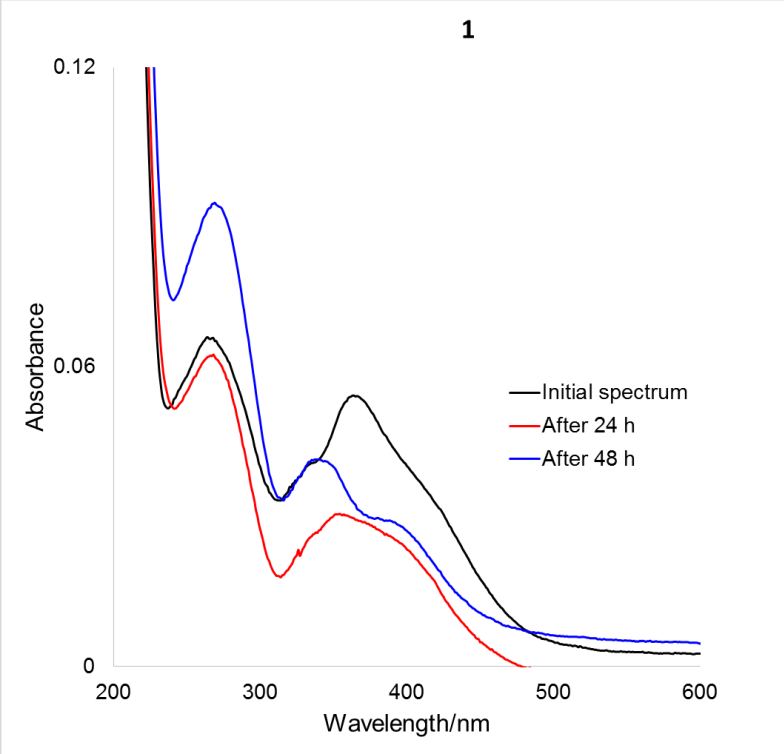
Anticancer, biophysical and computational investigations of half-sandwich ruthenium(II) thiosemicarbazone complexes: The effect of arene versus thiacrown face-cap

Supplementary Information



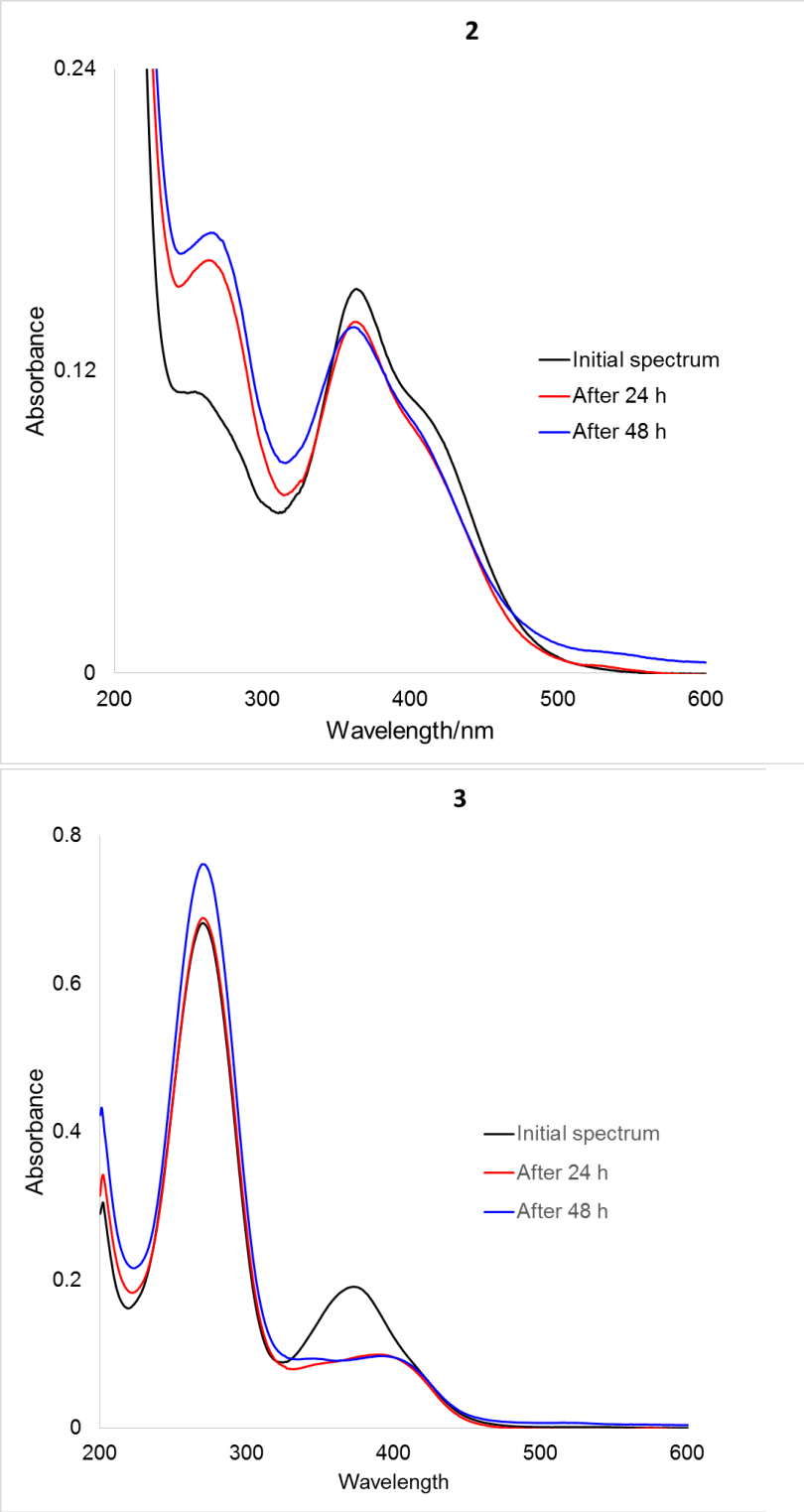


Figure S1. UV-Vis spectra of **1**, **2**, and **3** as a function of time.

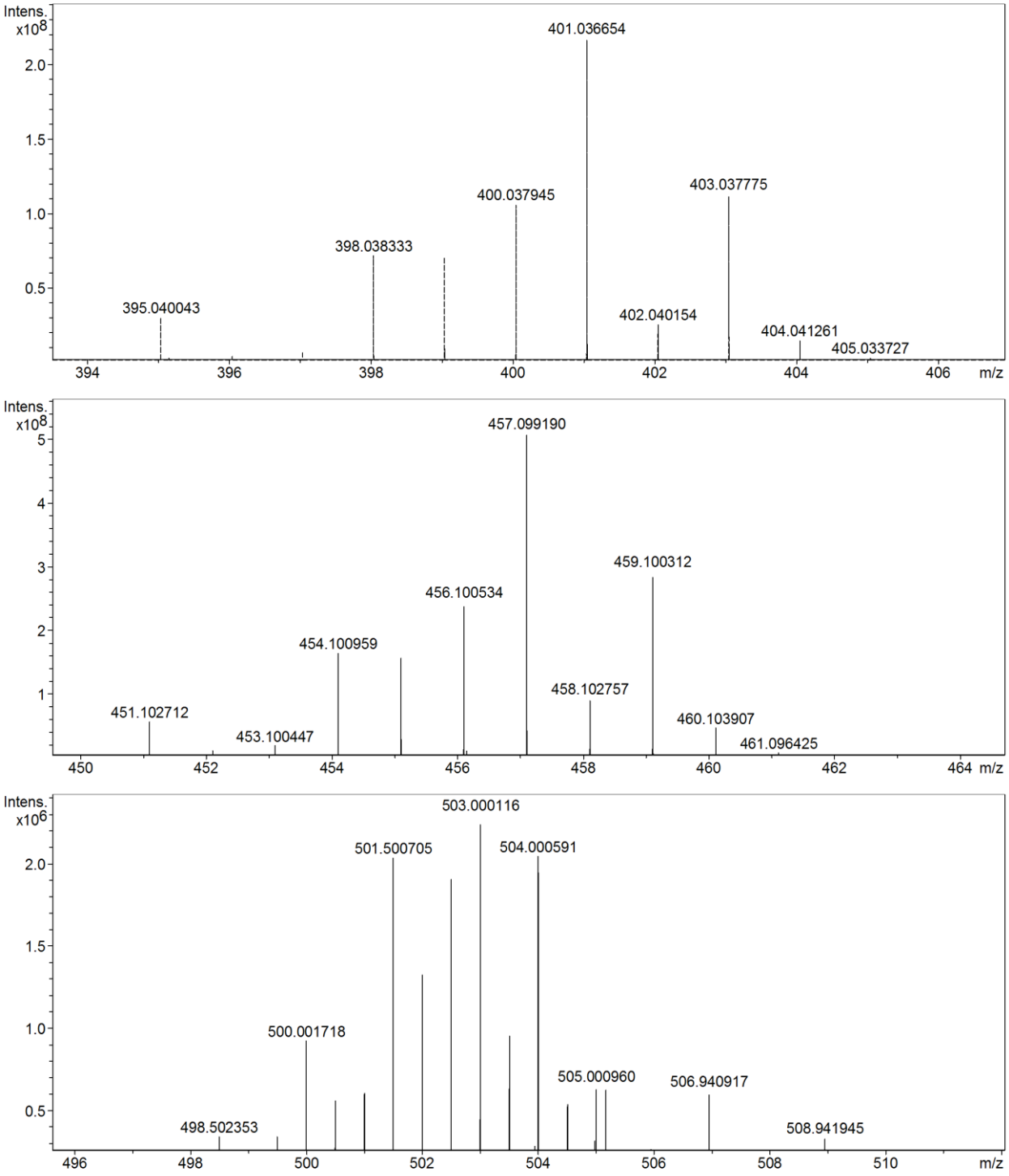


Figure S2. High resolution mass spectra of the complexes (**1, 2** and **3b** from top to bottom)

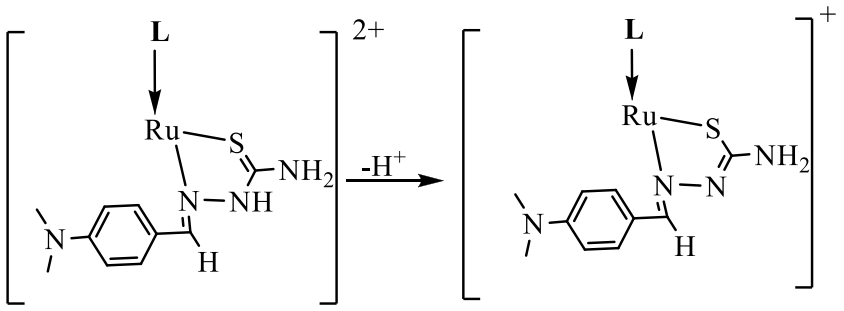
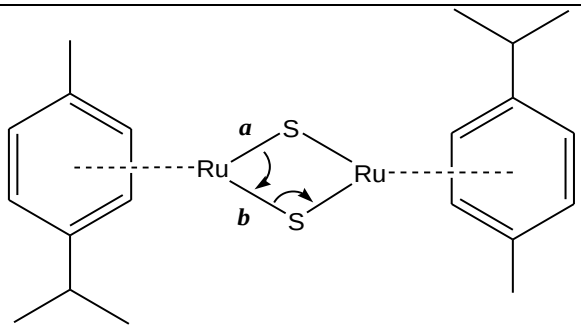
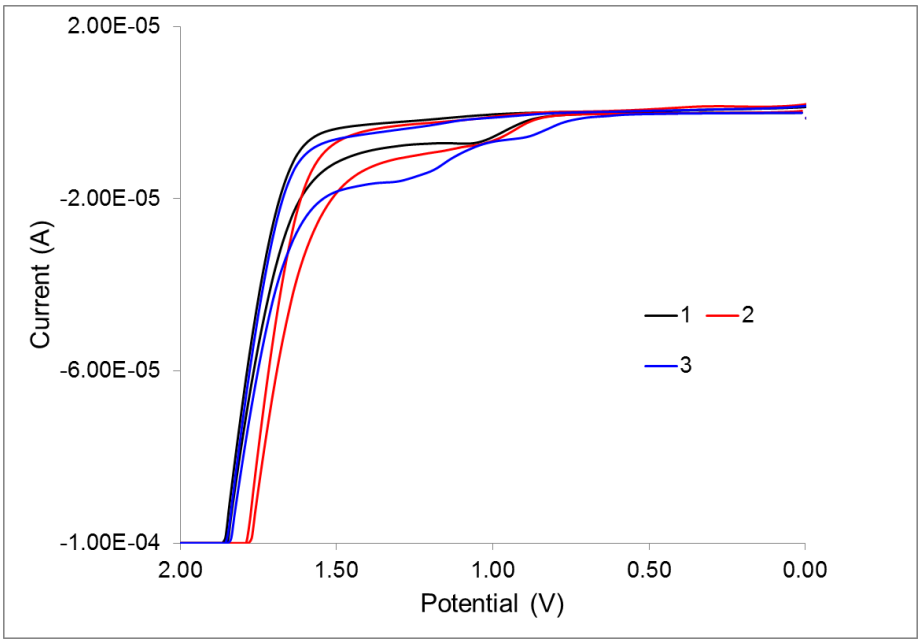


Figure S3. Tautomerisation and deprotonation of the [(**L**)Ru(dmabTSC)Cl]$^{2+}$ cation (where L = (η^6-C_6H_6) **1,** (η^6-*p*-cymene) **2**, and ([9]aneS_3) **3**)

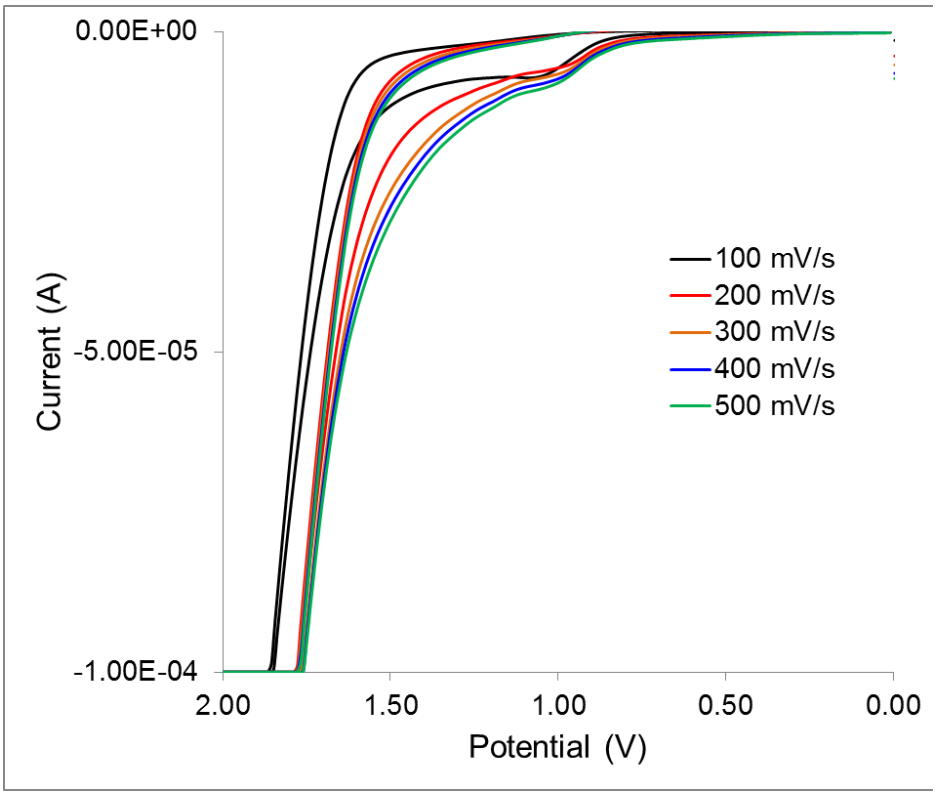
Table of geometrical parameters in structures of "true" Ru_2S_2 dimers.

								
Refcode, CCDC	Geometrical parameters of the dimer: distance (Å), or angle (^{o})						Comment	Refs.
	a	*b*	S-S	Ru-Ru	Ru-S-Ru	S-Ru-S		
NASXOW	2.349	2.401	3.150	3.557	96.18	83.06	practically planar asymmetric rhomb	38
NASXIQ	2.344	2.417	3.140	3.565	96.89	82.50	practically planar asymmetric rhomb	38
HUKNEG	2.416	2.429	3.119	3.648	98.53	80.14	practically planar asymmetric rhomb	Ref a
n/a	*2.356*	*2.406*	*3.081*	*3.631*	*99.36*	*80.63*	Planar asymmetric rhomb	*This work*

Ref. a Henderson, W., Nicholson, B.K., Dinger, M.B. and Bennett, R.L. (2002) *Inorg.Chim.Acta*, **338**, 210 – 218.



A



B

Figure S4. (A) Cyclic voltammograms of complexes **1**, **2**, and **3**; (B) Cyclic voltammogram of **1** as a function of scan rate

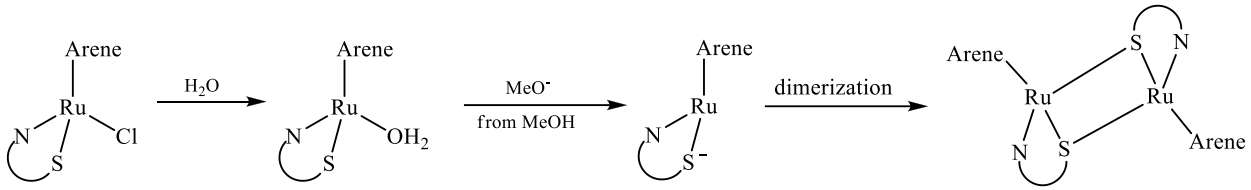


Figure S5. Proposal for how the dimeric complex could have formed.

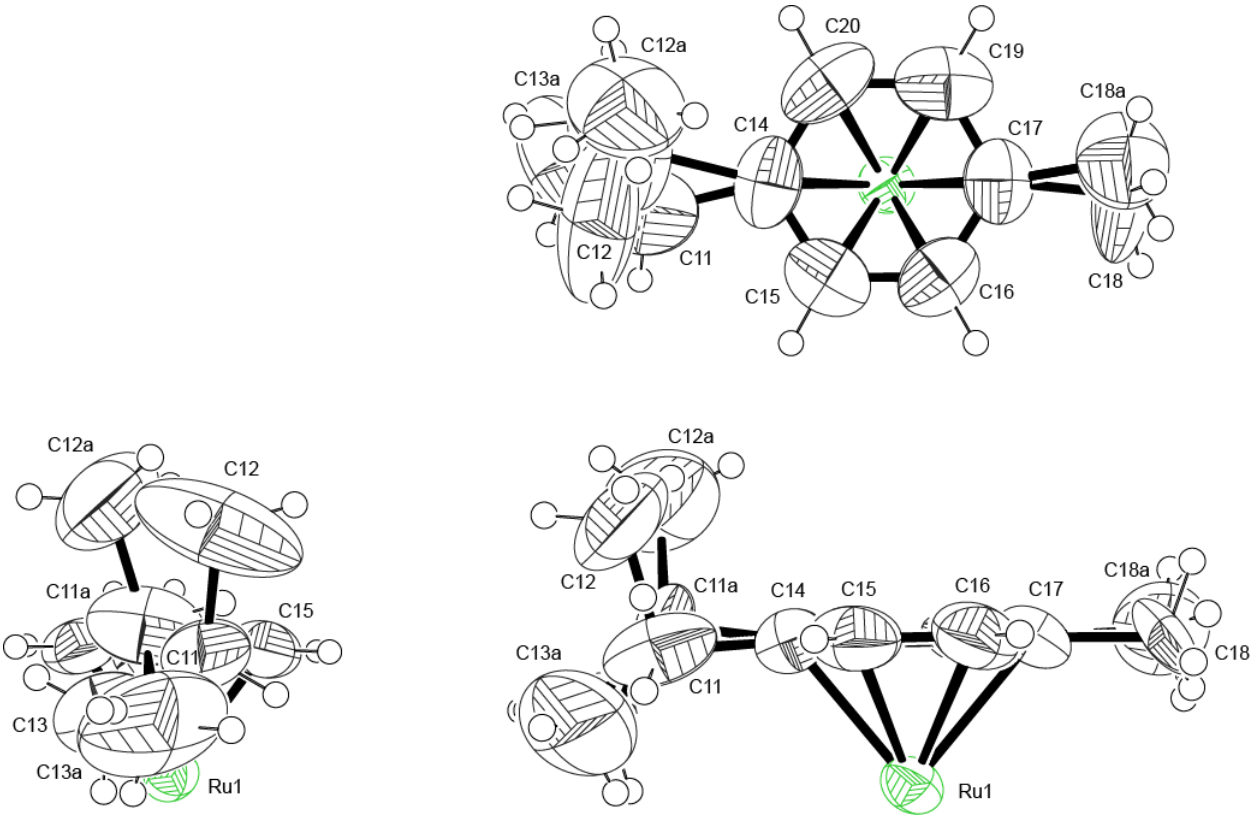
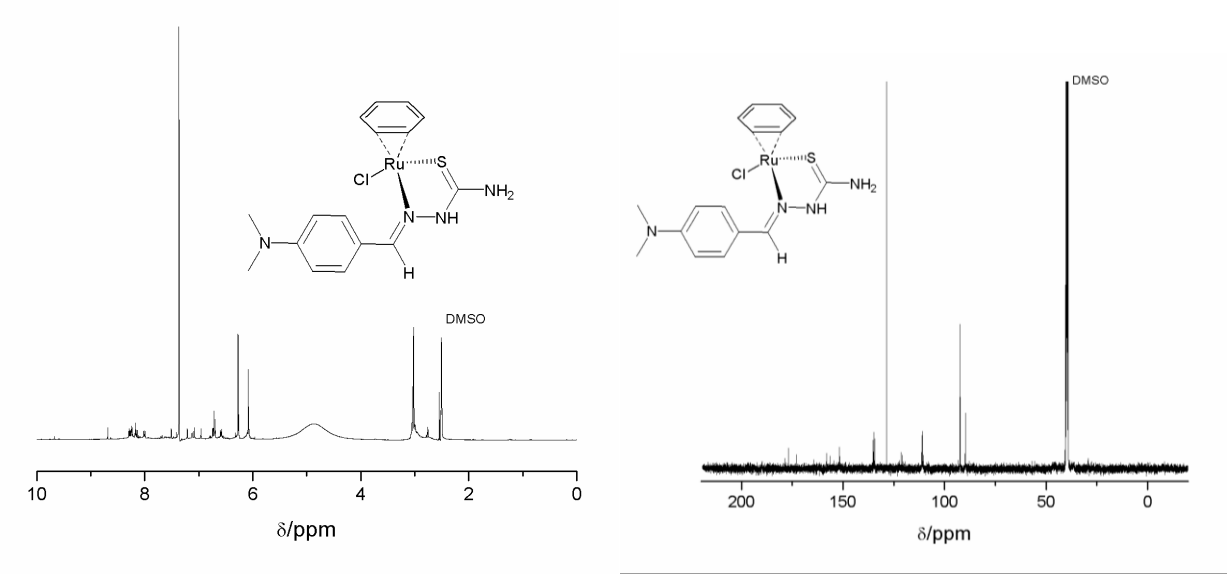
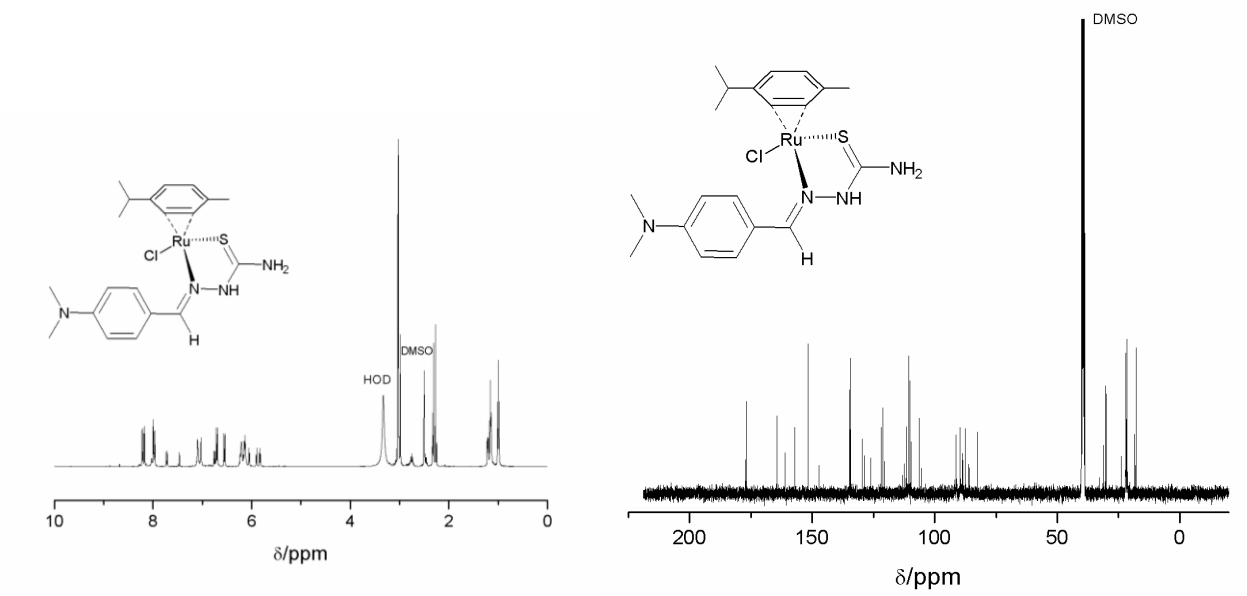


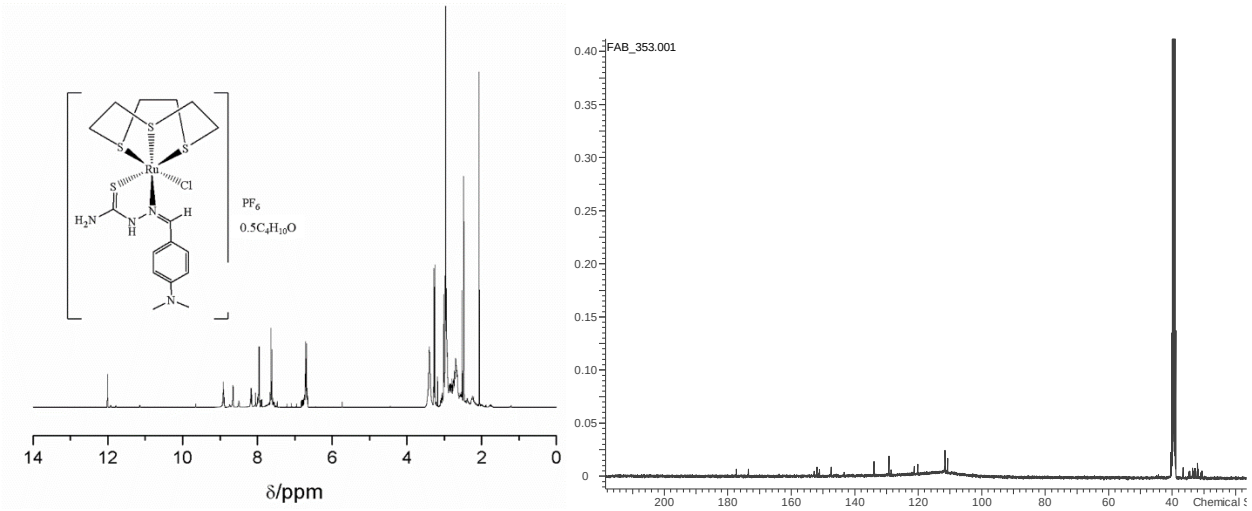
Figure S6. Three orthogonal projections of Ru-*p*-cymene fragment in which two positional disorder has been successfully resolved and modeled. Upper – top view, down – two 90-degrees apart side views. An ORTEP drawing showing 50% thermal ellipsoids probability level.



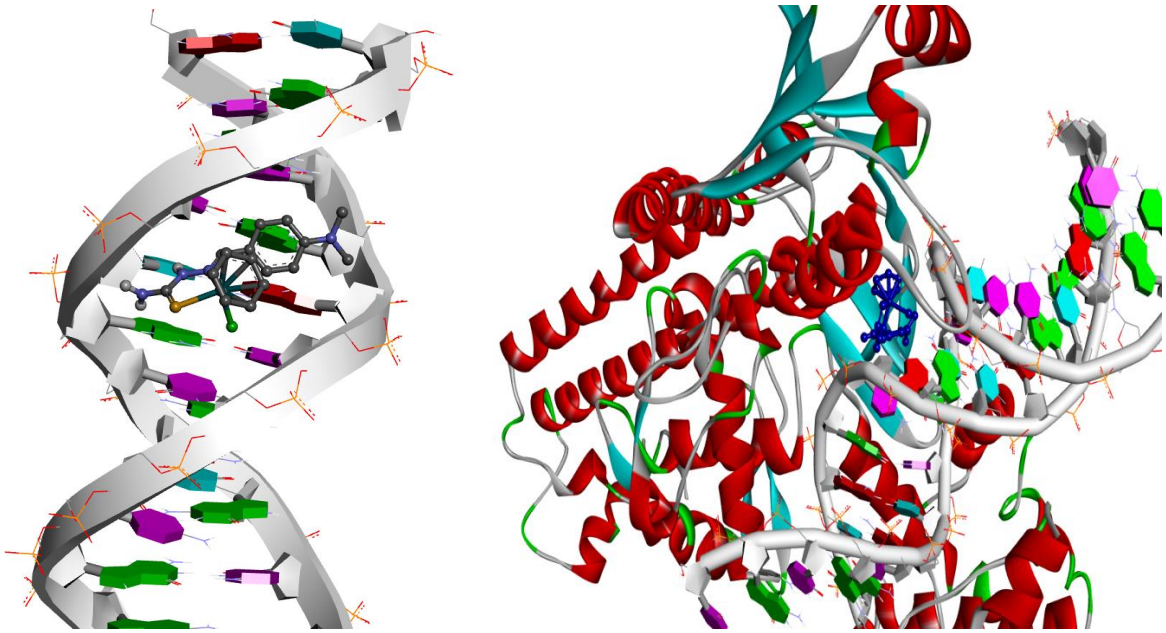
^{1}H NMR and ^{13}C NMR of **1** in DMSO-d_6



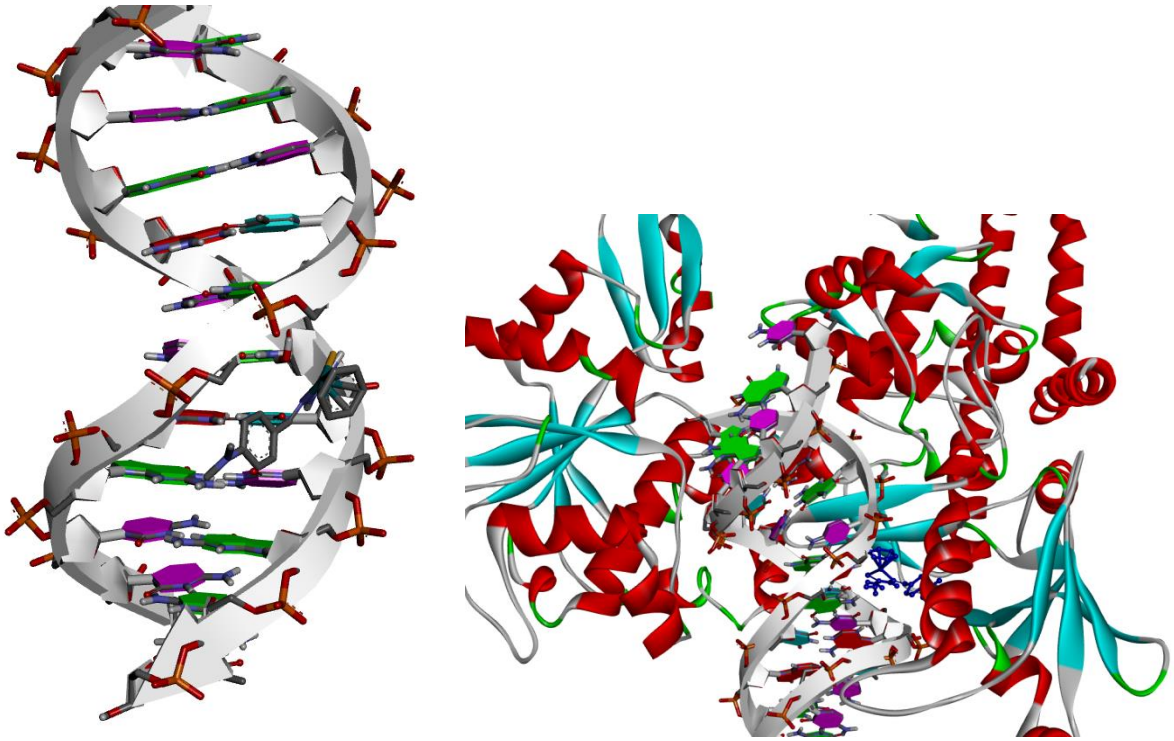
^{1}H NMR and ^{13}C NMR spectrum of **2** in DMSO-d_6



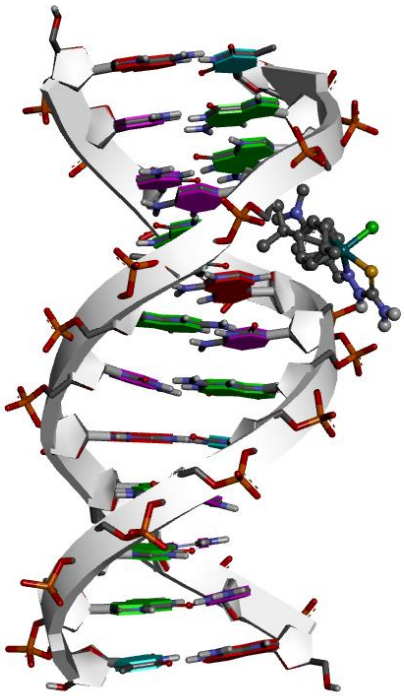
^{1}H NMR and ^{13}C NMR spectrum of **3** in DMSO-d_6

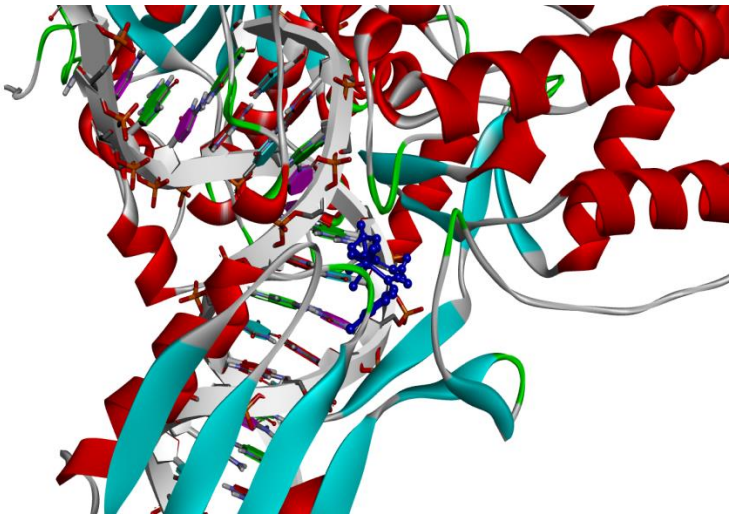


View of complex **1**

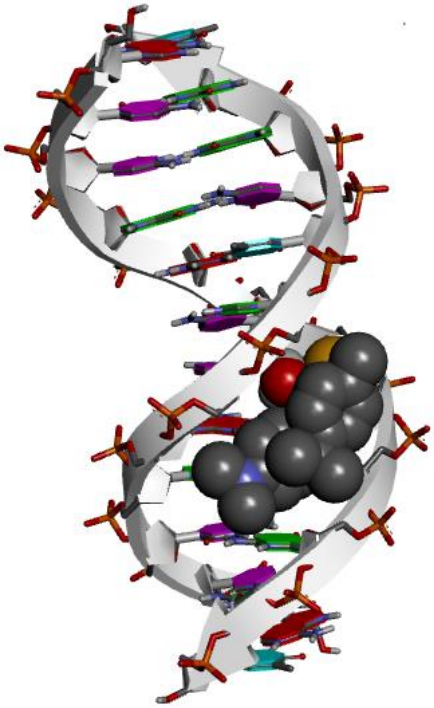


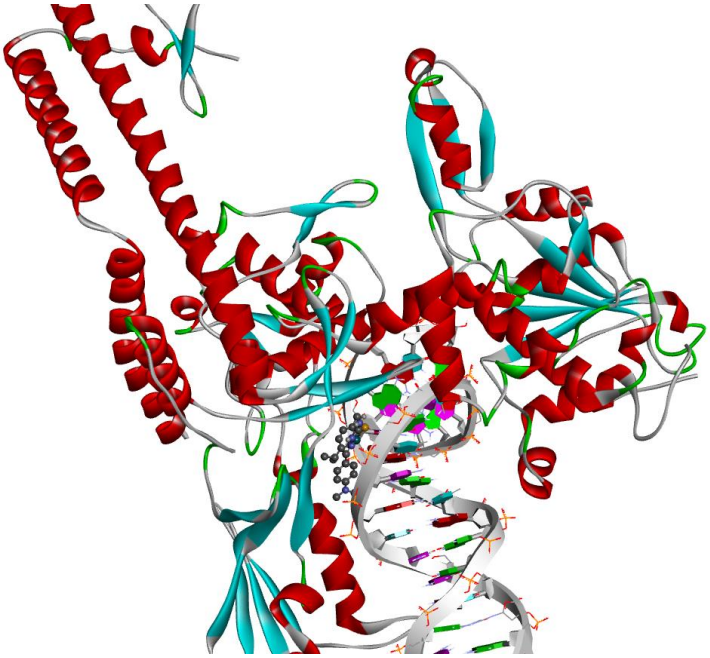
and **1-aq** docked with DNA and topo II



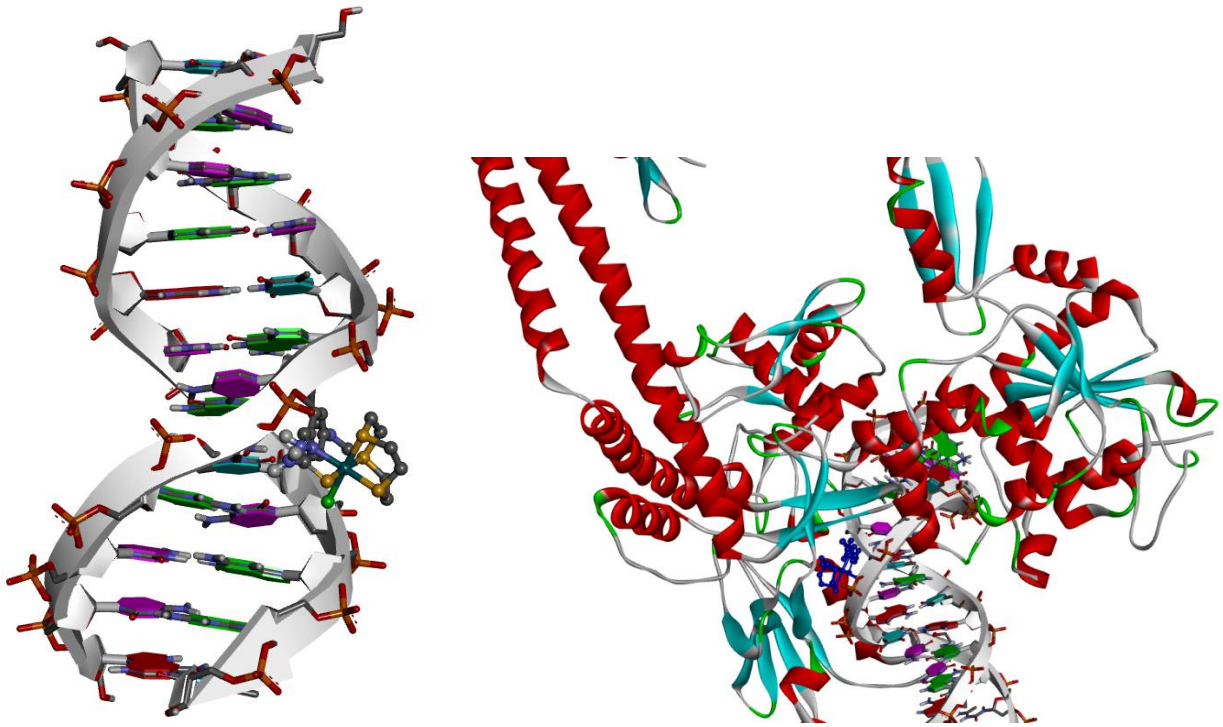


View of complex **2**

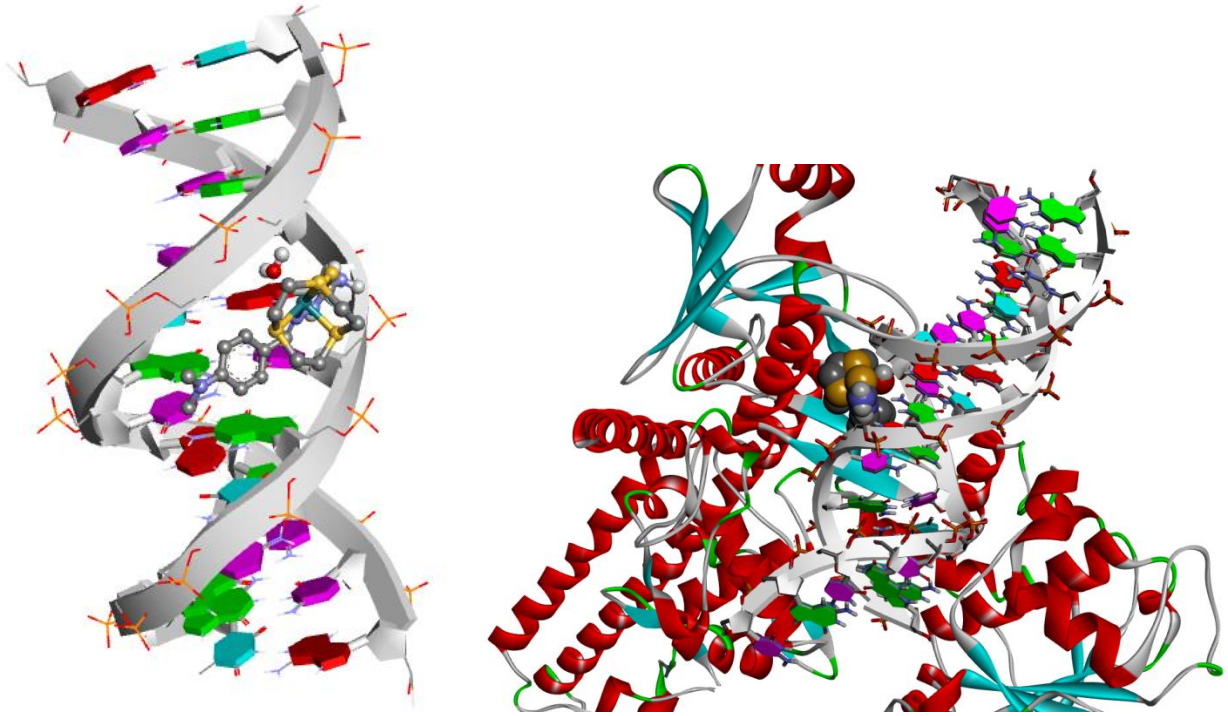




and **2-aq** docked with DNA and topo II



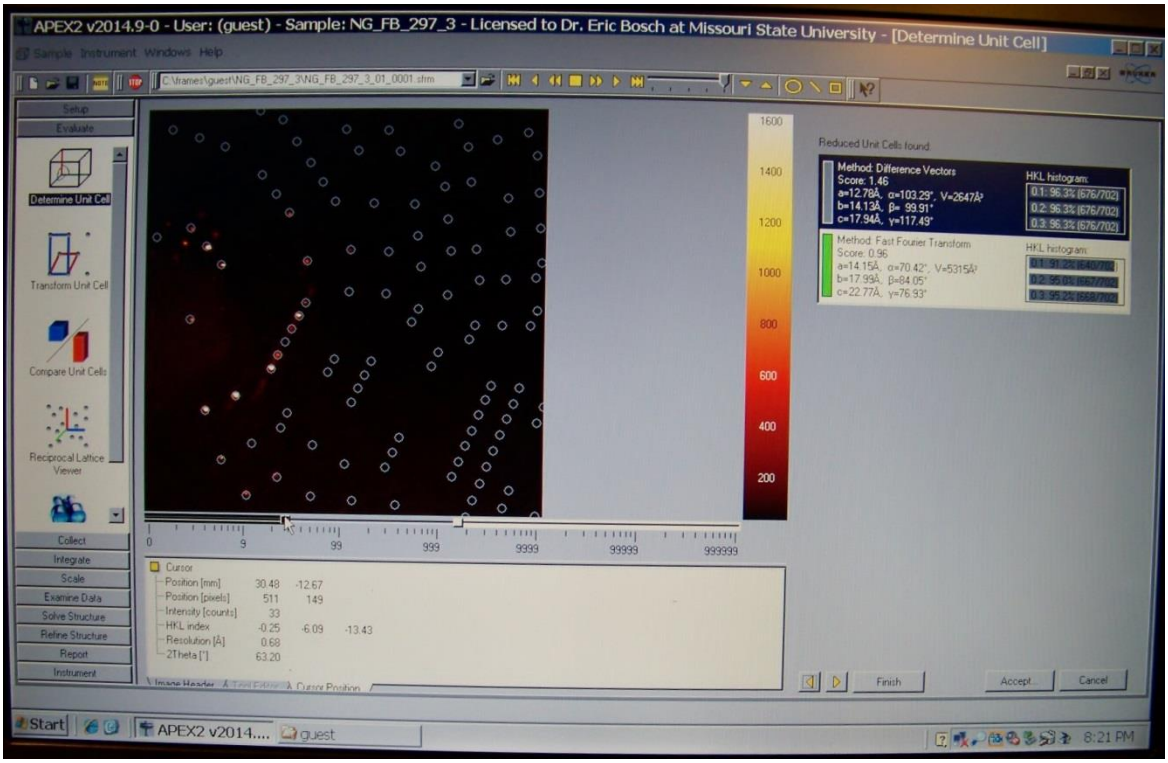
View of complex **2**



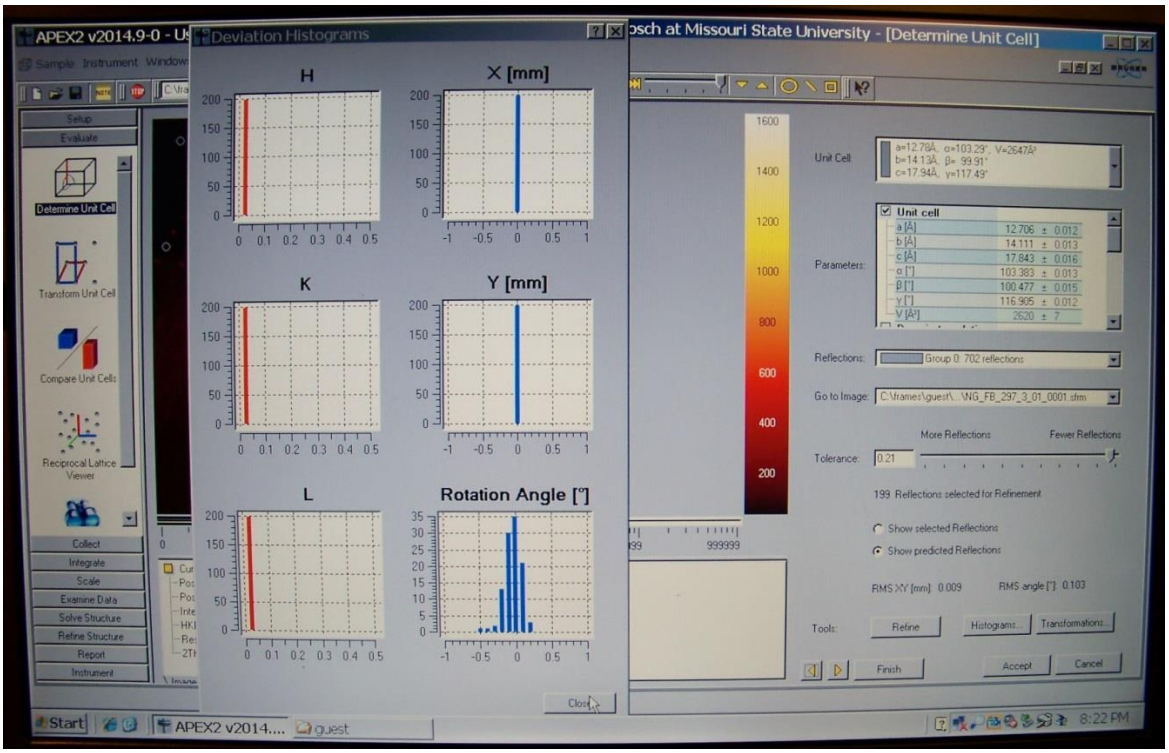
and **2-aq** docked with DNA and topo II

Ru-dimer crystal: step-by-step data processing.

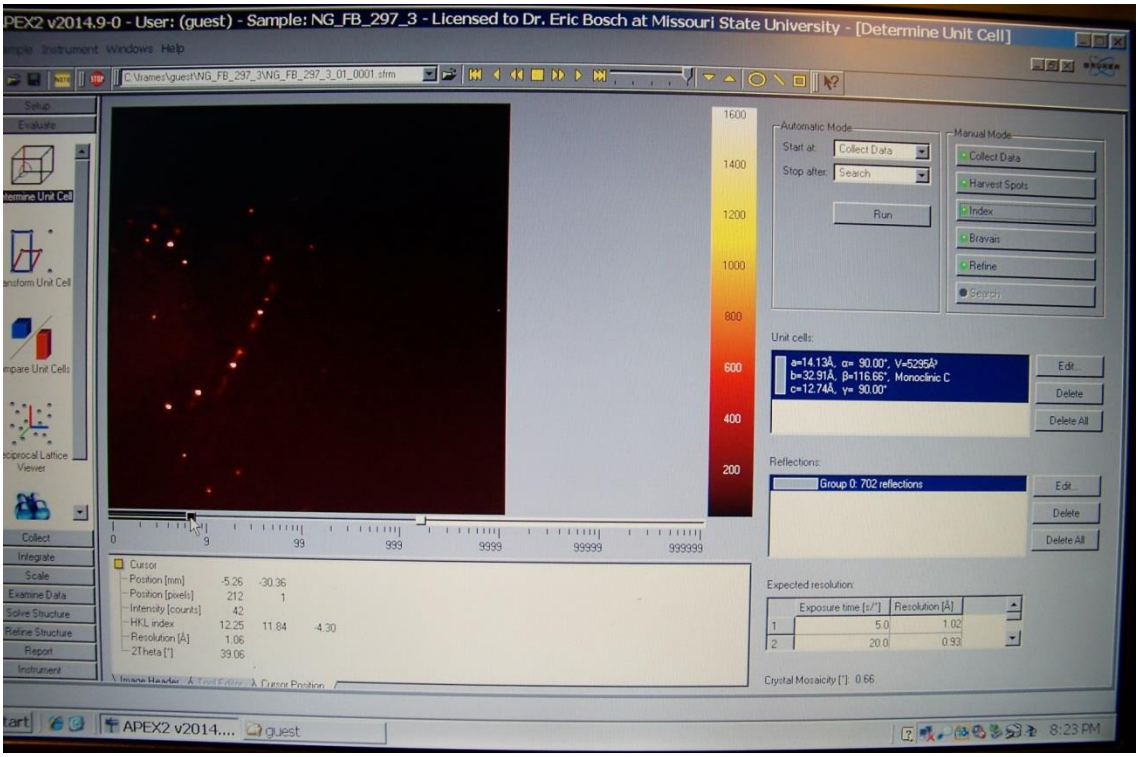
1) Reflections harvesting for unit cell determination and indexing



2) Cell refinement and histograms viewing.

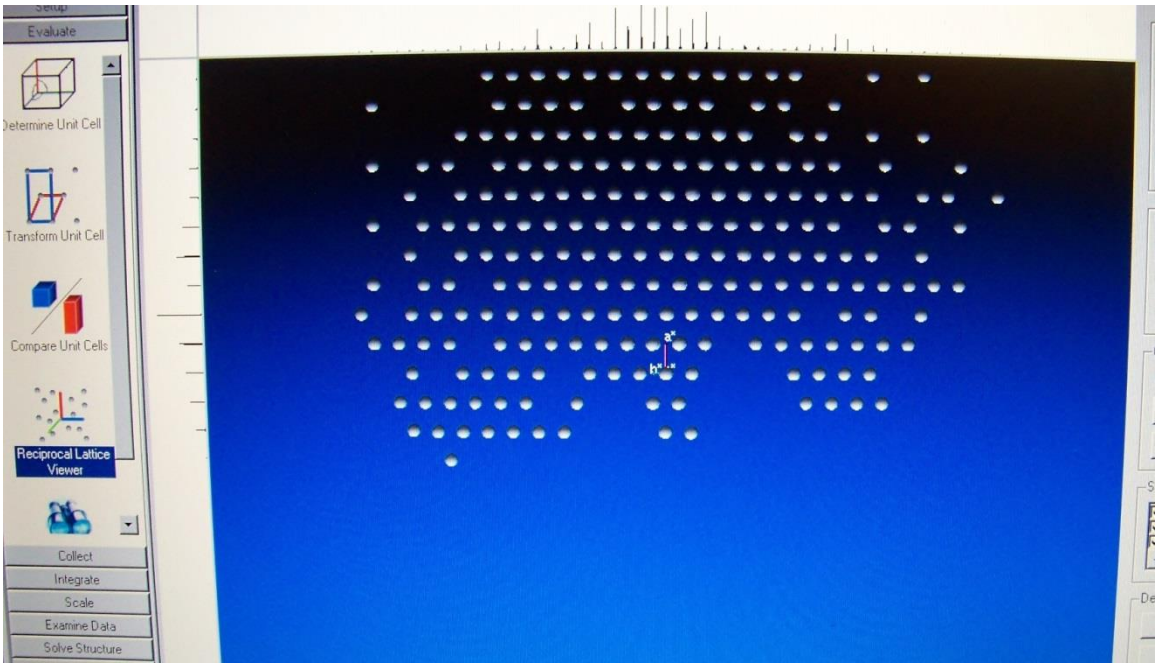


3) Unit cell determined, crystal mozaicity obtained!

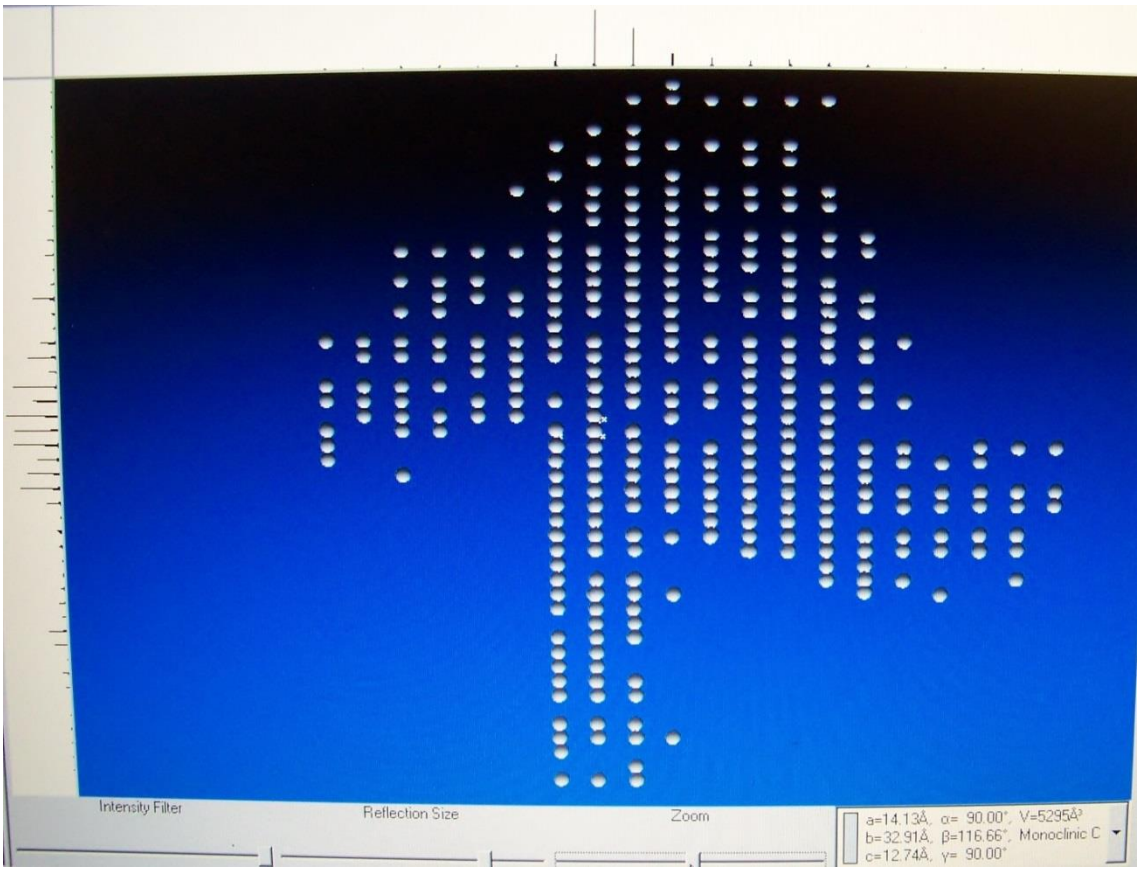


4) Analysis of harvested 702 reflections using the RLAT viewer: reciprocal lattice along a*:

RLAT along b*:

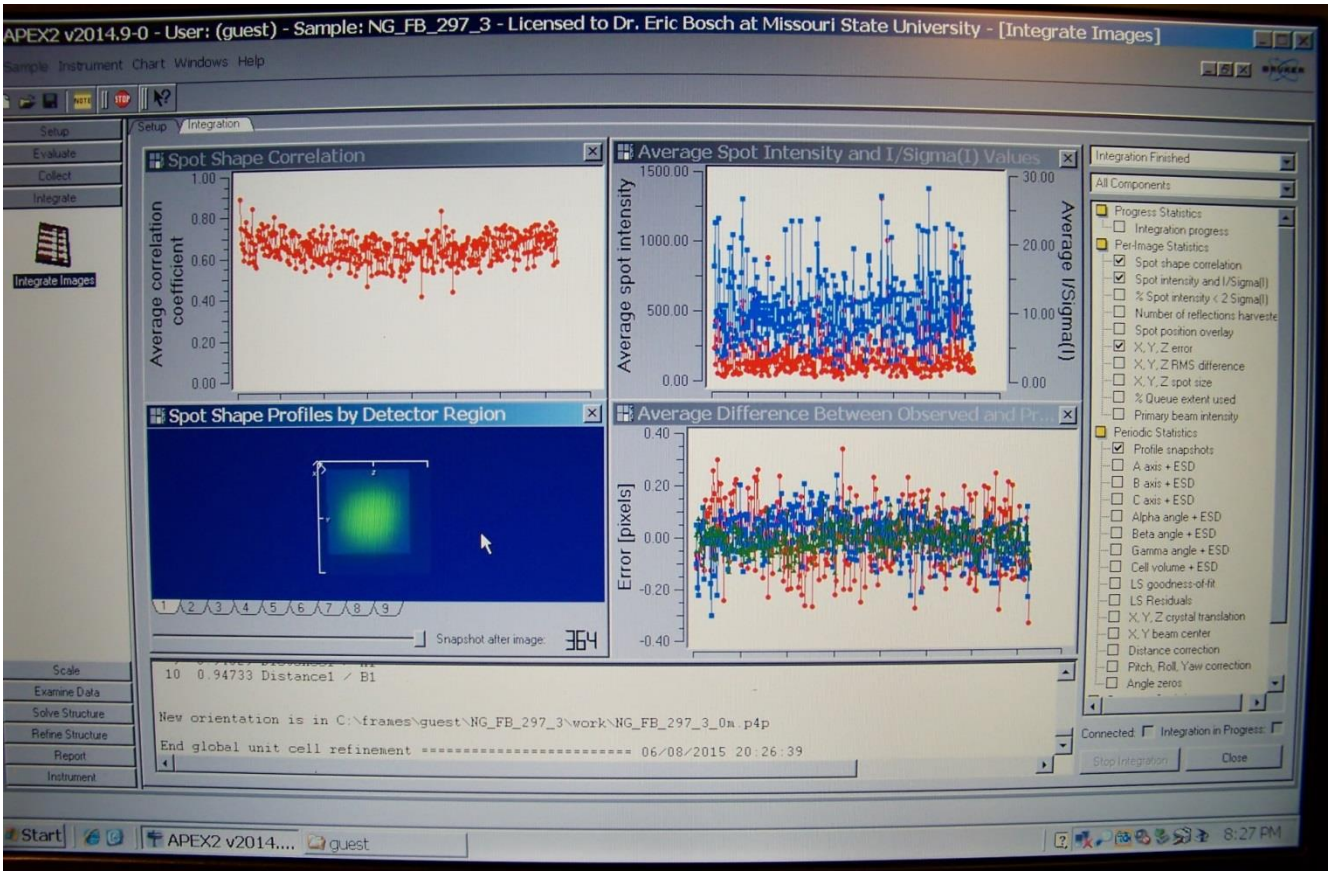


RLAT along c*:



All clearly evidence a SINGLE DOMAIN in the crystalline specimen.

5) Results of integration of full-sphere data set: single spot correlation profile, high, over 65% correlation coefficient.


APEX2 v2014.9-0 - User: (guest) - Sample: NG_FB_297_3 - Licensed to Dr. Eric Bosch at Missouri State University - [Integrate Images]
Spot Shape Correlation
Average correlation coefficient
Average Spot Intensity and I/Sigma(I) Values
Average spot intensity
Average I/Sigma(I)
Spot Shape Profiles by Detector Region
Average Difference Between Observed and Pr...
Error [pixels]
Integration Finished
All Components
Progress Statistics
Integration progress
Per-Image Statistics
Spot shape correlation
Spot intensity and I/Sigma(I)
Spot position overlay
X, Y, Z error
X, Y, Z RMS difference
X, Y, Z spot size
Primary beam intensity
Periodic Statistics
Profile snapshots
A axis + ESD
B axis + ESD
C axis + ESD
Alpha angle + ESD
Beta angle + ESD
Gamma angle + ESD
Cell volume + ESD
LS goodness-of-fit
LS Residuals
X, Y, Z crystal translation
X, Y beam center
Distance correction
Pitch, Roll, Yaw correction
Angle zeros
Snapshot after image:
10 0.94733 Distance1 / B1
New orientation is in C:\frames\guest\NG_FB_297_3\work\NG_FB_297_3_0m.p4p
End global unit cell refinement ========== 06/08/2015 20:26:39
Connected:
Integration in Progress:
Stop Integration
Close
Integrate Images
Scale
Examine Data
Solve Structure
Refine Structure
Report
Instrument
Start
APEX2 v2014....
guest
8:27 PM

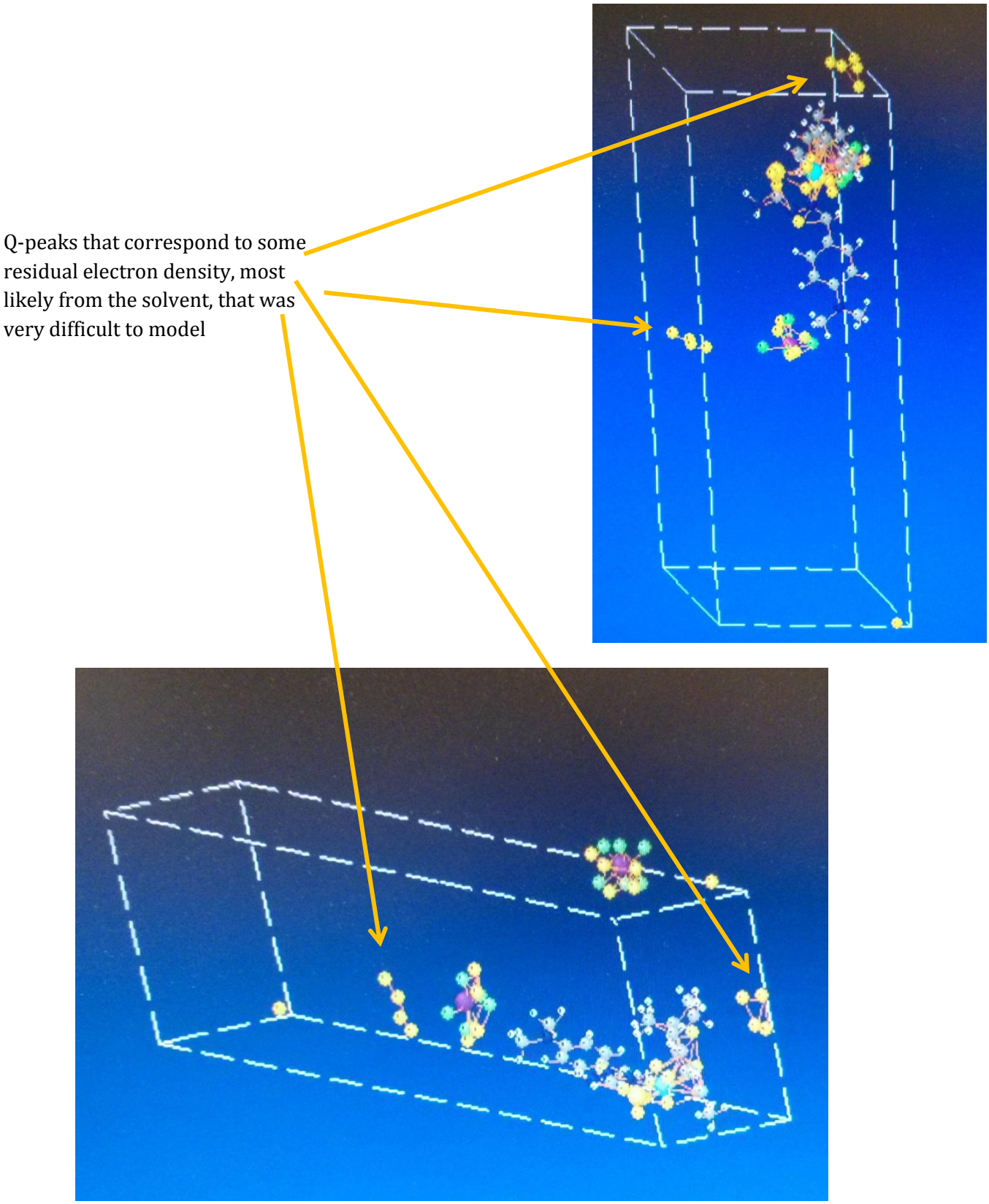

Q-peaks that correspond to some residual electron density, most likely from the solvent, that was very difficult to model

Figure. S6

checkCIF/PLATON (full publication check)

Structure factors have been supplied for datablock(s) I

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary

Please wait while processing .... Interpreting this report

Structure factor report

Datablock: I NG_FB_297_3

Bond precision: C-C = 0.0159 A Wavelength=0.71073

Cell: a=14.140(2) b=32.808(5) c=12.7477(18)
alpha=90 beta=116.616(2) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	5287.0(13)	5286.9(13)
Space group	C 2/m	C 2/m
Hall group	-C 2y	-C 2y
Moiety formula	C40 H54 N8 Ru2 S2, 2(F6 P)	C40 H54 N8 Ru2 S2, 2(P F6)
Sum formula	C40 H54 F12 N8 P2 Ru2 S2	C40 H54 F12 N8 P2 Ru2 S2
Mr	1203.13	1203.11
Dx,g cm-3	1.512	1.512
Z	4	4
Mu (mm-1)	0.789	0.789
F000	2432.0	2432.0
F000'	2424.91	
h,k,lmax	18,42,16	18,42,16
Nref	5986	5946
Tmin,Tmax	0.810,0.857	0.802,0.960
Tmin'	0.711	

Correction method= NUMERICAL

Data completeness= 0.993 Theta(max)= 27.163

R(reflections)= 0.0827(3864) wR2(reflections)= 0.2787(5946)

S = 1.034 Npar= Npar = 331

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

SHFSU01_ALERT_2_A The absolute value of parameter shift to su ratio > 0.20
Absolute value of the parameter shift to su ratio given 0.415
Additional refinement cycles may be required.

PLAT080_ALERT_2_A Maximum Shift/Error 0.41

PLAT601_ALERT_2_A Structure Contains Solvent Accessible VOIDS of . 311 Ang3

Alert level B

Crystal system given = monoclinic
PLAT722_ALERT_1_B Angle Calc 91.00, Rep 88.40 Dev... 2.60 Degree
C19A -C18A -H18A 1.555 1.555 1.555 # 171
And 4 other PLAT722 Alerts
Less ...

PLAT722_ALERT_1_B Angle Calc 91.00, Rep 88.80 Dev... 2.20 Degree

C15 -C18A -H18A 1.555 1.555 1.555 # 172

PLAT722_ALERT_1_B Angle Calc 110.00, Rep 107.60 Dev... 2.40 Degree

C18A -C20A -H20E 1.555 1.555 1.555 # 174

PLAT722_ALERT_1_B Angle Calc 110.00, Rep 112.10 Dev... 2.10 Degree

C18A -C19A -H19D 1.555 1.555 1.555 # 179

PLAT722_ALERT_1_B Angle Calc 110.00, Rep 107.20 Dev... 2.80 Degree

C18A -C19A -H19E 1.555 1.555 1.555 # 180

PLAT971_ALERT_2_B Check Calcd Residual Density 0.16A From P2 3.45 eA-3

Alert level C

DIFMX01_ALERT_2_C The maximum difference density is > 0.1*ZMAX*0.75
_refine_diff_density_max given = 3.491
Test value = 3.300
DIFMX02_ALERT_1_C The maximum difference density is > 0.1*ZMAX*0.75
The relevant atom site should be identified.
RFACR01_ALERT_3_C The value of the weighted R factor is > 0.25
Weighted R factor given 0.279
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ..... 0.28 Why ?
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.37 Why ?
PLAT097_ALERT_2_C Large Reported Max. (Positive) Residual Density 3.49 eA-3
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 5.2 Ratio
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 6.3 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C15 -- C16 .. 0.17
Ang.
PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for ..... C7 Check

And 2 other PLAT241 Alerts
Less ...
PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for .....
C16 Check
PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for .....
C17 Check
PLAT242_ALERT_2_C Low Ueq as Compared to Neighbors for .....
Ru1 Check

And 3 other PLAT242 Alerts
More ...
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0159 Ang.
PLAT413_ALERT_2_C Short Inter XH3 .. XHn H7 .. H20D .. 2.13 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor N1 - H1A ... Please Check
PLAT713_ALERT_1_C TORSION Unknown or Inconsistent Label ..... C2_A
N3 C2_A C3_A C4_A
PLAT721_ALERT_1_C Bond Calc 0.95000, Rep 0.96020 Dev... 0.01 Ang.
C19 -H19B 1.555 1.555 # 44

PLAT721_ALERT_1_C Bond Calc 0.95000, Rep 0.96070 Dev... 0.01 Ang.
C20A -H20D 1.555 1.555 # 73
PLAT722_ALERT_1_C Angle Calc 91.00, Rep 89.00 Dev... 2.00 Degree
C20A -C18A -H18A 1.555 1.555 1.555 # 170

And 4 other PLAT722 Alerts
Less ...

PLAT722_ALERT_1_C Angle Calc 110.00, Rep 111.40 Dev... 1.40 Degree

C18A -C20A -H20D 1.555 1.555 1.555 # 173

PLAT722_ALERT_1_C Angle Calc 108.00, Rep 109.40 Dev... 1.40 Degree

H20E -C20A -H20F 1.555 1.555 1.555 # 178

PLAT722_ALERT_1_C Angle Calc 110.00, Rep 108.80 Dev... 1.20 Degree

H19D -C19A -H19E 1.555 1.555 1.555 # 181

PLAT722_ALERT_1_C Angle Calc 109.00, Rep 110.10 Dev... 1.10 Degree

C18A -C19A -H19F 1.555 1.555 1.555 # 182

PLAT905_ALERT_3_C Negative K value in the Analysis of Variance ... -3.727 Why ?
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 20 Why ?
PLAT973_ALERT_2_C Check Calcd Positive Residual Density on Ru1 1.03 eA-3

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 18 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 9 Why ?
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 2 Why ?
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large. 0.16 Why ?
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 24.77 Why ?
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of P1 Check
PLAT301_ALERT_3_G Main Residue Disorder ..... Percentage = 12 Note
PLAT302_ALERT_4_G Anion/Solvent Disorder ..... Percentage = 33 Note
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 37 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 19 Note

3 **ALERT level A** = Most likely a serious problem - resolve or explain
6 **ALERT level B** = A potentially serious problem, consider carefully
30 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
12 **ALERT level G** = General information/check it is not something unexpected

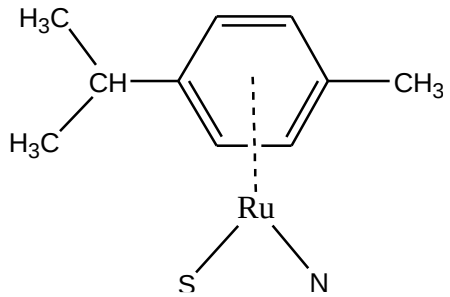
15 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
22 ALERT type 2 Indicator that the structure model may be wrong or deficient
8 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

PLATON version of 05/02/2014; check.def file version of 05/02/2014

Datablock I - ellipsoid plot

Download CIF editor (publCIF) from the IUCr
Download CIF editor (enCIFer) from the CCDC
Test a new CIF entry

Search of the CCDC for the fragment below resulted in 59 hits.



Refcodes for Ru-sulfides in dimeric and polymeric complexes:
RIMLAA, RIMNUW, WEKXOB, BEKYEW, COYQAI

Refcodes for dinuclear Ru-complexes with S-bridging ligands:
FILCAG, BACSUU, YASCEA, QOKBIB

Refcodes for "true dimers" are:
HAZKOK, HUKNEG, NASXIQ, NASXOW

Table S1. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for 2. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.8751(6)	0.7956(2)	0.5392(6)	0.0626(18)
C2	0.8801(6)	0.7580(3)	0.2924(7)	0.0653(19)
C3	0.8622(6)	0.7148(2)	0.2864(7)	0.0635(18)
C4	0.8352(8)	0.6960(3)	0.1788(8)	0.087(3)
C5	0.8158(10)	0.6556(3)	0.1622(10)	0.108(4)
C6	0.8265(9)	0.6308(3)	0.2538(13)	0.105(4)
C7	0.8568(14)	0.6494(3)	0.3618(13)	0.122(5)
C8	0.8748(9)	0.6897(3)	0.3801(9)	0.091(3)
C11	0.0122(9)	0.8869(5)	0.1786(13)	0.139(5)
C12	0.9177(7)	0.8826(3)	0.2067(9)	0.090(3)
C13	0.9007(8)	0.9094(3)	0.2799(8)	0.087(3)
C14	0.8164(10)	0.9062(3)	0.3046(9)	0.092(3)
C15	0.7407(8)	0.8753(4)	0.2526(11)	0.095(3)
C16	0.7567(9)	0.8473(3)	0.1798(10)	0.105(4)
C17	0.8472(12)	0.8510(3)	0.1555(8)	0.100(4)
C18	0.6535(16)	0.8784(6)	0.303(2)	0.110(8)
C19	0.568(2)	0.9092(10)	0.222(4)	0.22(3)
C20	0.6178(16)	0.8338(6)	0.307(2)	0.109(8)
P1	0.6706(10)	0.5	0.4554(11)	0.182(3)
F1	0.654(3)	0.5	0.3326(19)	0.305(15)
F2	0.786(2)	0.5	0.499(2)	0.320(15)
F3	0.702(3)	0.5	0.601(2)	0.299(14)
F4	0.566(4)	0.5	0.439(5)	0.43(3)
F5	0.6622(15)	0.5466(3)	0.4506(13)	0.242(7)
P2	0.0050(7)	0.76223(19)	0.0061(7)	0.15
F7	0.9151(8)	0.7743(3)	0.0444(10)	0.15
F8	0.9349(9)	0.7808(3)	0.8788(7)	0.15
F9	0.9524(9)	0.7187(2)	0.9638(9)	0.15
F7A	0.0962(8)	0.7510(3)	0.9698(10)	0.15
F8A	0.0590(9)	0.8061(2)	0.0511(9)	0.15
F9A	0.0759(8)	0.7442(3)	0.1350(7)	0.15
N1	0.8633(7)	0.7832(3)	0.6331(6)	0.095(3)
N2	0.8618(6)	0.7706(2)	0.4572(5)	0.0679(17)
N3	0.8825(5)	0.7856(2)	0.3679(5)	0.0613(15)
N4	0.8077(13)	0.5894(4)	0.2354(14)	0.166(6)
Ru1	0.89900(4)	0.84824(2)	0.34855(4)	0.0546(3)
S1	0.91156(15)	0.84752(5)	0.53921(16)	0.0557(4)
C18A	0.626(2)	0.864(2)	0.240(3)	0.119(19)
C20A	0.609(7)	0.847(3)	0.344(5)	0.23(4)

C19A	0.538(4)	0.874(3)	0.115(4)	0.21(4)
C9	0.7716(15)	0.5706(5)	0.1263(15)	0.199(9)
C10	0.827(3)	0.5630(6)	0.328(2)	0.33(2)

Table S2. Bond lengths (Å) for 2.

C1-N2	1.275(10)	C1-N1	1.344(10)
C1-S1	1.781(8)	C2-N3	1.311(10)
C2-C3	1.436(11)	C2-H2	0.93
C3-C4	1.393(11)	C3-C8	1.395(12)
C4-C5	1.350(14)	C4-H4	0.93
C5-C6	1.374(16)	C5-H5	0.93
C6-N4	1.385(15)	C6-C7	1.386(17)
C7-C8	1.349(14)	C7-H7	0.93
C8-H8	0.93	C11-C12	1.538(5)
C11-H11A	0.96	C11-H11C	0.96
C11-H11B	0.96	C12-C13	1.380(14)
C12-C17	1.381(15)	C12-Ru1	2.243(8)
C13-C14	1.366(15)	C13-Ru1	2.195(9)
C13-H13	0.93	C14-C15	1.406(16)
C14-Ru1	2.169(10)	C14-H14	0.93
C15-C16	1.395(18)	C15-C18A	1.60(4)
C15-C18	1.63(3)	C15-Ru1	2.201(9)
C16-C17	1.451(19)	C16-Ru1	2.191(10)
C16-H16	0.93	C17-Ru1	2.234(9)
C17-H17	0.93	C18-C20	1.559(5)
C18-C19	1.560(5)	C18-H18	0.98
C19-H19A	0.9602	C19-H19B	0.9602
C19-H19C	0.9602	C20-H20A	0.96
C20-H20B	0.96	C20-H20C	0.96
P1-F4	1.40(3)	P1-F2	1.47(3)
P1-F1	1.47(2)	P1-F5	1.532(11)
P1-F5	1.533(11)	P1-F3	1.70(3)
P2-F9	1.589(4)	P2-F8	1.596(4)
P2-F7A	1.596(4)	P2-F7	1.602(4)
P2-F9A	1.606(4)	P2-F8A	1.610(4)
N1-H1A	0.86	N1-H1B	0.86
N2-N3	1.387(8)	N3-Ru1	2.094(6)
N4-C10	1.390(5)	N4-C9	1.393(5)
Ru1-S1	2.3564(18)	Ru1-S1	2.406(2)
S1-Ru1	2.406(2)	C18A-C20A	1.561(7)
C18A-C19A	1.562(7)	C18A-H18A	0.98
C20A-H20D	0.9607	C20A-H20E	0.9604

C20A-H20F	0.9605	C19A-H19D	0.9642
C19A-H19E	0.9625	C19A-H19F	0.9634
C9-H9A	0.96	C9-H9B	0.96
C9-H9C	0.96	C10-H10A	0.96
C10-H10B	0.96	C10-H10C	0.96

Table S3. Bond angles (°) for 2.

N2-C1-N1	120.2(8)	N2-C1-S1	123.5(6)
N1-C1-S1	116.2(6)	N3-C2-C3	131.9(7)
N3-C2-H2	114.1	C3-C2-H2	114.1
C4-C3-C8	117.0(9)	C4-C3-C2	117.0(7)
C8-C3-C2	125.8(8)	C5-C4-C3	122.4(10)
C5-C4-H4	118.8	C3-C4-H4	118.8
C4-C5-C6	120.8(11)	C4-C5-H5	119.6
C6-C5-H5	119.6	C5-C6-N4	119.9(13)
C5-C6-C7	116.9(10)	N4-C6-C7	123.3(13)
C8-C7-C6	123.5(11)	C8-C7-H7	118.2
C6-C7-H7	118.2	C7-C8-C3	119.3(10)
C7-C8-H8	120.3	C3-C8-H8	120.3
C12-C11-H11A	109.5	C12-C11-H11C	109.4
H11A-C11-H11C	109.5	C12-C11-H11B	109.5
H11A-C11-H11B	109.5	H11C-C11-H11B	109.5
C13-C12-C17	119.5(10)	C13-C12-C11	122.0(11)
C17-C12-C11	118.5(12)	C13-C12-Ru1	70.0(5)
C17-C12-Ru1	71.7(5)	C11-C12-Ru1	131.5(8)
C14-C13-C12	122.7(10)	C14-C13-Ru1	70.8(5)
C12-C13-Ru1	73.8(5)	C14-C13-H13	118.7
C12-C13-H13	118.7	Ru1-C13-H13	129.4
C13-C14-C15	120.4(10)	C13-C14-Ru1	72.8(6)
C15-C14-Ru1	72.4(6)	C13-C14-H14	119.8
C15-C14-H14	119.8	Ru1-C14-H14	127.0
C16-C15-C14	118.2(10)	C16-C15-C18A	103.(2)
C14-C15-C18A	138.(2)	C16-C15-C18	133.0(13)
C14-C15-C18	108.6(13)	C16-C15-Ru1	71.1(6)
C14-C15-Ru1	70.0(6)	C18A-C15-Ru1	133.3(16)
C18-C15-Ru1	124.6(9)	C15-C16-C17	120.6(10)
C15-C16-Ru1	71.9(6)	C17-C16-Ru1	72.5(6)
C15-C16-H16	119.7	C17-C16-H16	119.7
Ru1-C16-H16	128.2	C12-C17-C16	118.6(11)
C12-C17-Ru1	72.4(5)	C16-C17-Ru1	69.3(6)
C12-C17-H17	120.7	C16-C17-H17	120.7
Ru1-C17-H17	130.0	C20-C18-C19	117.9(19)
C20-C18-C15	105.3(16)	C19-C18-C15	106.0(18)
C20-C18-H18	109.4	C19-C18-H18	108.8
C15-C18-H18	109.1	C18-C19-H19A	109.8
C18-C19-H19B	109.7	H19A-C19-H19B	109.5

C18-C19-H19C	109.0	H19A-C19-H19C	109.5
H19B-C19-H19C	109.4	C18-C20-H20A	109.6
C18-C20-H20B	109.2	H20A-C20-H20B	109.5
C18-C20-H20C	109.6	H20A-C20-H20C	109.5
H20B-C20-H20C	109.5	F4-P1-F2	168.(3)
F4-P1-F1	101.(3)	F2-P1-F1	91.6(16)
F4-P1-F5	86.3(8)	F2-P1-F5	93.9(8)
F1-P1-F5	89.2(7)	F4-P1-F5	86.3(8)
F2-P1-F5	93.9(8)	F1-P1-F5	89.2(7)
F5-P1-F5	172.0(17)	F4-P1-F3	84.(2)
F2-P1-F3	83.4(19)	F1-P1-F3	175.(2)
F5-P1-F3	91.2(7)	F5-P1-F3	91.2(7)
F9-P2-F8	90.8(3)	F9-P2-F7A	90.6(3)
F8-P2-F7A	90.5(3)	F9-P2-F7	90.7(3)
F8-P2-F7	89.9(3)	F7A-P2-F7	178.7(4)
F9-P2-F9A	90.0(3)	F8-P2-F9A	179.1(4)
F7A-P2-F9A	89.8(3)	F7-P2-F9A	89.8(3)
F9-P2-F8A	179.1(4)	F8-P2-F8A	90.0(3)
F7A-P2-F8A	89.7(3)	F7-P2-F8A	89.1(3)
F9A-P2-F8A	89.2(3)	C1-N1-H1A	120.0
C1-N1-H1B	120.0	H1A-N1-H1B	120.0
C1-N2-N3	115.8(7)	C2-N3-N2	114.2(7)
C2-N3-Ru1	124.0(5)	N2-N3-Ru1	121.4(5)
C6-N4-C10	121.2(16)	C6-N4-C9	124.0(13)
C10-N4-C9	114.7(16)	N3-Ru1-C14	144.5(4)
N3-Ru1-C16	90.0(3)	C14-Ru1-C16	66.9(4)
N3-Ru1-C13	165.0(3)	C14-Ru1-C13	36.5(4)
C16-Ru1-C13	77.9(4)	N3-Ru1-C15	108.8(4)
C14-Ru1-C15	37.5(4)	C16-Ru1-C15	37.0(5)
C13-Ru1-C15	66.4(4)	N3-Ru1-C17	99.8(3)
C14-Ru1-C17	78.9(4)	C16-Ru1-C17	38.3(5)
C13-Ru1-C17	65.2(4)	C15-Ru1-C17	67.8(5)
N3-Ru1-C12	130.3(4)	C14-Ru1-C12	66.2(4)
C16-Ru1-C12	66.6(4)	C13-Ru1-C12	36.2(4)
C15-Ru1-C12	78.9(4)	C17-Ru1-C12	35.9(4)
N3-Ru1-S1	80.18(16)	C14-Ru1-S1	93.3(3)
C16-Ru1-S1	128.6(4)	C13-Ru1-S1	114.3(3)
C15-Ru1-S1	99.5(3)	C17-Ru1-S1	166.7(4)
C12-Ru1-S1	148.7(3)	N3-Ru1-S1	94.22(18)
C14-Ru1-S1	119.3(3)	C16-Ru1-S1	150.7(4)
C13-Ru1-S1	92.2(3)	C15-Ru1-S1	156.8(3)
C17-Ru1-S1	112.5(4)	C12-Ru1-S1	89.0(3)
S1-Ru1-S1	80.63(7)	C1-S1-Ru1	97.0(2)
C1-S1-Ru1	104.8(3)	Ru1-S1-Ru1	99.36(7)
C20A-C18A-C19A	126.(5)	C20A-C18A-C15	124.(4)
C19A-C18A-C15	111.(3)	C20A-C18A-H18A	89.0
C19A-C18A-H18A	88.4	C15-C18A-H18A	88.8
C18A-C20A-H20D	111.4	C18A-C20A-H20E	107.6

H20D-C20A-H20E	109.5	C18A-C20A-H20F	109.6
H20D-C20A-H20F	109.4	H20E-C20A-H20F	109.4
C18A-C19A-H19D	112.1	C18A-C19A-H19E	107.2
H19D-C19A-H19E	108.8	C18A-C19A-H19F	110.1
H19D-C19A-H19F	109.3	H19E-C19A-H19F	109.4
N4-C9-H9A	109.5	N4-C9-H9B	109.5
H9A-C9-H9B	109.5	N4-C9-H9C	109.5
H9A-C9-H9C	109.5	H9B-C9-H9C	109.5
N4-C10-H10A	109.5	N4-C10-H10B	109.4
H10A-C10-H10B	109.5	N4-C10-H10C	109.5
H10A-C10-H10C	109.5	H10B-C10-H10C	109.5

Table S4. Torsion angles (°) for 2.

N3-C2_a-C3_a-C4_a	162.2(9)	N3-C2-C3-C8	-21.3(15)
C8-C3-C4-C5	3.7(15)	C2-C3-C4-C5	-179.5(10)
C3-C4-C5-C6	-2.9(19)	C4-C5-C6-N4	-179.1(13)
C4-C5-C6-C7	1.(2)	C5-C6-C7-C8	1.(2)
N4-C6-C7-C8	-179.7(14)	C6-C7-C8-C3	0.(2)
C4-C3-C8-C7	-2.4(16)	C2-C3-C8-C7	-178.8(11)
C17-C12-C13-C14	0.2(14)	C11-C12-C13-C14	179.3(10)
Ru1-C12-C13-C14	-53.6(8)	C17-C12-C13-Ru1	53.8(8)
C11-C12-C13-Ru1	-127.2(10)	C12-C13-C14-C15	-1.8(14)
Ru1-C13-C14-C15	-56.8(8)	C12-C13-C14-Ru1	54.9(9)
C13-C14-C15-C16	2.7(14)	Ru1-C14-C15-C16	-54.2(8)
C13-C14-C15-C18A	-169.(2)	Ru1-C14-C15-C18A	134.(2)
C13-C14-C15-C18	177.9(10)	Ru1-C14-C15-C18	121.0(9)
C13-C14-C15-Ru1	56.9(8)	C14-C15-C16-C17	-2.1(15)
C18A-C15-C16-C17	172.1(16)	C18-C15-C16-C17	-175.9(12)
Ru1-C15-C16-C17	-55.8(8)	C14-C15-C16-Ru1	53.7(8)
C18A-C15-C16-Ru1	-132.1(15)	C18-C15-C16-Ru1	-120.1(14)
C13-C12-C17-C16	0.4(14)	C11-C12-C17-C16	-178.7(10)
Ru1-C12-C17-C16	53.4(8)	C13-C12-C17-Ru1	-53.0(8)
C11-C12-C17-Ru1	127.9(9)	C15-C16-C17-C12	0.6(14)
Ru1-C16-C17-C12	-54.9(8)	C15-C16-C17-Ru1	55.5(9)
C16-C15-C18-C20	27.(2)	C14-C15-C18-C20	-147.1(15)
C18A-C15-C18-C20	50.(3)	Ru1-C15-C18-C20	-69.(2)
C16-C15-C18-C19	-98.(2)	C14-C15-C18-C19	87.(2)
C18A-C15-C18-C19	-75.(4)	Ru1-C15-C18-C19	166.(2)
N1-C1-N2-N3	-176.0(7)	S1-C1-N2-N3	3.0(10)
C3-C2-N3-N2	-1.5(12)	C3-C2-N3-Ru1	-175.0(7)
C1-N2-N3-C2	172.4(7)	C1-N2-N3-Ru1	-14.0(9)
C5-C6-N4-C10	174.(2)	C7-C6-N4-C10	-6.(3)
C5-C6-N4-C9	-4.(2)	C7-C6-N4-C9	176.3(16)
N2-C1-S1-Ru1	6.7(7)	N1-C1-S1-Ru1	-174.3(6)

N2-C1-S1-Ru1	-95.0(7)	N1-C1-S1-Ru1	84.1(7)
C16-C15-C18A-C20A	114.(7)	C14-C15-C18A-C20A	-73.(7)
C18-C15-C18A-C20A	-49.(5)	Ru1-C15-C18A-C20A	37.(9)
C16-C15-C18A-C19A	-69.(5)	C14-C15-C18A-C19A	104.(5)
C18-C15-C18A-C19A	129.(7)	Ru1-C15-C18A-C19A	-145.(4)

Table S5. Anisotropic atomic displacement parameters ($Å^2$) for 2.
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.061(4)	0.075(5)	0.055(4)	-0.005(4)	0.029(3)	-0.007(4)
C2	0.069(5)	0.080(5)	0.050(4)	-0.002(4)	0.030(3)	-0.009(4)
C3	0.064(4)	0.071(5)	0.059(4)	-0.003(4)	0.031(4)	-0.005(4)
C4	0.099(7)	0.080(6)	0.062(5)	-0.001(4)	0.019(5)	-0.002(5)
C5	0.116(9)	0.091(8)	0.076(7)	-0.017(6)	0.006(6)	-0.007(6)
C6	0.107(8)	0.071(6)	0.146(11)	-0.011(7)	0.066(8)	-0.012(6)
C7	0.208(15)	0.082(8)	0.134(11)	0.022(7)	0.130(12)	0.009(8)
C8	0.141(9)	0.074(6)	0.087(6)	0.009(5)	0.076(7)	0.011(6)
C11	0.132(8)	0.176(9)	0.140(8)	0.037(7)	0.088(7)	-0.008(7)
C12	0.105(7)	0.102(7)	0.077(6)	0.036(6)	0.053(5)	0.004(6)
C13	0.098(7)	0.080(6)	0.069(5)	0.016(5)	0.027(5)	-0.008(5)
C14	0.119(8)	0.078(6)	0.079(6)	0.015(5)	0.043(6)	0.026(6)
C15	0.073(6)	0.109(8)	0.103(8)	0.040(7)	0.038(6)	0.017(6)
C16	0.087(7)	0.097(8)	0.080(7)	0.023(6)	-0.008(6)	-0.021(6)
C17	0.145(11)	0.091(7)	0.043(4)	0.013(4)	0.023(6)	-0.006(7)
C18	0.076(14)	0.128(17)	0.100(17)	0.030(13)	0.017(12)	0.023(12)
C19	0.13(2)	0.18(3)	0.38(7)	0.12(4)	0.12(3)	0.05(2)
C20	0.075(11)	0.16(2)	0.102(14)	0.014(14)	0.048(11)	-0.017(11)
P1	0.239(10)	0.109(5)	0.249(11)	0	0.156(9)	0
F1	0.52(5)	0.20(2)	0.166(16)	0	0.13(2)	0
F2	0.18(2)	0.50(5)	0.24(2)	0	0.054(17)	0
F3	0.48(5)	0.195(19)	0.24(2)	0	0.18(3)	0
F4	0.45(5)	0.39(5)	0.71(8)	0	0.49(6)	0
F5	0.38(2)	0.112(7)	0.257(14)	-0.018(8)	0.159(14)	0.021(10)
N1	0.130(7)	0.106(6)	0.069(4)	-0.013(4)	0.063(5)	-0.041(5)
N2	0.084(4)	0.075(4)	0.056(3)	-0.006(3)	0.042(3)	-0.021(3)
N3	0.073(4)	0.074(4)	0.047(3)	0.002(3)	0.036(3)	-0.006(3)
N4	0.221(15)	0.076(7)	0.235(17)	-0.016(9)	0.133(14)	-0.026(8)
Ru1	0.0618(4)	0.0604(4)	0.0421(3)	0.0025(2)	0.0236(3)	-0.0023(3)
S1	0.0602(10)	0.0642(10)	0.0478(9)	-0.0022(7)	0.0287(8)	0.0012(8)

C18A	0.040(15)	0.18(5)	0.12(3)	0.03(3)	0.020(19)	0.00(2)
C20A	0.21(5)	0.24(5)	0.22(6)	-0.01(3)	0.08(4)	0.05(3)
C19A	0.14(4)	0.34(10)	0.08(3)	0.04(4)	-0.02(3)	-0.06(5)
C9	0.189(18)	0.089(10)	0.28(3)	-0.062(13)	0.065(18)	-0.020(10)
C10	0.64(6)	0.097(13)	0.44(5)	0.04(2)	0.42(5)	0.01(2)

Table S6. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for 2.

	x/a	**y/b**	**z/c**	**U(eq)**
H2	0.8923	0.7683	0.2316	0.078
H4	0.8304	0.7118	0.1160	0.104
H5	0.7949	0.6445	0.0881	0.13
H7	0.8652	0.6331	0.4252	0.146
H8	0.8953	0.7007	0.4544	0.11
H11A	1.0681	0.9015	0.2409	0.209
H11C	0.9906	0.9016	0.1064	0.209
H11B	1.0370	0.8604	0.1711	0.209
H13	0.9485	0.9306	0.3137	0.104
H14	0.8091	0.9245	0.3561	0.111
H16	0.7089	0.8261	0.1465	0.125
H17	0.8576	0.8325	0.1064	0.12
H18	0.6875	0.8894	0.3829	0.132
H19A	0.6019	0.9340	0.2163	0.337
H19B	0.5197	0.9150	0.2535	0.337
H19C	0.5302	0.8976	0.1447	0.337
H20A	0.5887	0.8222	0.2294	0.164
H20B	0.5650	0.8336	0.3347	0.164
H20C	0.6775	0.8179	0.3586	0.164
H1A	0.8466	0.7583	0.6380	0.114
H1B	0.8723	0.8001	0.6883	0.114
H18A	0.6324	0.8362	0.2150	0.143
H20D	0.6333	0.8661	0.4071	0.344
H20E	0.6476	0.8216	0.3714	0.344
H20F	0.5348	0.8415	0.3184	0.344
H19D	0.4796	0.8869	0.1205	0.316
H19E	0.5146	0.8495	0.0696	0.316
H19F	0.5661	0.8924	0.0766	0.316
H9A	0.8293	0.5674	0.1067	0.299
H9B	0.7176	0.5871	0.0679	0.299
H9C	0.7430	0.5443	0.1290	0.299
H10A	0.8187	0.5353	0.3006	0.488

H10B	0.7783	0.5684	0.3597	0.488
H10C	0.8983	0.5669	0.3882	0.488