX2. Agilent Technologies UK Ltd, Yarnton, Oxfordshire, England.] suite of programs implemented in the *CrysAlis* software, and then refined by full-matrix least-squares (*SHELXL2014*) on F^2 [G. M. Sheldrick, *Acta Cryst*., 2008, A**64**, 112–122]. The non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were positioned geometrically in idealized positions and refined with the riding model approximation, with U_{iso}(H) = 1.2 U_{eq}(C). For the molecular graphics the program SHELXTL was used [G. M. Sheldrick, *Acta Cryst*., 2008, A**64**, 112–122]. All geometric calculations were carried out using the *PLATON* software [A. L. Spek, *Acta Cryst*., 2009, D65, 148–155]. CCDC **2017460** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details

Density functional theory (DFT) calculations have been performed using the *Gaussian 09* package to perform geometry optimizations, the vibrational frequencies and the electronic structures of the complex [M. Frisch, *et al*., GAUSSIAN09. 2009. Gaussian Inc., Wallingford, CT, USA. http://www.gaussian.com]. A frequency calculation after each geometry optimization ensured that the calculated structures are real minima in the potential energy

surface of the molecules. The structure was optimized using the B3LYP exchange-correlation functionals with the LANL2DZ effective core pseudo-potential (ECP) and corresponding set of basic functions for Ru, 6-31G* (five pure d functions) for C, H, N, O, S and 6-311G* for Cl atom [D. Andrae, U. Häußermann, M. Dolg, H. Stoll & H. Preuß, *Theor. Chim. Acta*, **1990**, 77, 123–141]. The NBO program [K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, & T. L. Windus, *J. Chem. Info. & Model*., **2007**, 47, 1045–1052] embedded in Gaussian 09 package used for calculations was done at B3LYP/LANL2DZ level of theory. The natural bond orbital analysis emphasizes the role of intra- and intermolecular interaction or charge transfer in the title compound. It is performed by including all possible interaction between filled donor and empty acceptor NBOs and estimating the energetic importance by second-order perturbation theory. Single point calculations based on the experimental X-ray geometry have been carried out at the DFT level of theory using the M06 functional [Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc*., **2008**, 120, 215–241] with the help of the Gaussian09 program package. This functional was specifically developed to describe weak dispersion forces and non-covalent interactions. The Douglas-Kroll-Hess second-order scalar relativistic calculations requesting a relativistic core Hamiltonian were carried out using DZP-DKH basis sets [C. L. Barros, P. J. P. de Oliveira, F. E. Jorge, A. C. Neto and M. Campos, *Mol. Phys*., **2010**, 108, 1965–1972; F. E. Jorge, A. C. Neto, G. G. Camiletti and S. F. Machado, *J. Chem. Phys*., **2009**, 130, 6; A. C. Neto and F. E. Jorge, *Chem. Phys. Lett*., **2013**, 582, 158–162; 39 C. L. Barros, P. J. P. de Oliveira, F. E. Jorge, A. C. Neto and M. Campos, *Mol. Phys*., **2010**, 108, 1965–1972; 40 R. C. de Berredo and F. E. Jorge, *J. Mol. Struct*.: *THEOCHEM*, **2010**, 961, 107–112] for all atoms to calculate wave function for topological analysis of the electron density distribution with the help of atoms in molecules (QTAIM) method. The QTAIM calculations were performed using Multiwfn program (version 3.7) [T. Lu and F. W. Chen, *J. Comput. Chem*., 2012, 33, 580–592]. Molecular orbital (MO) compositions and the overlap populations were calculated using the AOMix 6.90 program [S. I. Gorelsky & A. B. P. Lever, *J. Organomet. Chem*., **2001**, 635, 187–196]. The analysis of the molecular orbital (MO) compositions in terms of the highest occupied orbitals (HOFO) and lowest unoccupied orbitals (LUFOs) of

the fragment species **F1** and **F2** {**F1** is [$RuCl_3NO$] and **F2** is $^{2,6isop}Ph_2Aceq$) were performed by the AOMix 6.90 program. Charge decomposition analysis (CDA) implemented in AOMix 6.90 program was used to provide better qualitative and quantitative understanding of the nature of the chemical bonding in the complex based on the electron donation and back-donation between the metal fragment and the coordinated ligand.

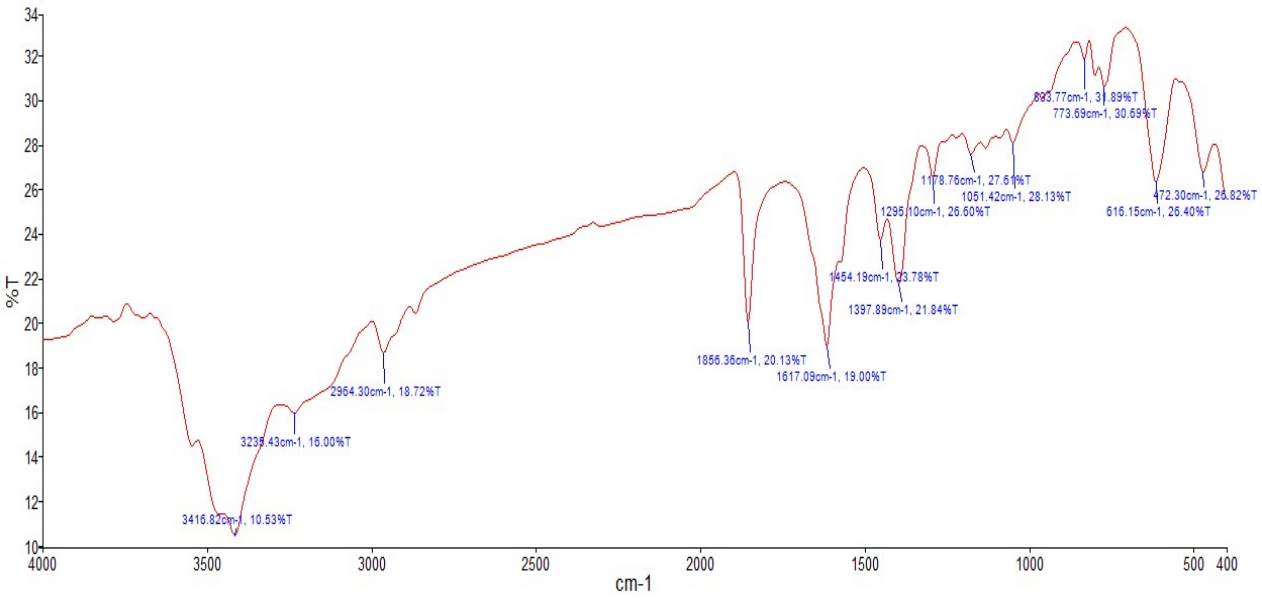

Fig. S1. The FTIR spectrum of the title complex.

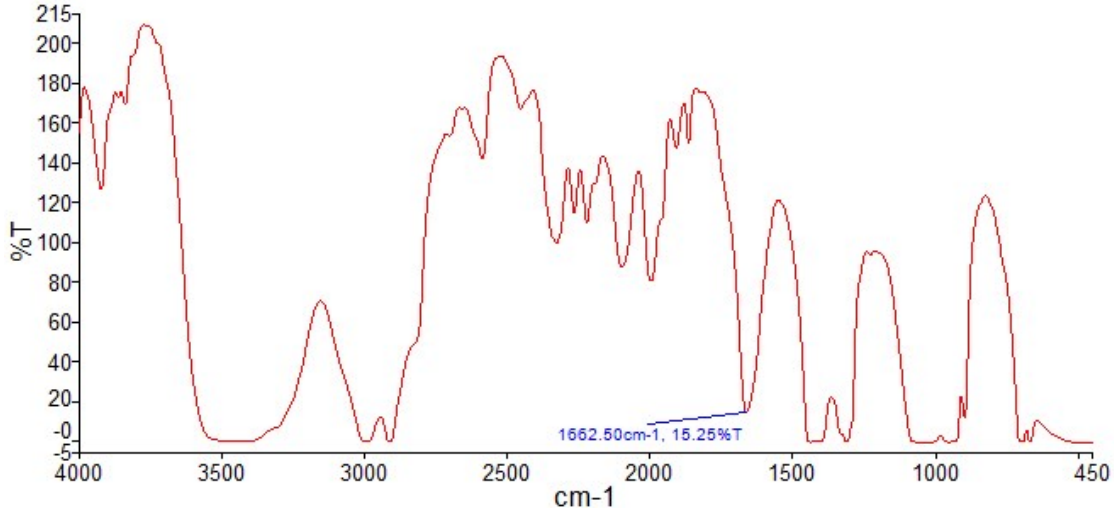

Fig. S2. The solution-phase FTIR spectrum of the title complex in DMSO.

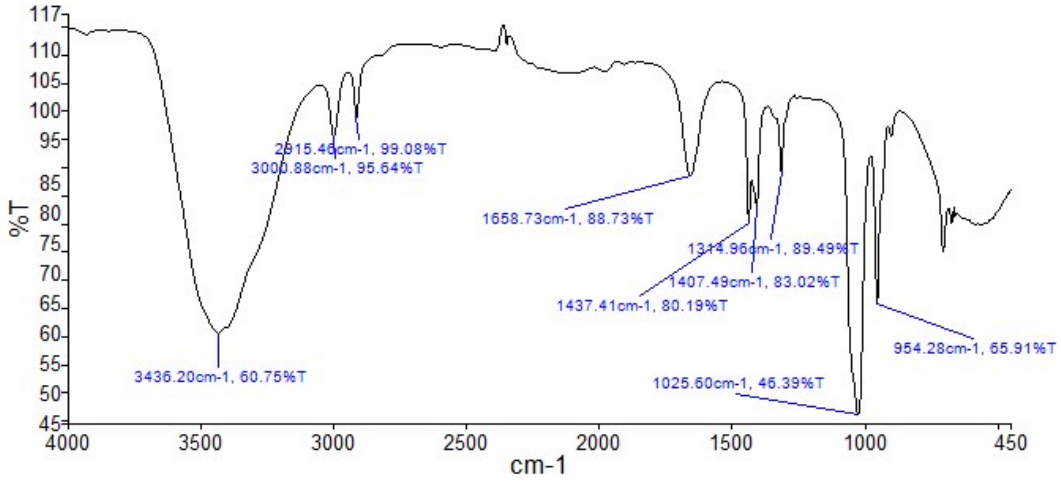

Fig. S3. The FTIR spectrum of the droplets of dissolved complex in DMSO on KBr.

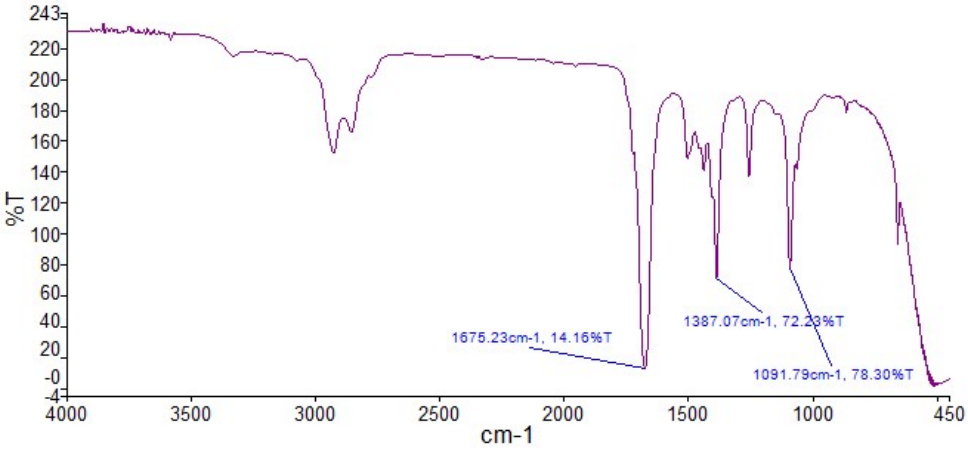

Fig. S4. The solution-phase FTIR spectrum of the title complex in DMF.

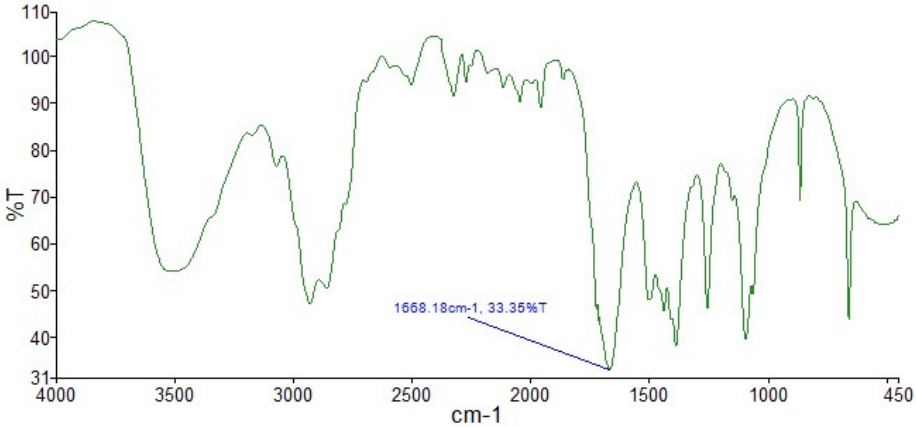

Fig. S5. The FTIR spectrum of the droplets of dissolved complex in DMF on KBr.

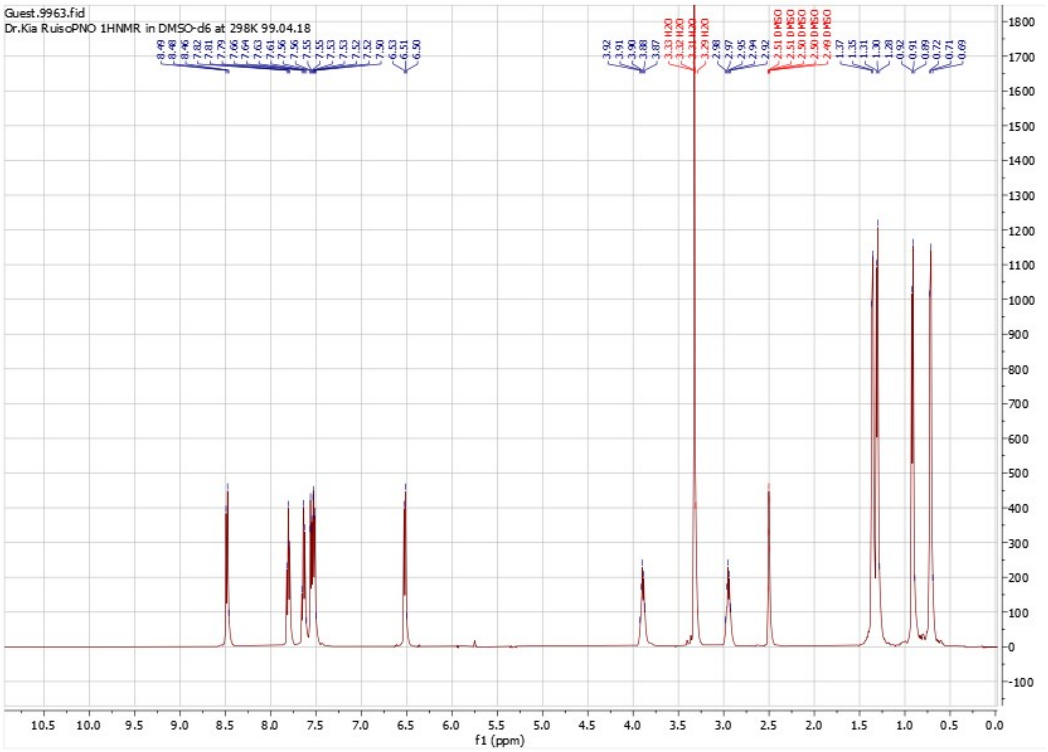

Figure S6. ^{1}H NMR (500 MHz), spectrum of the title complex in dmso-d6 at room temperature.

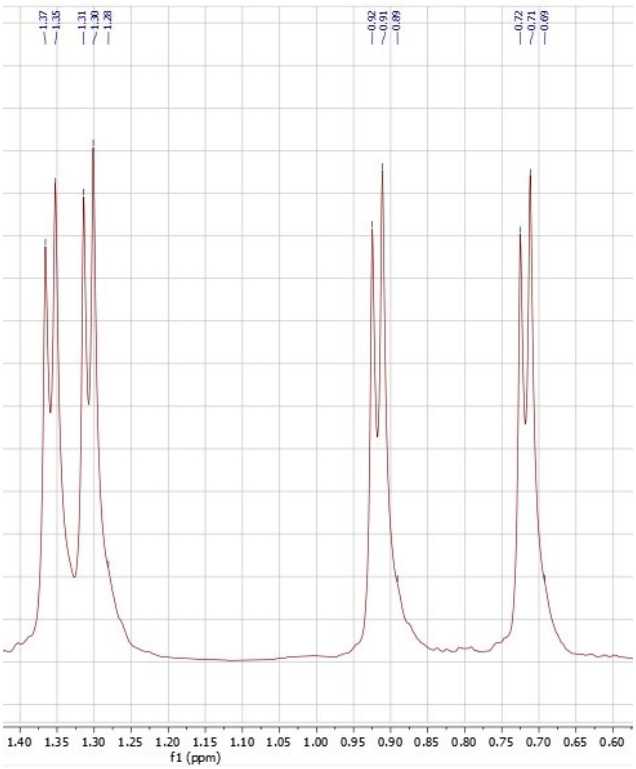

Figure S7. Expanded ^{1}H NMR spectrum of the title complex (0.6-1.40 ppm).

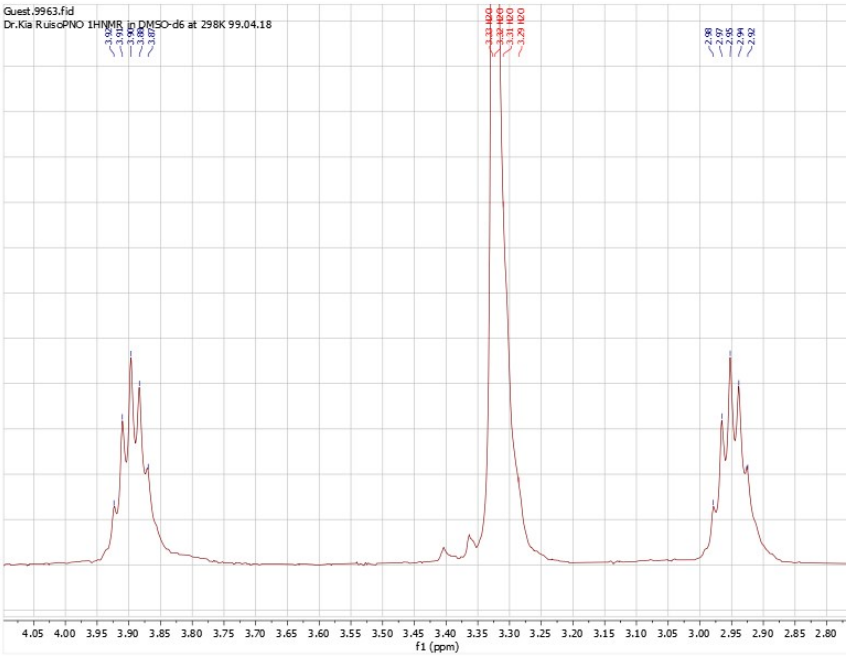

Figure S8. Expanded ^{1}H NMR spectrum of the title complex (2.80-4.00 ppm).

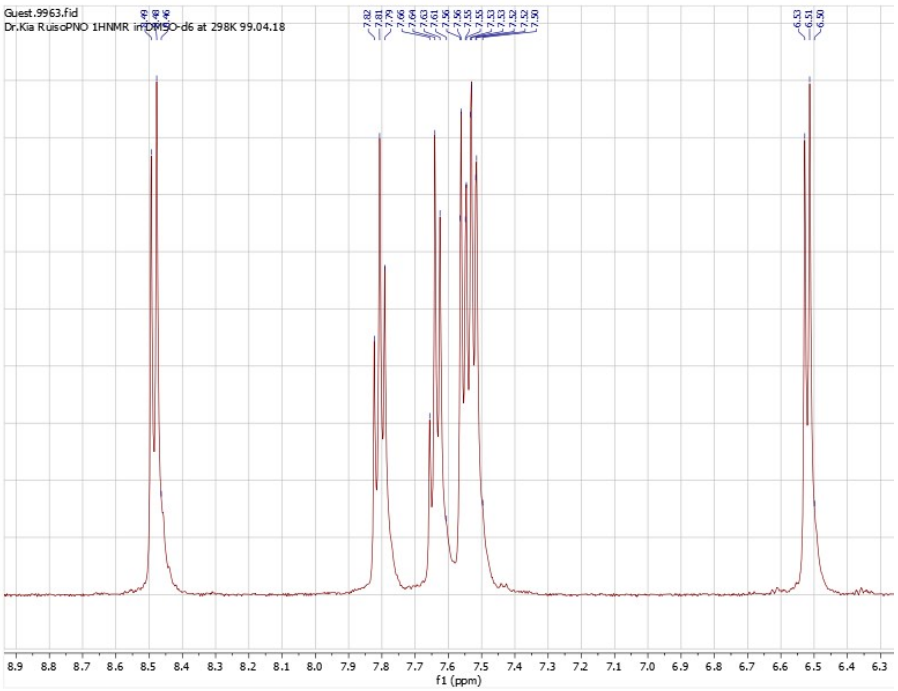

Figure S9. Expanded ^{1}H NMR spectrum of the title complex (6.30-8.60 ppm).

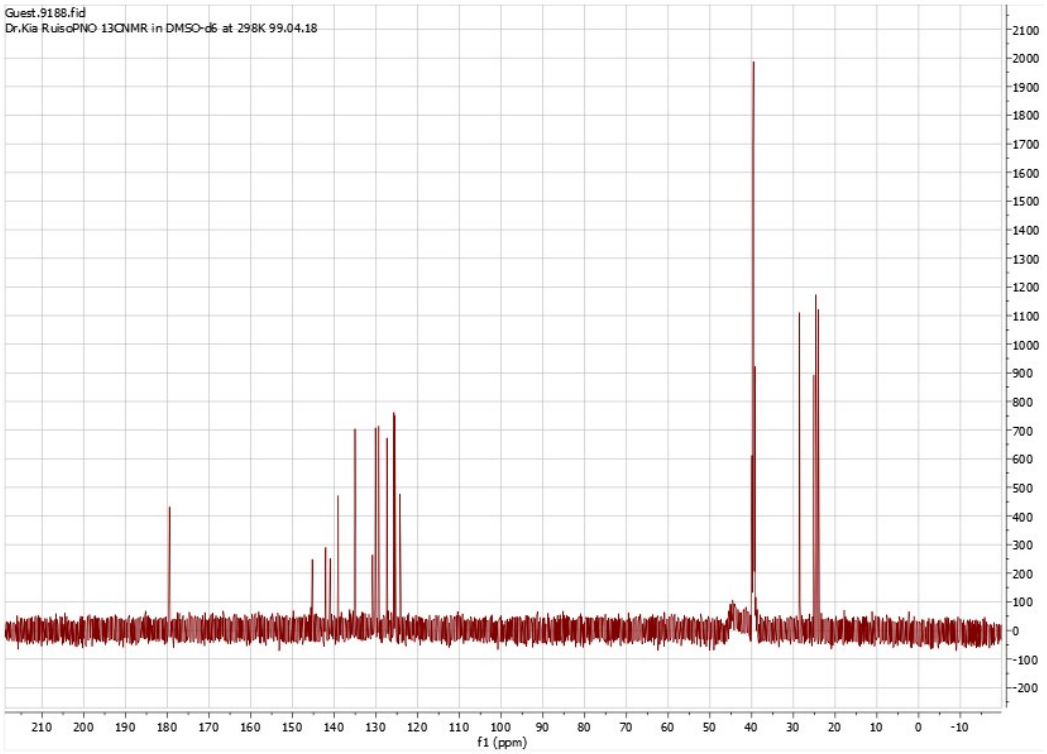

Figure S10. $^{13}C\{^{1}H\}$ NMR (150 MHz), spectrum of the title complex in dmso-d6 at room temperature.

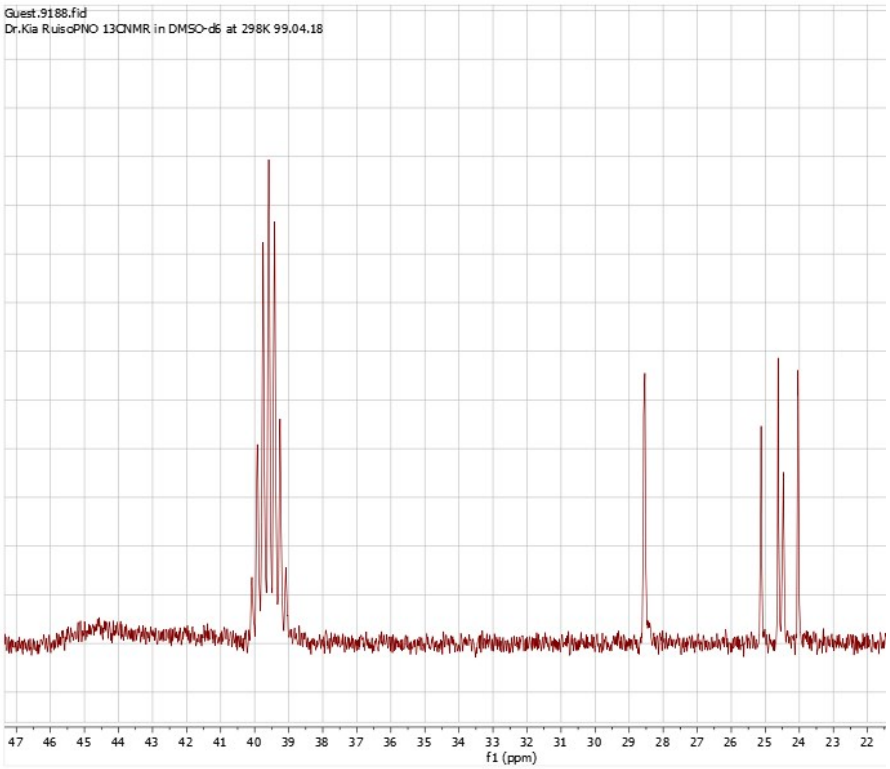

Figure S11. Expanded $^{13}C\{^{1}H\}$ NMR spectrum of the title complex (23-46 ppm).

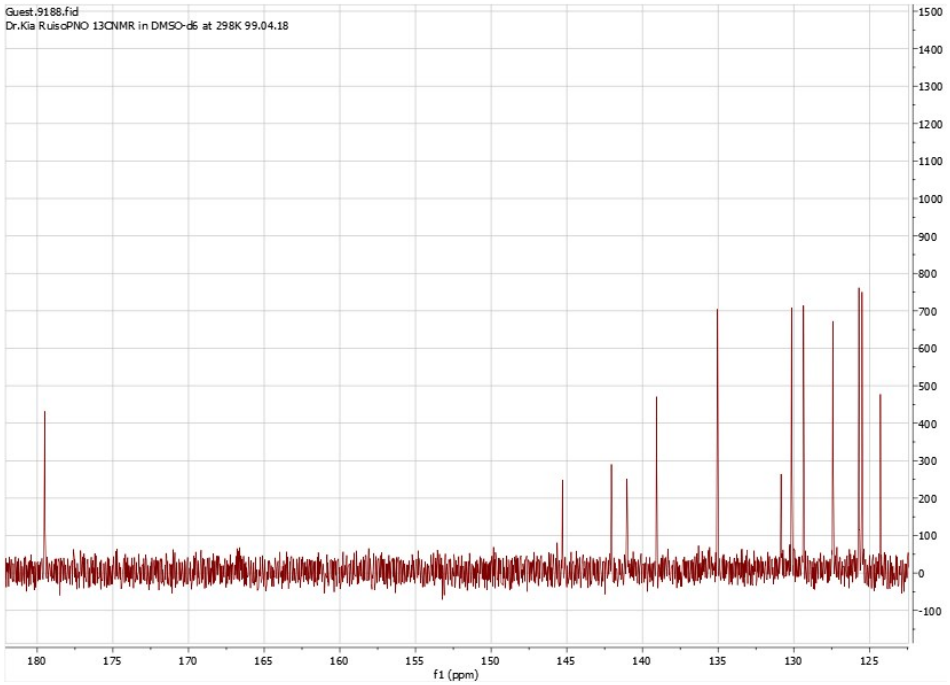

Figure S12. Expanded $^{13}C\{^{1}H\}$ NMR spectrum of the title complex (120-180 ppm).

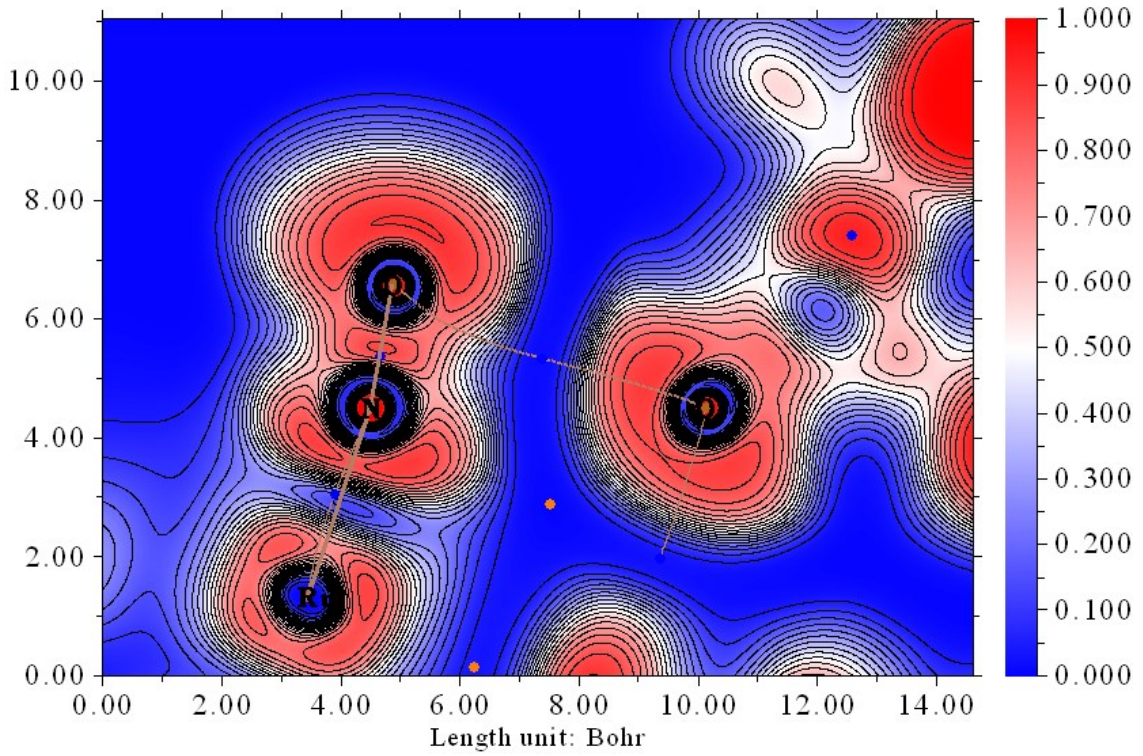

Fig. S13. Electron localization function (ELF) isodensity surface for O2···O1 interaction in the complex.

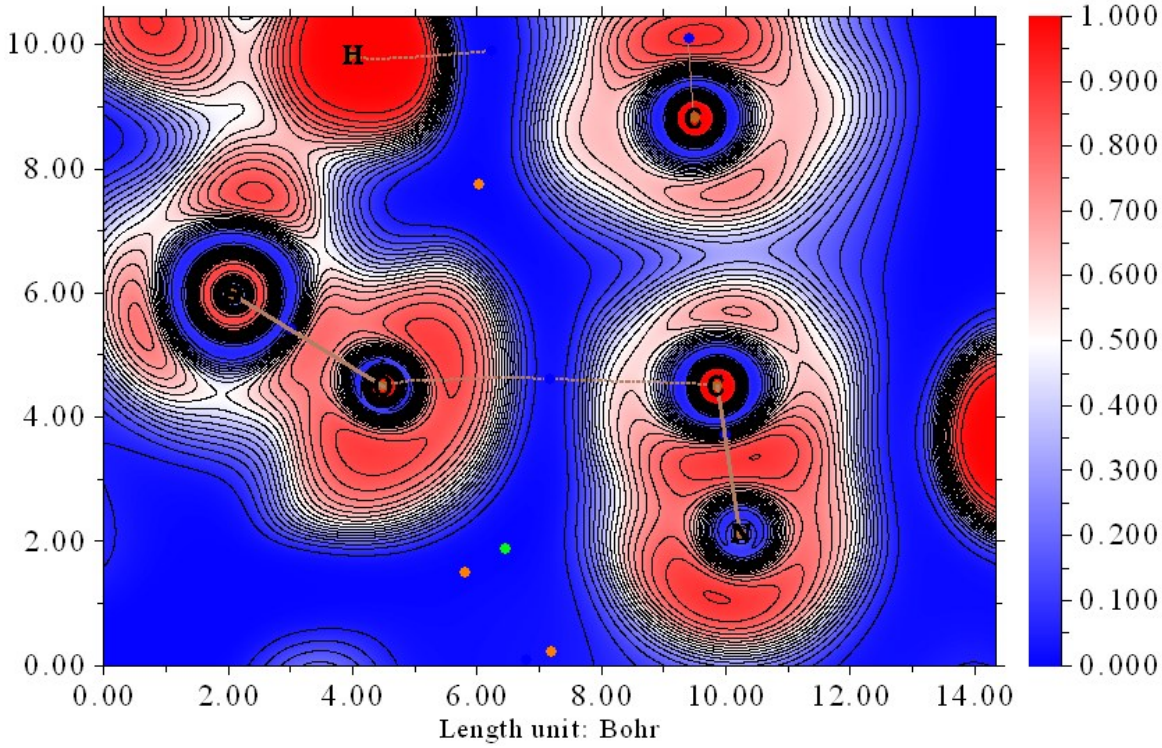

Fig. S14. Electron localization function (ELF) isodensity surface for O2···C17 interaction in the complex.

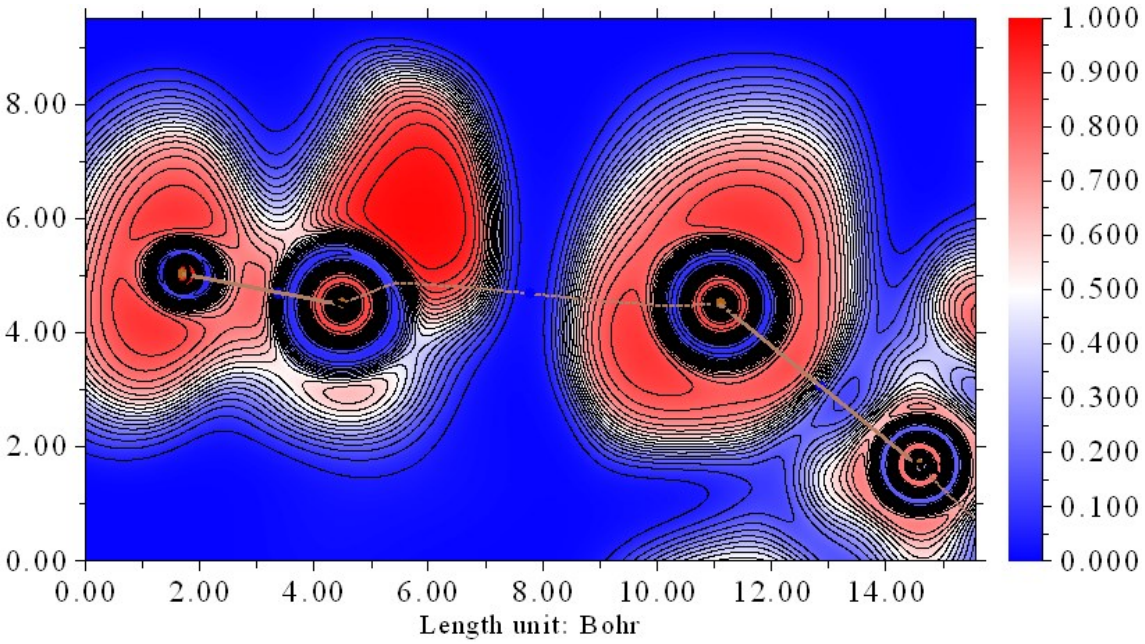

Fig. S15. Electron localization function (ELF) isodensity surface for Cl3···S1 interaction in the complex.

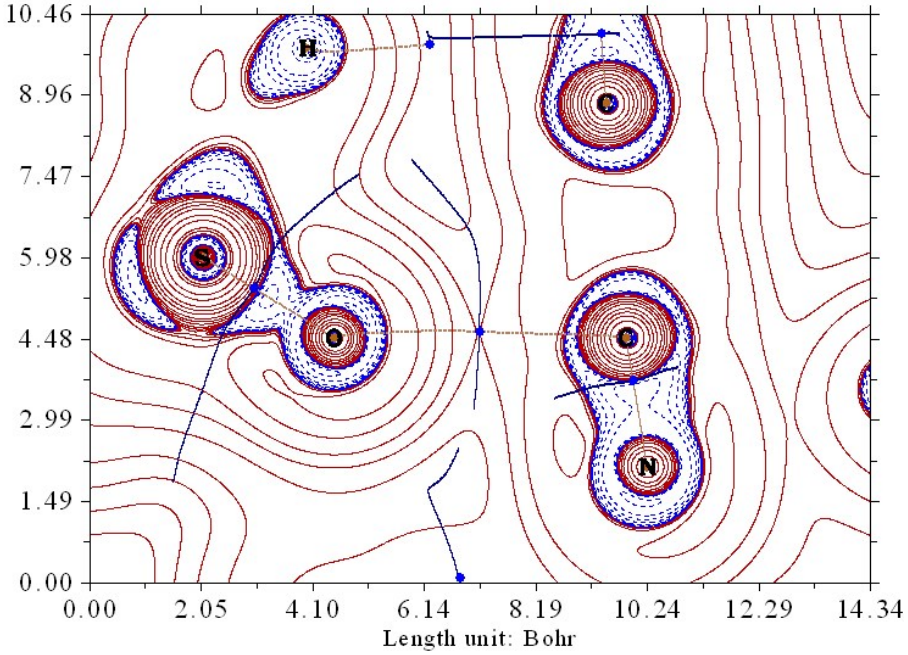

Fig. S16. Contour line diagram of the Laplacian distribution, bond paths and selected zero-flux surfaces for O2···C17 interaction.

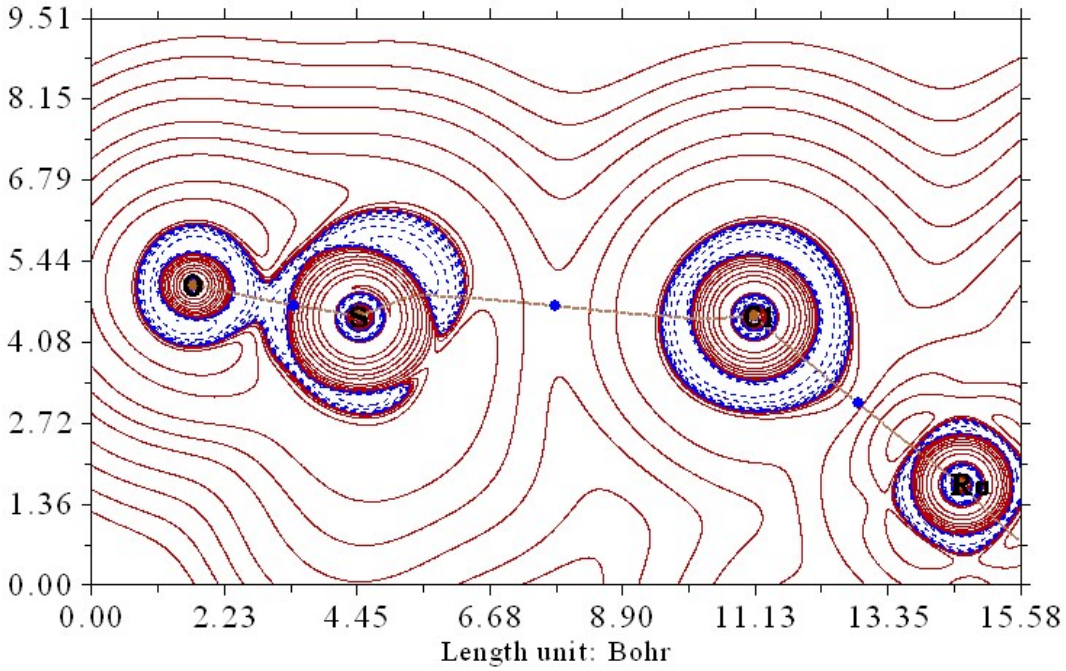

Fig. S17. Contour line diagram of the Laplacian distribution, bond paths and selected zero-flux surfaces for Cl3···S1 interaction.

Table S1. Crystal data and structure refinement for the Complex.

Identification code	Complex	
Empirical formula	$C_{38}H_{46}Cl_3N_3O_2RuS$	
Formula weight	816.26	
Temperature	150(2) K	
Wavelength	1.54184Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.2664(1) Å	α= 90°
	b = 25.5555(2) Å	β= 95.385(1)°
	c = 14.0136(1) Å	γ = 90°
Volume	4373.51(6) Å^3	
Z	4	
Density (calculated)	1.240 Mg/m^3	
Absorption coefficient	5.283 mm^{-1}	
F(000)	1688	
Crystal size	0.110 x 0.080 x 0.040 mm^3	
Theta range for data collection	3.609 to 73.105°	
Index ranges	-12<=h<=15, -31<=k<=31, -17<=l<=16	
Reflections collected	34889	
Independent reflections	8702 [R(int) = 0.0388]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.68975	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8702 / 0 / 443	
Goodness-of-fit on F^2	1.288	
Final R indices [I>2sigma(I)]	R1 = 0.0617, wR2 = 0.1424	
R indices (all data)	R1 = 0.0641, wR2 = 0.1434	
Largest diff. peak and hole	1.368 and -0.923 e. Å^{-3}	

Bond lengths [Å] and angles [^{0}] for the complex.

C(1)-C(6)	1.392(7)
C(1)-C(2)	1.413(7)
C(1)-N(1)	1.459(6)
C(2)-C(3)	1.392(7)
C(2)-C(28)	1.517(8)
C(3)-C(4)	1.391(9)
C(3)-H(3)	0.9300
C(4)-C(5)	1.360(10)
C(4)-H(4)	0.9300
C(5)-C(6)	1.400(8)
C(5)-H(5)	0.9300
C(6)-C(25)	1.523(8)
C(7)-N(1)	1.292(6)
C(7)-C(8)	1.465(7)
C(7)-C(17)	1.497(7)
C(8)-C(9)	1.384(7)
C(8)-C(18)	1.416(7)
C(9)-C(10)	1.396(8)
C(9)-H(9)	0.9300
C(10)-C(11)	1.382(8)
C(10)-H(10)	0.9300
C(11)-C(12)	1.409(8)
C(11)-H(11)	0.9300
C(12)-C(18)	1.410(7)
C(12)-C(13)	1.421(8)
C(13)-C(14)	1.378(9)
C(13)-H(13)	0.9300
C(14)-C(15)	1.419(8)
C(14)-H(14)	0.9300
C(15)-C(16)	1.381(7)
C(15)-H(15)	0.9300
C(16)-C(18)	1.405(7)
C(16)-C(17)	1.462(6)
C(17)-N(2)	1.286(6)

C(19)-C(20)	1.395(8)
C(19)-C(24)	1.404(8)
C(19)-N(2)	1.461(6)
C(20)-C(21)	1.382(8)
C(20)-C(31)	1.537(9)
C(21)-C(22)	1.396(10)
C(21)-H(21)	0.9300
C(22)-C(23)	1.372(10)
C(22)-H(22)	0.9300
C(23)-C(24)	1.400(8)
C(23)-H(23)	0.9300
C(24)-C(34)	1.505(9)
C(25)-C(27)	1.538(9)
C(25)-C(26)	1.538(9)
C(25)-H(25)	0.9800
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
C(28)-C(30)	1.532(8)
C(28)-C(29)	1.537(8)
C(28)-H(28)	0.9800
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600
C(30)-H(30A)	0.9600
C(30)-H(30B)	0.9600
C(30)-H(30C)	0.9600
C(31)-C(32)	1.535(9)
C(31)-C(33)	1.538(9)
C(31)-H(31)	0.9800
C(32)-H(32A)	0.9600
C(32)-H(32B)	0.9600
C(32)-H(32C)	0.9600

C(33)-H(33A)	0.9600
C(33)-H(33B)	0.9600
C(33)-H(33C)	0.9600
C(34)-C(36)	1.530(9)
C(34)-C(35)	1.537(9)
C(34)-H(34)	0.9800
C(35)-H(35A)	0.9600
C(35)-H(35B)	0.9600
C(35)-H(35C)	0.9600
C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600
C(37)-S(1)	1.770(8)
C(37)-H(37A)	0.9600
C(37)-H(37B)	0.9600
C(37)-H(37C)	0.9600
C(38)-S(1)	1.774(8)
C(38)-H(38A)	0.9600
C(38)-H(38B)	0.9600
C(38)-H(38C)	0.9600
N(1)-Ru(1)	2.110(4)
N(2)-Ru(1)	2.144(4)
N(3)-O(1)	1.113(6)
N(3)-Ru(1)	1.779(5)
O(2)-S(1)	1.500(4)
Cl(1)-Ru(1)	2.3078(14)
Cl(2)-Ru(1)	2.3512(12)
Cl(3)-Ru(1)	2.3698(13)

C(6)-C(1)-C(2)	122.7(5)
C(6)-C(1)-N(1)	118.5(5)
C(2)-C(1)-N(1)	118.8(4)
C(3)-C(2)-C(1)	116.7(5)
C(3)-C(2)-C(28)	119.6(5)
C(1)-C(2)-C(28)	123.8(4)
C(4)-C(3)-C(2)	121.7(6)

C(4)-C(3)-H(3)	119.1
C(2)-C(3)-H(3)	119.1
C(5)-C(4)-C(3)	119.7(5)
C(5)-C(4)-H(4)	120.2
C(3)-C(4)-H(4)	120.2
C(4)-C(5)-C(6)	121.9(6)
C(4)-C(5)-H(5)	119.0
C(6)-C(5)-H(5)	119.0
C(1)-C(6)-C(5)	117.3(5)
C(1)-C(6)-C(25)	123.7(5)
C(5)-C(6)-C(25)	119.1(5)
N(1)-C(7)-C(8)	134.2(5)
N(1)-C(7)-C(17)	118.0(4)
C(8)-C(7)-C(17)	107.7(4)
C(9)-C(8)-C(18)	119.4(5)
C(9)-C(8)-C(7)	135.4(5)
C(18)-C(8)-C(7)	105.1(4)
C(8)-C(9)-C(10)	118.6(5)
C(8)-C(9)-H(9)	120.7
C(10)-C(9)-H(9)	120.7
C(11)-C(10)-C(9)	122.6(5)
C(11)-C(10)-H(10)	118.7
C(9)-C(10)-H(10)	118.7
C(10)-C(11)-C(12)	120.3(5)
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-H(11)	119.9
C(11)-C(12)-C(18)	117.1(5)
C(11)-C(12)-C(13)	127.1(5)
C(18)-C(12)-C(13)	115.8(5)
C(14)-C(13)-C(12)	120.3(5)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(13)-C(14)-C(15)	123.0(5)
C(13)-C(14)-H(14)	118.5
C(15)-C(14)-H(14)	118.5
C(16)-C(15)-C(14)	117.6(5)

C(16)-C(15)-H(15)	121.2
C(14)-C(15)-H(15)	121.2
C(15)-C(16)-C(18)	119.5(5)
C(15)-C(16)-C(17)	134.5(5)
C(18)-C(16)-C(17)	106.0(4)
N(2)-C(17)-C(16)	134.2(5)
N(2)-C(17)-C(7)	118.6(4)
C(16)-C(17)-C(7)	107.0(4)
C(16)-C(18)-C(12)	123.7(5)
C(16)-C(18)-C(8)	114.2(4)
C(12)-C(18)-C(8)	122.0(5)
C(20)-C(19)-C(24)	122.1(5)
C(20)-C(19)-N(2)	119.0(5)
C(24)-C(19)-N(2)	118.8(5)
C(21)-C(20)-C(19)	118.3(6)
C(21)-C(20)-C(31)	116.3(6)
C(19)-C(20)-C(31)	125.3(5)
C(20)-C(21)-C(22)	121.1(6)
C(20)-C(21)-H(21)	119.5
C(22)-C(21)-H(21)	119.5
C(23)-C(22)-C(21)	119.5(6)
C(23)-C(22)-H(22)	120.2
C(21)-C(22)-H(22)	120.2
C(22)-C(23)-C(24)	121.8(6)
C(22)-C(23)-H(23)	119.1
C(24)-C(23)-H(23)	119.1
C(23)-C(24)-C(19)	117.1(6)
C(23)-C(24)-C(34)	119.0(5)
C(19)-C(24)-C(34)	123.6(5)
C(6)-C(25)-C(27)	109.9(5)
C(6)-C(25)-C(26)	112.2(5)
C(27)-C(25)-C(26)	110.4(5)
C(6)-C(25)-H(25)	108.1
C(27)-C(25)-H(25)	108.1
C(26)-C(25)-H(25)	108.1
C(25)-C(26)-H(26A)	109.5

C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(2)-C(28)-C(30)	112.0(5)
C(2)-C(28)-C(29)	109.1(5)
C(30)-C(28)-C(29)	109.8(5)
C(2)-C(28)-H(28)	108.6
C(30)-C(28)-H(28)	108.6
C(29)-C(28)-H(28)	108.6
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(28)-C(30)-H(30A)	109.5
C(28)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(28)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(32)-C(31)-C(20)	110.2(6)
C(32)-C(31)-C(33)	108.5(6)
C(20)-C(31)-C(33)	111.5(6)
C(32)-C(31)-H(31)	108.9
C(20)-C(31)-H(31)	108.9
C(33)-C(31)-H(31)	108.9
C(31)-C(32)-H(32A)	109.5

C(31)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(31)-C(33)-H(33A)	109.5
C(31)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(31)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(24)-C(34)-C(36)	109.9(5)
C(24)-C(34)-C(35)	112.5(6)
C(36)-C(34)-C(35)	108.6(6)
C(24)-C(34)-H(34)	108.6
C(36)-C(34)-H(34)	108.6
C(35)-C(34)-H(34)	108.6
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(34)-C(36)-H(36A)	109.5
C(34)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(34)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
S(1)-C(37)-H(37A)	109.5
S(1)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
S(1)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
S(1)-C(38)-H(38A)	109.5

S(1)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
S(1)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(7)-N(1)-C(1)	117.7(4)
C(7)-N(1)-Ru(1)	111.7(3)
C(1)-N(1)-Ru(1)	130.4(3)
C(17)-N(2)-C(19)	118.5(4)
C(17)-N(2)-Ru(1)	110.5(3)
C(19)-N(2)-Ru(1)	130.9(3)
O(1)-N(3)-Ru(1)	171.1(4)
N(3)-Ru(1)-N(1)	94.13(17)
N(3)-Ru(1)-N(2)	96.04(17)
N(1)-Ru(1)-N(2)	79.48(16)
N(3)-Ru(1)-Cl(1)	172.33(14)
N(1)-Ru(1)-Cl(1)	93.51(12)
N(2)-Ru(1)-Cl(1)	85.99(12)
N(3)-Ru(1)-Cl(2)	91.53(14)
N(1)-Ru(1)-Cl(2)	91.78(11)
N(2)-Ru(1)-Cl(2)	168.81(12)
Cl(1)-Ru(1)-Cl(2)	87.59(5)
N(3)-Ru(1)-Cl(3)	85.75(14)
N(1)-Ru(1)-Cl(3)	176.90(12)
N(2)-Ru(1)-Cl(3)	97.44(12)
Cl(1)-Ru(1)-Cl(3)	86.65(5)
Cl(2)-Ru(1)-Cl(3)	91.32(5)
O(2)-S(1)-C(37)	108.4(3)
O(2)-S(1)-C(38)	106.8(3)
C(37)-S(1)-C(38)	98.6(5)

Torsion angles [^{0}] for the complex.

C(6)-C(1)-C(2)-C(3)	0.7(8)
N(1)-C(1)-C(2)-C(3)	-177.2(4)
C(6)-C(1)-C(2)-C(28)	-178.6(5)
N(1)-C(1)-C(2)-C(28)	3.5(7)
C(1)-C(2)-C(3)-C(4)	0.1(8)
C(28)-C(2)-C(3)-C(4)	179.4(5)
C(2)-C(3)-C(4)-C(5)	-1.1(9)
C(3)-C(4)-C(5)-C(6)	1.5(10)
C(2)-C(1)-C(6)-C(5)	-0.3(8)
N(1)-C(1)-C(6)-C(5)	177.5(5)
C(2)-C(1)-C(6)-C(25)	-178.8(5)
N(1)-C(1)-C(6)-C(25)	-0.9(8)
C(4)-C(5)-C(6)-C(1)	-0.8(9)
C(4)-C(5)-C(6)-C(25)	177.7(6)
N(1)-C(7)-C(8)-C(9)	-5.7(11)
C(17)-C(7)-C(8)-C(9)	178.3(6)
N(1)-C(7)-C(8)-C(18)	175.6(6)
C(17)-C(7)-C(8)-C(18)	-0.4(5)
C(18)-C(8)-C(9)-C(10)	0.7(8)
C(7)-C(8)-C(9)-C(10)	-177.9(6)
C(8)-C(9)-C(10)-C(11)	-0.2(9)
C(9)-C(10)-C(11)-C(12)	-0.5(9)
C(10)-C(11)-C(12)-C(18)	0.6(8)
C(10)-C(11)-C(12)-C(13)	-179.9(6)
C(11)-C(12)-C(13)-C(14)	-178.4(6)
C(18)-C(12)-C(13)-C(14)	1.0(8)
C(12)-C(13)-C(14)-C(15)	-0.2(9)
C(13)-C(14)-C(15)-C(16)	-0.6(9)
C(14)-C(15)-C(16)-C(18)	0.5(8)
C(14)-C(15)-C(16)-C(17)	178.1(6)
C(15)-C(16)-C(17)-N(2)	6.3(11)
C(18)-C(16)-C(17)-N(2)	-175.8(6)
C(15)-C(16)-C(17)-C(7)	-178.8(6)
C(18)-C(16)-C(17)-C(7)	-1.0(5)

N(1)-C(7)-C(17)-N(2)	-0.1(7)
C(8)-C(7)-C(17)-N(2)	176.7(4)
N(1)-C(7)-C(17)-C(16)	-175.9(4)
C(8)-C(7)-C(17)-C(16)	0.9(5)
C(15)-C(16)-C(18)-C(12)	0.4(8)
C(17)-C(16)-C(18)-C(12)	-177.9(5)
C(15)-C(16)-C(18)-C(8)	179.0(5)
C(17)-C(16)-C(18)-C(8)	0.8(6)
C(11)-C(12)-C(18)-C(16)	178.4(5)
C(13)-C(12)-C(18)-C(16)	-1.1(8)
C(11)-C(12)-C(18)-C(8)	-0.1(8)
C(13)-C(12)-C(18)-C(8)	-179.6(5)
C(9)-C(8)-C(18)-C(16)	-179.2(5)
C(7)-C(8)-C(18)-C(16)	-0.2(6)
C(9)-C(8)-C(18)-C(12)	-0.5(8)
C(7)-C(8)-C(18)-C(12)	178.5(5)
C(24)-C(19)-C(20)-C(21)	-0.5(8)
N(2)-C(19)-C(20)-C(21)	-178.4(5)
C(24)-C(19)-C(20)-C(31)	178.9(5)
N(2)-C(19)-C(20)-C(31)	1.0(8)
C(19)-C(20)-C(21)-C(22)	1.1(9)
C(31)-C(20)-C(21)-C(22)	-178.3(6)
C(20)-C(21)-C(22)-C(23)	-0.6(9)
C(21)-C(22)-C(23)-C(24)	-0.6(9)
C(22)-C(23)-C(24)-C(19)	1.2(8)
C(22)-C(23)-C(24)-C(34)	175.3(6)
C(20)-C(19)-C(24)-C(23)	-0.6(8)
N(2)-C(19)-C(24)-C(23)	177.3(5)
C(20)-C(19)-C(24)-C(34)	-174.4(5)
N(2)-C(19)-C(24)-C(34)	3.5(8)
C(1)-C(6)-C(25)-C(27)	118.2(6)
C(5)-C(6)-C(25)-C(27)	-60.2(7)
C(1)-C(6)-C(25)-C(26)	-118.6(6)
C(5)-C(6)-C(25)-C(26)	63.0(7)
C(3)-C(2)-C(28)-C(30)	52.5(7)
C(1)-C(2)-C(28)-C(30)	-128.3(5)

C(3)-C(2)-C(28)-C(29)	-69.3(6)
C(1)-C(2)-C(28)-C(29)	109.9(6)
C(21)-C(20)-C(31)-C(32)	-58.9(7)
C(19)-C(20)-C(31)-C(32)	121.7(6)
C(21)-C(20)-C(31)-C(33)	61.7(7)
C(19)-C(20)-C(31)-C(33)	-117.7(6)
C(23)-C(24)-C(34)-C(36)	-65.1(7)
C(19)-C(24)-C(34)-C(36)	108.6(6)
C(23)-C(24)-C(34)-C(35)	56.0(7)
C(19)-C(24)-C(34)-C(35)	-130.4(6)
C(8)-C(7)-N(1)-C(1)	-0.6(8)
C(17)-C(7)-N(1)-C(1)	175.0(4)
C(8)-C(7)-N(1)-Ru(1)	174.6(5)
C(17)-C(7)-N(1)-Ru(1)	-9.7(6)
C(6)-C(1)-N(1)-C(7)	-92.0(6)
C(2)-C(1)-N(1)-C(7)	85.9(6)
C(6)-C(1)-N(1)-Ru(1)	93.7(5)
C(2)-C(1)-N(1)-Ru(1)	-88.3(5)
C(16)-C(17)-N(2)-C(19)	8.0(8)
C(7)-C(17)-N(2)-C(19)	-166.4(4)
C(16)-C(17)-N(2)-Ru(1)	-176.1(5)
C(7)-C(17)-N(2)-Ru(1)	9.6(5)
C(20)-C(19)-N(2)-C(17)	72.0(6)
C(24)-C(19)-N(2)-C(17)	-106.0(6)
C(20)-C(19)-N(2)-Ru(1)	-103.1(5)
C(24)-C(19)-N(2)-Ru(1)	78.9(6)

Table S2. Hydrogen Bonds (Å, ^{0})

C22−H22···Cl2	0.9300	2.8300	3.495(7)	130.00	4_555
C25−H25···Cl1	0.9800	2.6500	3.423(6)	136.00	
C28−H28···N3	0.9800	2.6200	3.380(7)	135.00	
C31−H31··· Cl1	0.9800	2.7900	3.397(7)	121.00	
C32− H32B···Cl1	0.9600	2.7800	3.393(7)	122.00	
C34−H34···N3	0.9800	2.5900	3.531(7)	161.00	

4455 = Symmetry code; -1/2+x,1/2-y,1/2+z

Table S3. Comparison of important bond lengths and angles of the X-ray structure and theoretically optimized structure of the title complex

Bond/Interaction	Experimental (Å)	Theoretical (Å)
Ru1—N1	2.110(4)	2.198
Ru1—N2	2.143(4)	2.196
Ru1—N3	1.778(4)	1.770
Ru1—Cl1	2.3079(15)	2.368
Ru1—Cl2	2.3512(14)	2.425
Ru1—Cl3	2.3699(14)	2.425
N3—O1	1.113(6)	1.151
N1—C1	1.460(7)	1.450
N1—C7	1.292(6)	1.290
N2—C17	1.287(6)	1.290
N2—C19	1.461(7)	1.450
Cl1−Ru1−Cl2	87.59(5)	86.93
Cl1−Ru1−Cl3	86.65(5)	87.07
Cl1−Ru1−N1	93.51(12)	88.30
Cl1−Ru1−N2	85.99(12)	88.42
Cl1−Ru1−N3	172.34(13)	171.63
N1−Ru1−N2	79.49(15)	78.80

Table S4. Optimized Cartesian coordinates of the title complex without DMSO.

Ru	-0.13271400	-1.81441900	-0.92161200
N	-0.07917800	-0.99166900	-2.48737900
O	-0.05825300	-0.64470300	-3.58477800
Cl	-0.22703000	-3.20758100	0.99032100
Cl	-1.97000900	-3.12594400	-1.80694300
Cl	1.50789900	-3.36111600	-1.81440500
C	-2.88426100	-0.34546400	0.16761300
C	-3.57360000	0.25899300	-0.90929400
C	-4.97216200	0.28531400	-0.86258500
H	-5.51740000	0.74116100	-1.68369100
C	-5.67463000	-0.25908500	0.20600000
H	-6.76082900	-0.23101100	0.21940700
C	-4.97565000	-0.84500700	1.25445300
H	-5.52448500	-1.27660300	2.08603800
C	-3.57626900	-0.91186700	1.26685200
C	-0.73662200	0.47841900	0.77924500
C	-1.09060500	1.64848600	1.59851300
C	-2.27524300	2.26985200	1.95211900
H	-3.23541200	1.88746300	1.62839700
C	-2.21517500	3.43262300	2.76420200
H	-3.14660900	3.91521500	3.04504000
C	-1.01664600	3.96463500	3.20855300
H	-1.01472000	4.85530400	3.83176900
C	0.21780800	3.35450300	2.85250500
C	1.52438300	3.79145300	3.20737300
H	1.64386000	4.67307600	3.83216400
C	2.63999400	3.10001100	2.76403500
H	3.62835100	3.45038700	3.04675600
C	2.54115200	1.93897200	1.95306600
H	3.43983200	1.42959000	1.62813500
C	1.28277800	1.48598600	1.59922400
C	0.77265000	0.37597300	0.77849200
C	0.13913700	2.19715400	2.05058200
C	2.79045800	-0.72040100	0.15514700
C	3.40908300	-1.37987600	1.24587900

C	4.80648900	-1.48204700	1.23172900
H	5.29991800	-1.98510300	2.05782500
C	5.57064800	-0.97282100	0.18870800
H	6.65245100	-1.07489700	0.20106200
C	4.93813200	-0.33853600	-0.87392300
H	5.53356900	0.05619300	-1.69183000
C	3.54646500	-0.19519300	-0.91877300
C	-2.90418300	-1.59794600	2.45304400
H	-1.82424200	-1.58269700	2.30019000
C	-3.31652700	-3.08180700	2.52991600
H	-4.38616900	-3.18977800	2.74875100
H	-2.75764000	-3.58289300	3.32853800
H	-3.09701000	-3.59629100	1.59122700
C	-3.20541200	-0.88102300	3.78513900
H	-2.88435200	0.16642000	3.76942600
H	-2.67764100	-1.38268700	4.60470400
H	-4.27561200	-0.89926000	4.02375600
C	-2.87823800	0.90551900	-2.10310000
H	-1.79786100	0.85216200	-1.94945500
C	-3.22311000	0.17100000	-3.41428200
H	-4.29018800	0.26434300	-3.64805800
H	-2.98773800	-0.89482700	-3.34547300
H	-2.66169000	0.60215500	-4.25222300
C	-3.22817000	2.40312400	-2.21122600
H	-4.29874400	2.55736000	-2.38871900
H	-2.69140300	2.85403200	-3.05501500
H	-2.95556900	2.94765200	-1.30095400
C	2.66002400	-1.99640000	2.42437400
H	1.58912500	-1.85241600	2.27490500
C	2.89063600	-3.52025400	2.47845900
H	3.94043000	-3.76093000	2.68702500
H	2.60386200	-3.99030600	1.53455400
H	2.27959200	-3.96097000	3.27442400
C	3.04561900	-1.33976600	3.76568300
H	2.46585000	-1.79021400	4.57982500
H	2.84732100	-0.26207000	3.76821400

H	4.10728800	-1.48470300	3.99936400
C	2.93467200	0.53729300	-2.10892100
H	1.85727300	0.62480500	-1.95314500
C	3.18062300	-0.23382600	-3.42151900
H	4.24976400	-0.26855000	-3.66253800
H	2.66917100	0.26131100	-4.25600500
H	2.81997500	-1.26411700	-3.35010900
C	3.46933000	1.97884300	-2.21470600
H	3.26625700	2.54191000	-1.29817900
H	2.98103600	2.49614300	-3.04917000
H	4.54972200	1.99891900	-2.39832300
N	-1.43528700	-0.39133900	0.13193400
N	1.34760200	-0.57762100	0.12764000

Table S5. X-ray and optimized Cartesian coordinates of the title complex with DMSO.

X-ray

C	2.76520000	11.02220000	3.94030000
C	2.80490000	10.74850000	2.55440000
C	2.78120000	11.84720000	1.69950000
H	2.80470000	11.70660000	0.78050000
C	2.72330000	13.14990000	2.18440000
H	2.72450000	13.86850000	1.59400000
C	2.66490000	13.36770000	3.52580000
H	2.60540000	14.24140000	3.83890000
C	2.69180000	12.31550000	4.44920000
C	4.02590000	9.49440000	5.21660000
C	5.39010000	9.88940000	4.85580000
C	5.95440000	10.77700000	3.95600000
H	5.41780000	11.31580000	3.42080000
C	7.34590000	10.84630000	3.86890000
H	7.72670000	11.43990000	3.26270000
C	8.17960000	10.06720000	4.64830000
H	9.10200000	10.13950000	4.55480000
C	7.63830000	9.16390000	5.58390000
C	8.35540000	8.30000000	6.45410000
H	9.28530000	8.31150000	6.45500000
C	7.67880000	7.44460000	7.29700000
H	8.17320000	6.88790000	7.85430000
C	6.26260000	7.37440000	7.35360000
H	5.83230000	6.78170000	7.92660000
C	5.54630000	8.21800000	6.52740000
C	4.12370000	8.42870000	6.26330000
C	6.23290000	9.09210000	5.66800000
C	3.12980000	7.16740000	7.99550000
C	3.45280000	7.79330000	9.20010000
C	3.56900000	7.01250000	10.33440000
H	3.76840000	7.41530000	11.14860000
C	3.39180000	5.62850000	10.27760000
H	3.48040000	5.11310000	11.04660000
C	3.08600000	5.03470000	9.07940000

H	2.97800000	4.11150000	9.04670000
C	2.93200000	5.78010000	7.90410000
C	2.67500000	12.63710000	5.93730000
H	2.73070000	11.79270000	6.43160000
C	1.38160000	13.35420000	6.36150000
H	1.31710000	14.19540000	5.90340000
H	1.39610000	13.50620000	7.30920000
H	0.62460000	12.80840000	6.13640000
C	3.90360000	13.48640000	6.30350000
H	4.70330000	13.01140000	6.06610000
H	3.90280000	13.65990000	7.24770000
H	3.87160000	14.31820000	5.82530000
C	2.85380000	9.34830000	1.97290000
H	2.98730000	8.71000000	2.70430000
C	1.51070000	9.04080000	1.29170000
H	1.34850000	9.68500000	0.59870000
H	0.80510000	9.08470000	1.94110000
H	1.53980000	8.16050000	0.90980000
C	3.99690000	9.18530000	0.96610000
H	3.85140000	9.77050000	0.21910000
H	4.02600000	8.27610000	0.65930000
H	4.82980000	9.40710000	1.38890000
C	3.70790000	9.29800000	9.37900000
H	3.56930000	9.74740000	8.51920000
C	2.73120000	9.88340000	10.40810000
H	2.88660000	9.47720000	11.26400000
H	1.82950000	9.70770000	10.12960000
H	2.86660000	10.83140000	10.47460000
C	5.14330000	9.57300000	9.85840000
H	5.29190000	10.52070000	9.89660000
H	5.76680000	9.17580000	9.24600000
H	5.26710000	9.19420000	10.73180000
C	2.70270000	5.05560000	6.60490000
H	2.55630000	5.71870000	5.89830000
C	1.48390000	4.12120000	6.66120000
H	1.67880000	3.37520000	7.23310000

H	1.28330000	3.80330000	5.77780000
H	0.72840000	4.60130000	7.00780000
C	3.93700000	4.22520000	6.24750000
H	4.68380000	4.80970000	6.09850000
H	3.76260000	3.71930000	5.45040000
H	4.13920000	3.62540000	6.96930000
N	2.84970000	9.90800000	4.87880000
N	3.03760000	7.97320000	6.78080000
N	1.40880000	7.48950000	4.39880000
O	1.30420000	6.67890000	3.64350000
Cl	0.99220000	10.10020000	7.50300000
Cl	-0.34330000	9.90080000	4.57470000
Cl	-0.28260000	7.26910000	6.68920000
Ru	1.33160000	8.69650000	5.70280000
C	5.09100000	4.47440000	2.86020000
H	5.44790000	4.18490000	3.70310000
H	5.64410000	4.14450000	2.14820000
H	4.19930000	4.13430000	2.75650000
C	6.76720000	6.55300000	3.16740000
H	6.90810000	7.49770000	3.26400000
H	7.30970000	6.22040000	2.44870000
H	7.00910000	6.10840000	3.98320000
O	4.27230000	6.73530000	3.98910000
S	5.05740000	6.24370000	2.80990000

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Optimised

C	-2.87220000	-0.40150000	0.14400000
C	-3.59720000	0.40390000	-0.76460000
C	-4.98190000	0.43430000	-0.61100000
H	-5.50590000	0.96770000	-1.20890000
C	-5.62250000	-0.29160000	0.38970000
H	-6.57390000	-0.24190000	0.48540000
C	-4.88770000	-1.07400000	1.23340000
H	-5.33870000	-1.58620000	1.90500000
C	-3.49120000	-1.14940000	1.14490000
C	-0.76400000	0.49940000	0.69810000

C	-1.15790000	1.63820000	1.53360000
C	-2.35750000	2.23250000	1.88750000
H	-3.19040000	1.87280000	1.58250000
C	-2.32640000	3.37070000	2.70130000
H	-3.15450000	3.78510000	2.94470000
C	-1.14530000	3.92020000	3.16740000
H	-1.16830000	4.70390000	3.71690000
C	0.09260000	3.33040000	2.83630000
C	1.38450000	3.77030000	3.23380000
H	1.47340000	4.53370000	3.80480000
C	2.51110000	3.10180000	2.80010000
H	3.36900000	3.42120000	3.08080000
C	2.45600000	1.96130000	1.95640000
H	3.25530000	1.52270000	1.66490000
C	1.20900000	1.50720000	1.57170000
C	0.73240000	0.42350000	0.71100000
C	0.05810000	2.18580000	2.01310000
C	2.72030000	-0.80240000	0.34550000
C	3.10060000	-1.35140000	1.57520000
C	4.44950000	-1.55620000	1.81370000
H	4.72690000	-1.94560000	2.64300000
C	5.41120000	-1.20470000	0.86430000
H	6.34090000	-1.34480000	1.04540000
C	5.01360000	-0.65670000	-0.33240000
H	5.67850000	-0.40980000	-0.97560000
C	3.66190000	-0.44900000	-0.63740000
C	-2.73330000	-2.00330000	2.15230000
H	-1.75810000	-1.91550000	1.96180000
C	-3.10840000	-3.49310000	2.04600000
H	-4.06230000	-3.60700000	2.25080000
H	-2.57250000	-4.01120000	2.68520000
H	-2.92930000	-3.81190000	1.13470000
C	-2.98960000	-1.48460000	3.57990000
H	-2.71200000	-0.54460000	3.64280000
H	-2.47360000	-2.02140000	4.22040000
H	-3.94640000	-1.55700000	3.78910000

C	-2.95230000	1.20330000	-1.88220000
H	-1.96170000	1.16720000	-1.76950000
C	-3.31660000	0.56370000	-3.23440000
H	-4.29290000	0.55490000	-3.34050000
H	-2.97670000	-0.35710000	-3.26430000
H	-2.91330000	1.08520000	-3.96250000
C	-3.39450000	2.67280000	-1.86420000
H	-4.36170000	2.72680000	-2.02530000
H	-2.91820000	3.16630000	-2.56690000
H	-3.18670000	3.06790000	-0.98930000
C	2.13970000	-1.74310000	2.70870000
H	1.20260000	-1.57820000	2.40910000
C	2.29670000	-3.23430000	3.04730000
H	3.20460000	-3.40100000	3.38270000
H	2.14270000	-3.77220000	2.24060000
H	1.64290000	-3.48380000	3.73630000
C	2.40720000	-0.92110000	3.98390000
H	1.73570000	-1.14630000	4.66450000
H	2.35280000	0.03690000	3.77600000
H	3.30330000	-1.13010000	4.32730000
C	3.30880000	0.25370000	-1.92380000
H	2.31600000	0.26610000	-2.01940000
C	3.91240000	-0.44450000	-3.15540000
H	4.88680000	-0.32130000	-3.15810000
H	3.53130000	-0.05400000	-3.97210000
H	3.70440000	-1.40350000	-3.12380000
C	3.81530000	1.70100000	-1.88580000
H	3.35360000	2.19690000	-1.17730000
H	3.63880000	2.13350000	-2.74710000
H	4.78160000	1.70290000	-1.71060000
N	-1.41500000	-0.41740000	0.06140000
N	1.30510000	-0.54900000	0.09120000
N	-0.10160000	-0.52270000	-2.47800000
O	-0.02080000	0.04150000	-3.44300000
Cl	0.01510000	-3.26800000	0.54030000
Cl	-1.93590000	-2.83140000	-1.99770000

Cl	1.42790000	-2.93330000	-2.32820000
Ru	-0.12370000	-1.63330000	-1.08830000
C	1.48840000	4.23960000	-2.98180000
H	2.31720000	4.20250000	-2.45580000
H	1.31690000	5.16620000	-3.25880000
H	1.57980000	3.67120000	-3.77720000
C	0.32330000	4.76470000	-0.61560000
H	-0.31500000	4.51790000	0.08840000
H	0.15040000	5.68640000	-0.90750000
H	1.23910000	4.69670000	-0.26700000
O	0.46010000	2.28000000	-1.50060000
S	0.13060000	3.66020000	-1.99640000

Table S6. G03/B3LYP calculated one-electron energy and percentage composition of selected frontier MOs of the title complex in terms of component fragments

MO	Orbital	Energy (eV)	$Ru(NO)Cl_3$	α-diimine (L)
180	LUMO + 3	-2.67	85.6	14.4
179	LUMO + 2	-2.71	87.1	12.9
178	LUMO + 1	-2.93	16.1	83.9
177	**LUMO**	**-3.56**	**13.9**	**86.1**
176	**HOMO**	**-6.40**	**90.9**	**9.1**
175	HOMO – 1	-6.62	87.8	12.2
174	HOMO – 2	-6.67	88.0	12.0
173	HOMO – 3	-6.73	86.1	13.9

E(HOMO-LUMO gap)= 2.844 eV