Supporting Information

Anti-cancer organoruthenium(II) complexes and their interactions with cysteine and its analogues. A mass-spectrometric study.

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Contents

Preparation of reaction mixtures

Stock solutions of ruthenium(II) complexes and different amino acids/tripeptide were prepared and stored for no longer than 2 days.

Table S1. Contents of the stock solutions of ruthenium(II) complexes.

Stock Solution	Reagent	Quantity (mg)	n (µmol)	Solvent	Quantity (µl)
I	[Ru(CYM)(*p*-Cl-dkt)]	1	2	3 % DMSO in water	5000
II	[Ru(CYM)(pta)(*p*-Cl-dkt)]PF_6	1	1	3 % DMSO in water	3200
IIa	[Ru(CYM)(pta)(*p*-Cl-dkt)]PF_6	1	1	Water	3200
III	RAPTA-C	1	2	3 % DMSO in water	5400

Stock solutions of NAC, GSH and Cys were prepared in two different concentrations. The higher concentration solutions were used in measurements with 1000 equivalents of amino acid/tripeptide to ruthenium(II) complexes.

Table S2. Contents of the stock solutions of different amino acids/tripeptide.

Stock Solution	Reagent	Quantity (mg)	n	Solvent	Quantity (µl)
NAC I	*N*-acetylcysteine	1	6 µmol	Water	2000
NAC II	*N*-acetylcysteine	100	0.6 mmol	Water	2000
GSH I	Glutathione	1	3 µmol	Water	1000
GSH II	Glutathione	100	0.3 mmol	Water	1000
Cys I	L-Cysteine	1	8 µmol	Water	2500
Cys II	L-Cysteine	100	0.8 mmol	Water	2500
Ala I	L-Alanine	1	10 µmol	Water	2500
Ser I	L-Serine	1	10 µmol	Water	2500
Glu I	L-Glutamic acid	1	7 µmol	Water	2500
Arg I	L-Arginine	1	6 µmol	Water	1000
His I	L-Histidine	1	6 µmol	Water	1600
Met I	L-Methionine	1	7 µmol	Water	1700
Asp I	L-Aspartic acid	1	8 µmol	Water	1900

ESI mass spectra and CID spectra

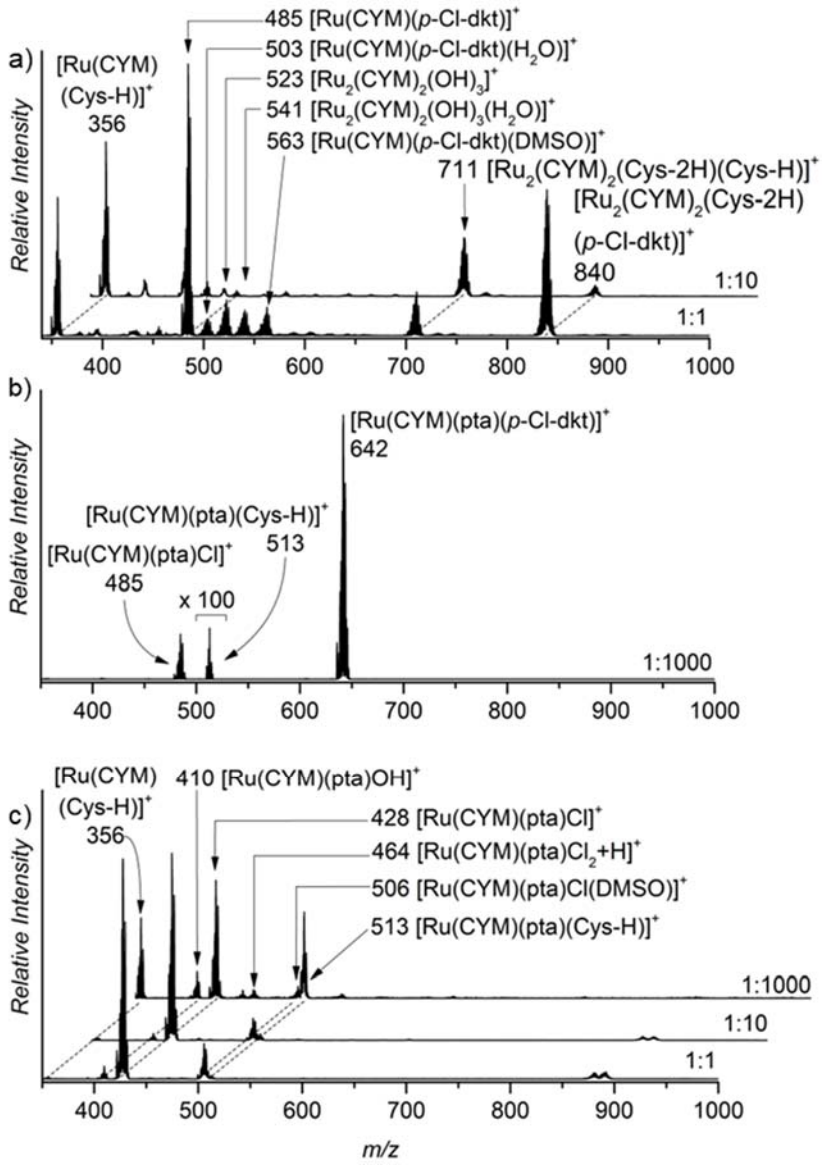


Figure S1. ESI mass spectra of 0.2 mM aqueous solution of a) [Ru(CYM)(*p*-Cl-dkt)]Cl, b) [Ru(CYM)(pta)(*p*-Cl-dkt)]PF_6 and c) RAPTA-C with Cys. The spectra were acquired immediately after preparing a solution with all components. The molar ratio of the ruthenium(II) complex to Cys was 1:1, 1:10 and 1:1000 as denoted in each ESI mass spectrum (right bottom).

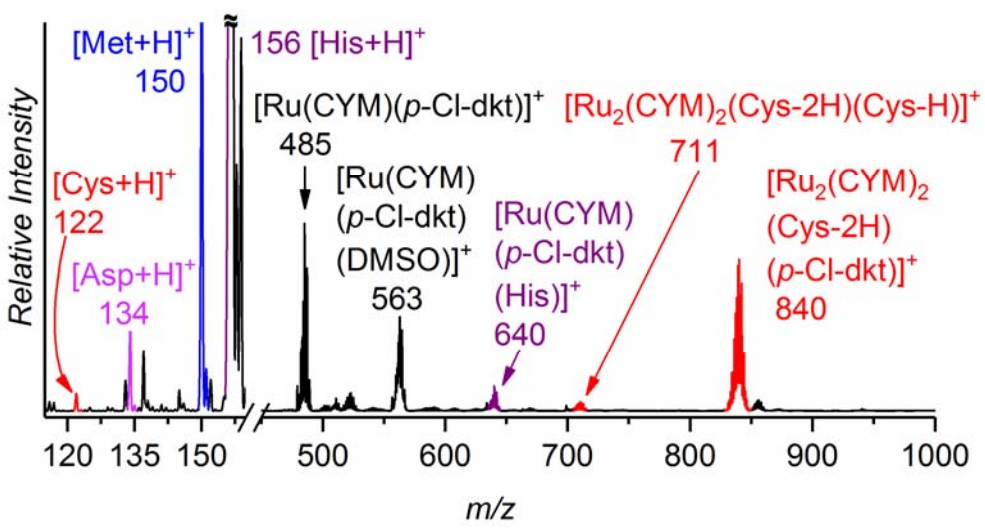


Figure S2. ESI mass spectrum of a 0.2 mM aqueous solution of [Ru(CYM)(*p*-Cl-dkt)]Cl with equimolar concentrations of Cys, Asp, Met, and His. The spectra were acquired immediately after preparing a solution with all components.

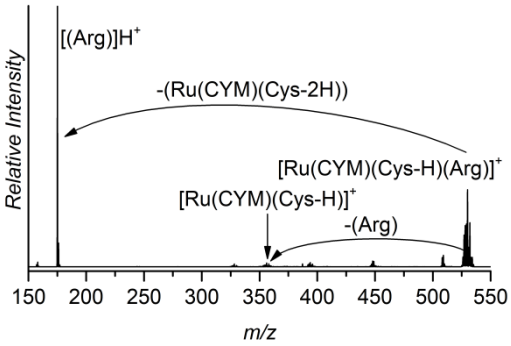


Figure S3. The CID spectrum of mass-selected ion [Ru(CYM)(Cys-H)(Ala)]$^+$.

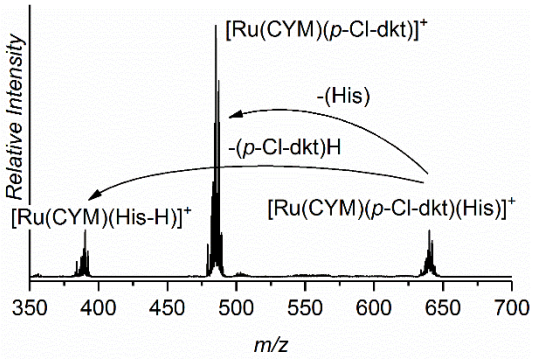


Figure S4. The CID spectrum of mass-selected ion [Ru(CYM)(*p*-Cl-dkt)(His)]$^+$.

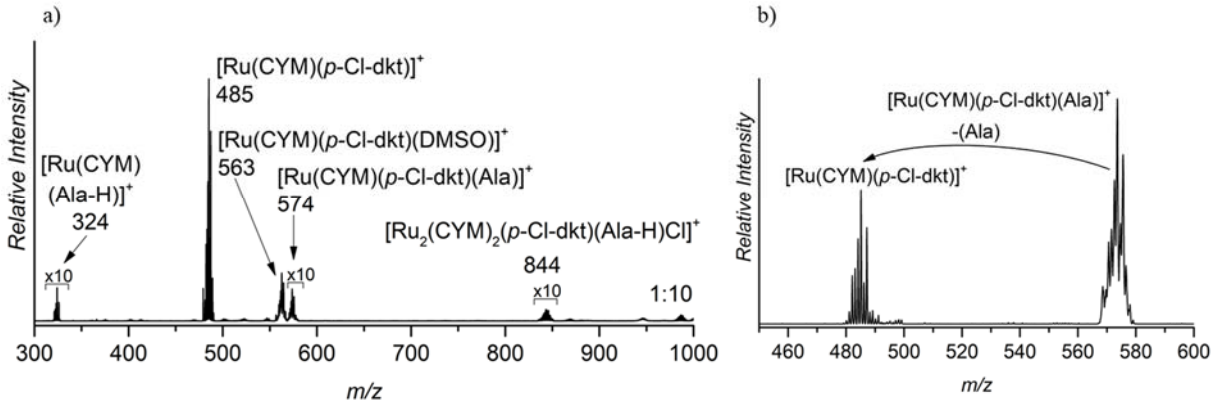


Figure S5. a) ESI mass spectra of 0.2 mM aqueous solution of [Ru(CYM)(*p*-Cl-dkt)]Cl with Ala and b) the CID spectrum of mass-selected ion [Ru(CYM)(*p*-Cl-dkt)(Ala)]$^+$. The spectra were acquired immediately after preparing a solution with all components. The [Ru(CYM)(*p*-Cl-dkt)]Cl to Ala ratio was 1 to 10.

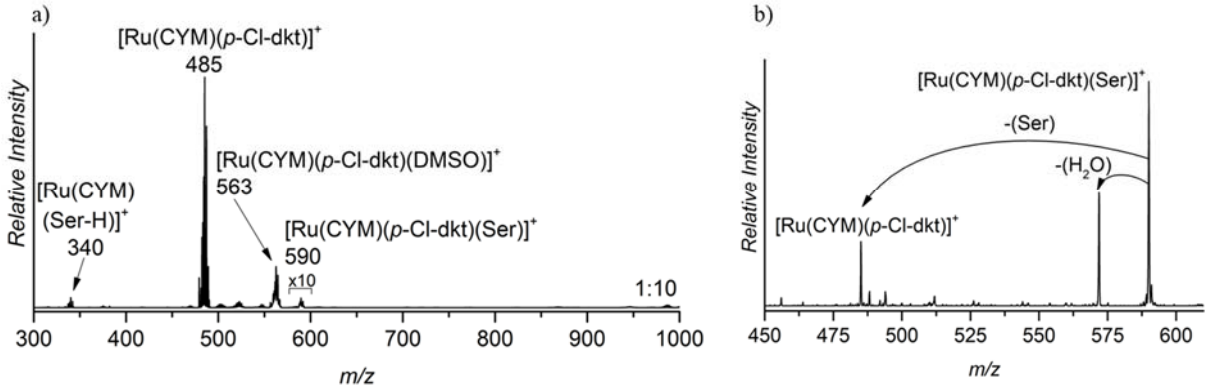


Figure S6. a) ESI mass spectra of 0.2 mM aqueous solution of [Ru(CYM)(*p*-Cl-dkt)]Cl with Ser and b) the CID spectrum of mass-selected ion [Ru(CYM)(*p*-Cl-dkt)(Ser)]$^+$. The spectra were acquired immediately after preparing a solution with all components. The [Ru(CYM)(*p*-Cl-dkt)]Cl to Ser ratio was 1 to 10.

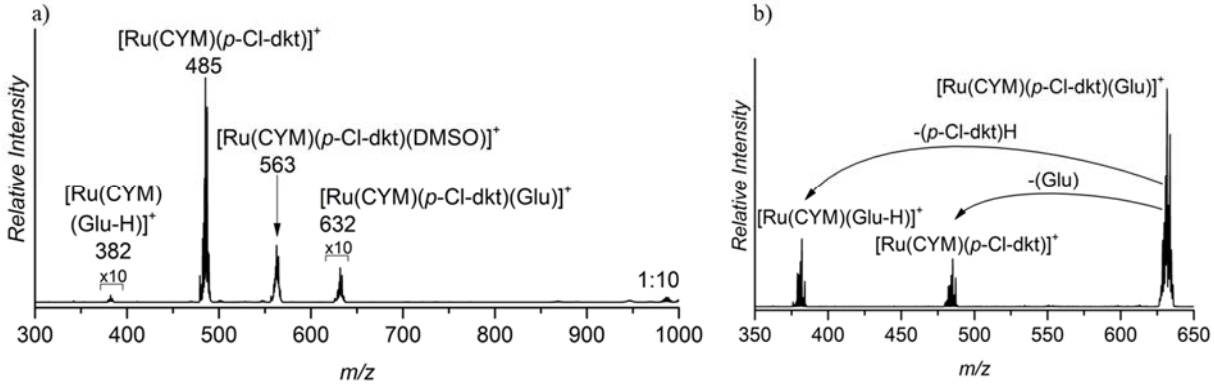


Figure S7. a) ESI mass spectra of 0.2 mM aqueous solution of [Ru(CYM)(*p*-Cl-dkt)]Cl with Glu and b) the CID spectrum of mass-selected ion [Ru(CYM)(*p*-Cl-dkt)(Glu)]$^+$. The spectra were acquired immediately after preparing a solution with all components. The [Ru(CYM)(*p*-Cl-dkt)]Cl to Glu ratio was 1 to 10.

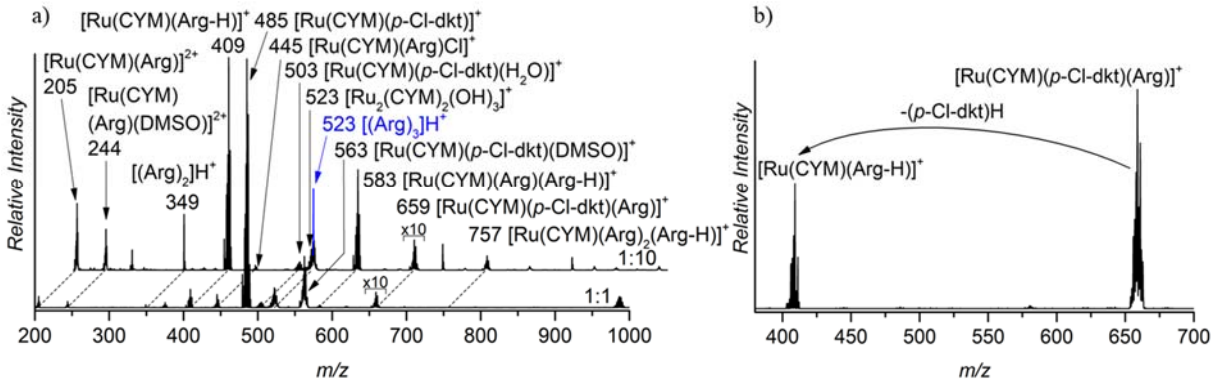


Figure S8. a) ESI mass spectra of 0.2 mM aqueous solution of [Ru(CYM)(*p*-Cl-dkt)]Cl with Arg and b) the CID spectrum of mass-selected ion [Ru(CYM)(*p*-Cl-dkt)(Arg)]$^{+}$. The spectra were acquired immediately after preparing a solution with all components. The molar ratio of the ruthenium(II) complex to Arg was 1:1 and 1:10 as denoted in each ESI mass spectrum (right bottom).

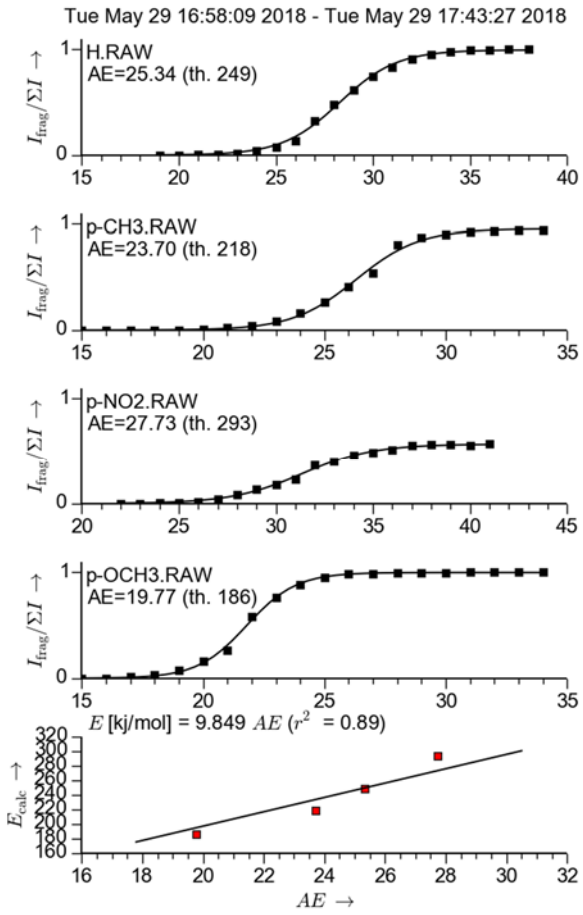


Figure S9. Calibration curves and sigmoidal fits of the relative intensities in dependence to normalised collision energies for positive-ion mode for substituted benzylpyridiunium ions $[RBnPy]^+$. The linear extrapolation of the sigmoidal fit rise gives appearance energy. Used $[RBnPy]^+$ were benzylpyridinium (R=H), *p*-methylbenzylpyridinium (R=*p*-CH_3), *p*-methoxybenzylpyridinium (R=*p*-OCH_3) and *p*-nitrobenzylpyridinium (R=*p*-NO2).

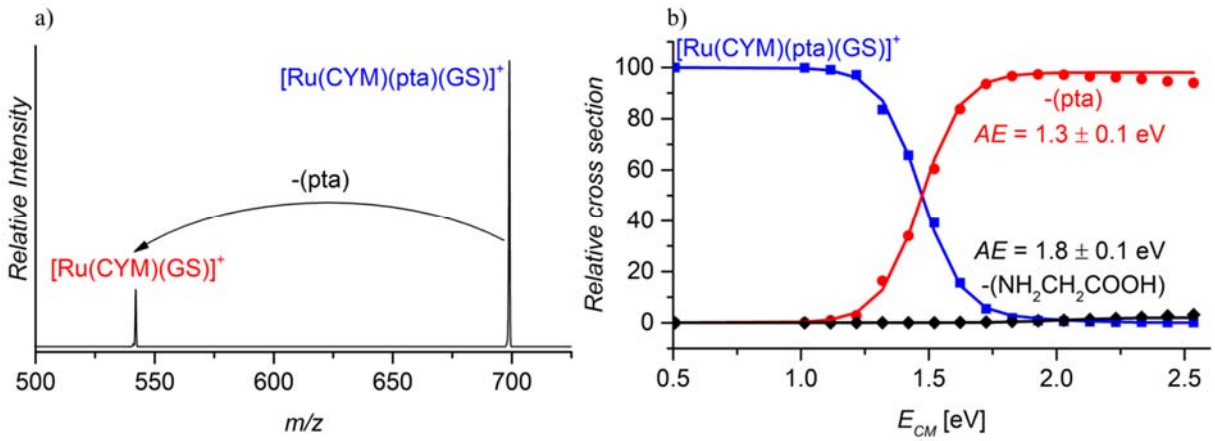


Figure S10. a) The CID spectrum of mass-selected ion $[Ru(CYM)(pta)(GS)]^+$ (E_{coll} 1.3 eV, c.m.) and b) the breakdown curve as function of collision energy.

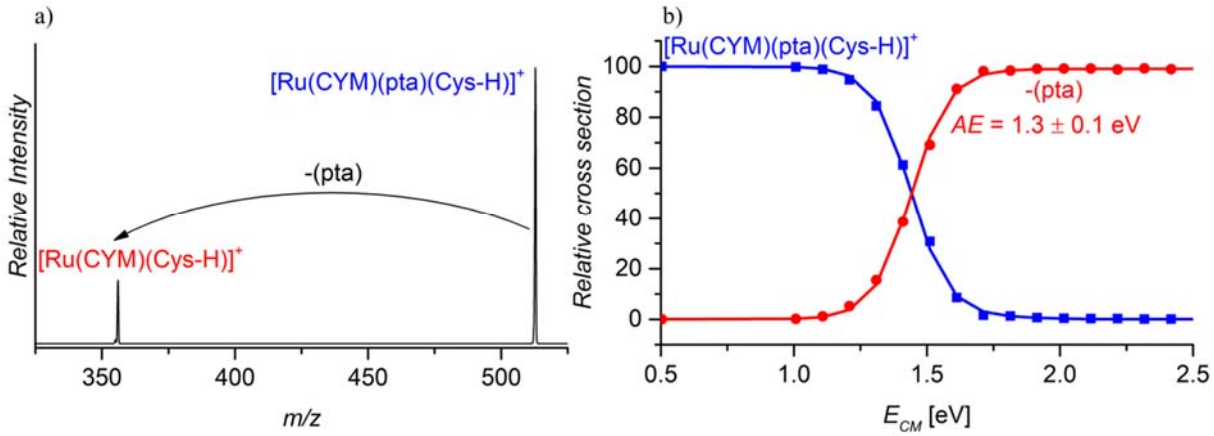


Figure S11. a) The CID spectrum of mass-selected ion $[Ru(CYM)(pta)(Cys\text{-}H)]^+$ (E_{coll} 1.3 eV, c.m.) and b) the breakdown curve as function of collision energy.

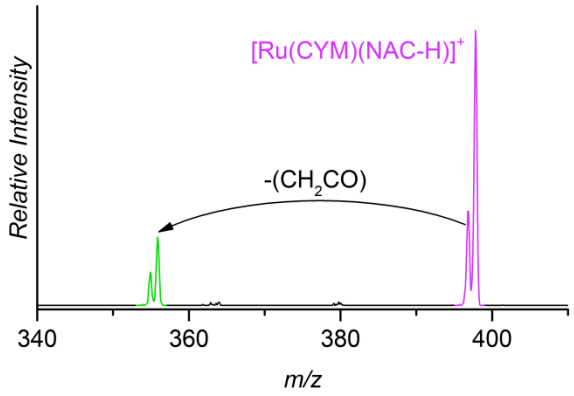


Figure S12. MS/MS/MS experiment of mass-selected ion $[Ru(CYM)(NAC\text{-}H)]^+$.

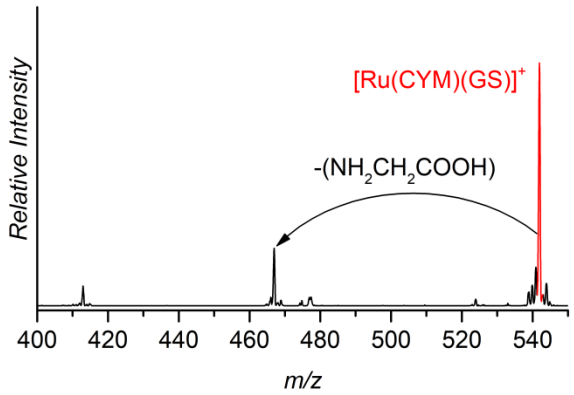


Figure S13. MS/MS/MS experiment of mass-selected ion $[Ru(CYM)(GS)]^+$.

IRPD and theoretical IR spectra

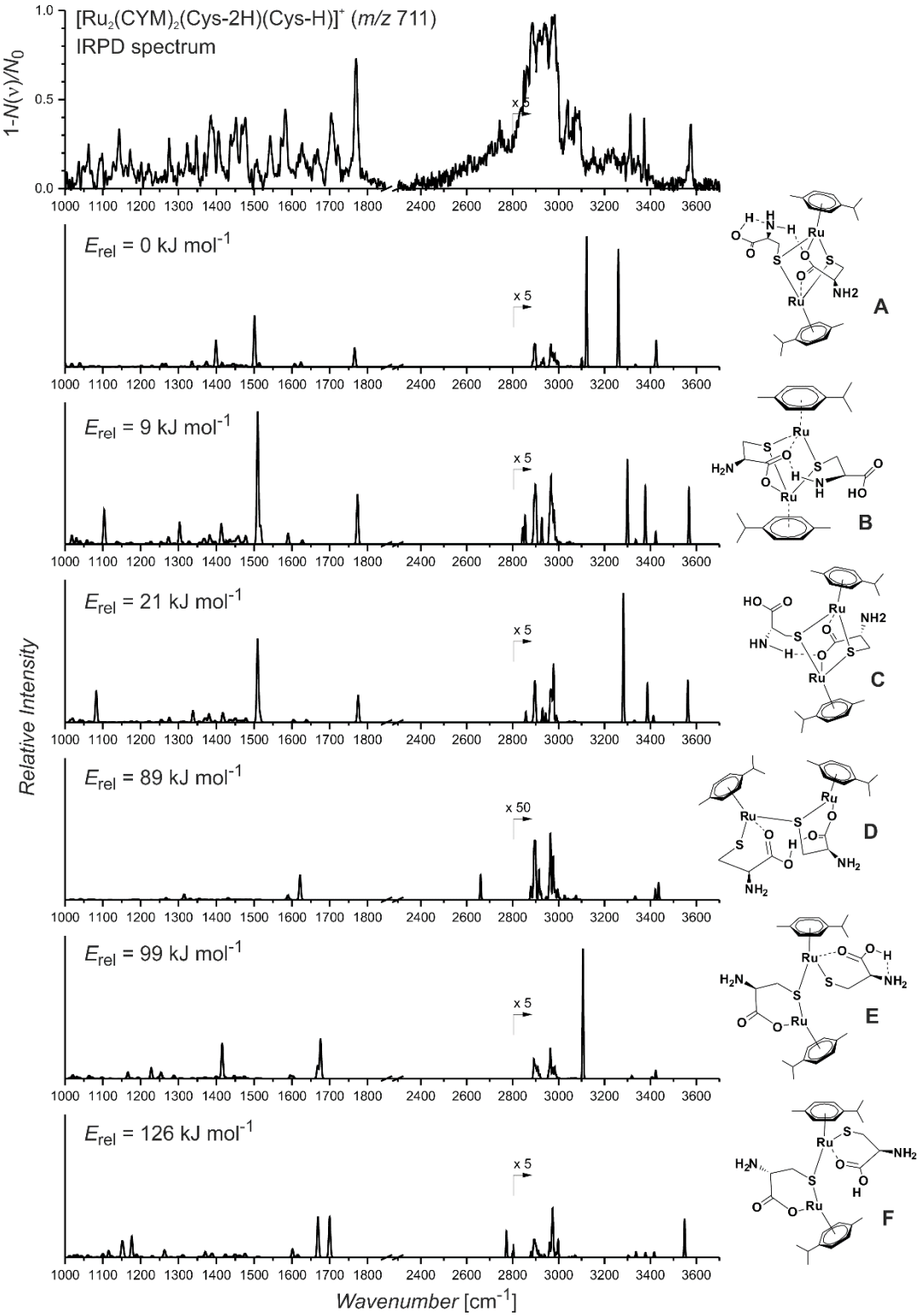


Figure S14. a) Helium tagging IRPD spectrum of mass-selected ion $[Ru_2(CYM)_2(Cys\text{-}2H)(Cys\text{-}H)]^+$ (*m/z* 711). b) Theoretical IR spectra (B3LYP-D3/6-31G**:SDD(Ru)) of possible isomers of $[Ru_2(CYM)_2(Cys\text{-}2H)(Cys\text{-}H)]^+$. The relative energies refer to energies at 0 K. The geometries and energetics of the optimised structures can be found in Table S3.

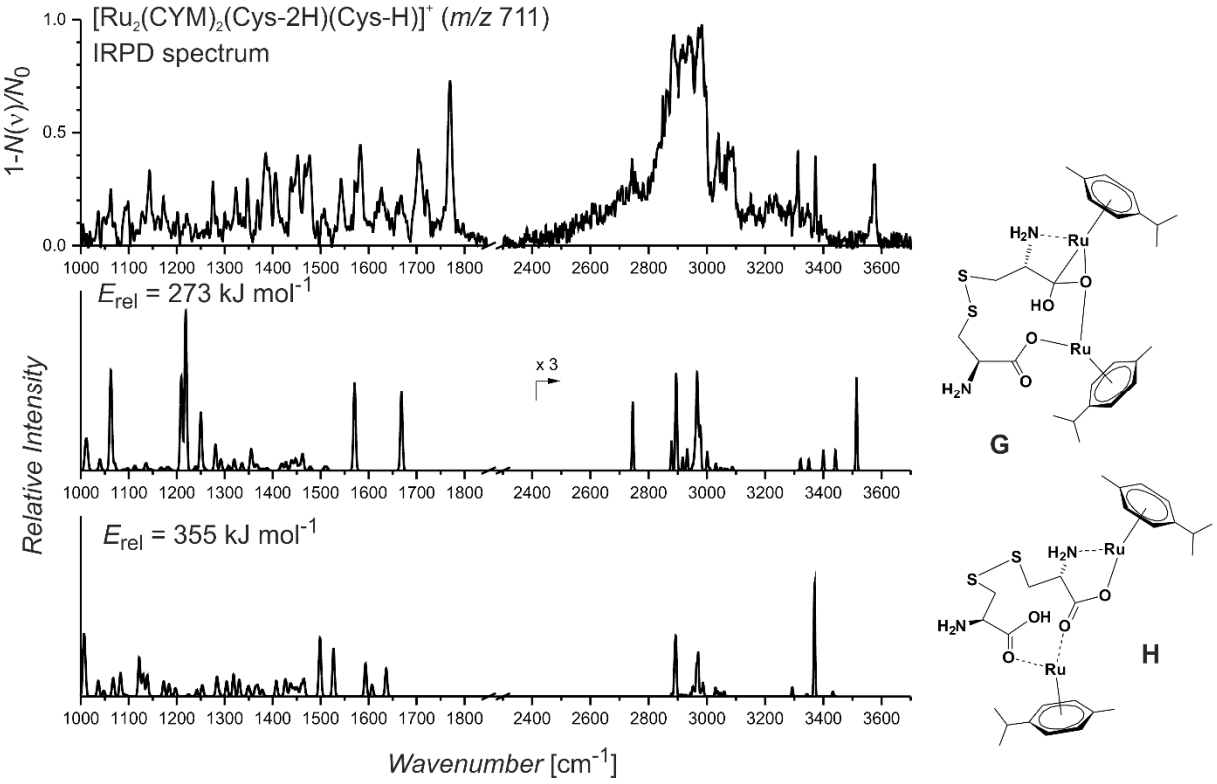


Figure S15. a) Helium tagging IRPD spectrum of mass-selected ion $[Ru_2(CYM)_2(Cys\text{-}2H)(Cys\text{-}H)]^+$ (*m/z* 711). b) Theoretical IR spectra (B3LYP-D3/6-31G**:SDD(Ru)) of possible isomers of $[Ru_2(CYM)_2(cystine)(Cys\text{-}H)]^+$. The relative energies refer to energies at 0 K and are given relative to the isomer **A** in Figure S12. The geometries and energetics of the optimised structures can be found in Table S3.

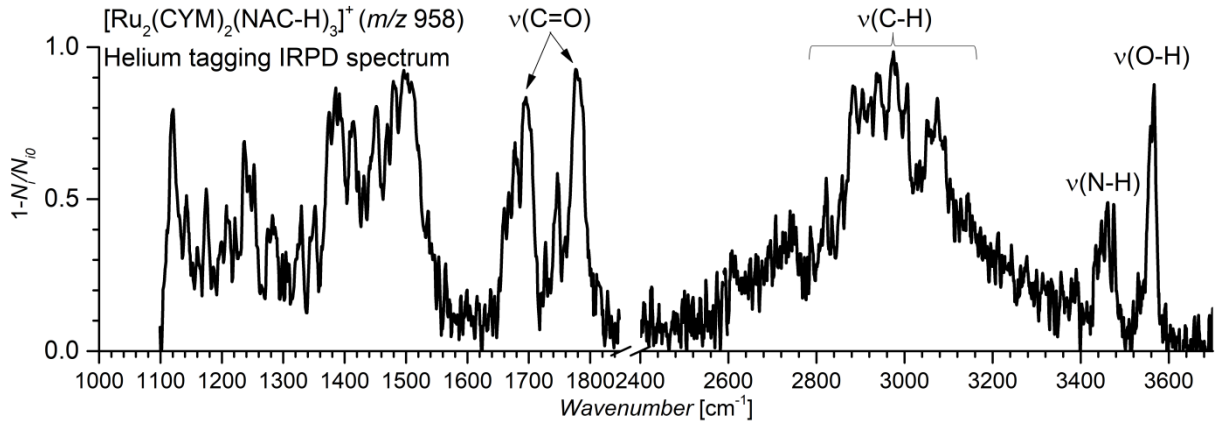
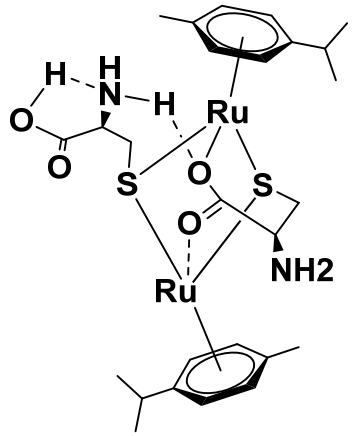


Figure S16. Helium tagging IRPD spectrum of mass-selected ions $[Ru_2(CYM)_2(NAC\text{-}H)_3]^+$ (*m/z* 958).

Computational results

Table S3. XYZ coordinates and energies of optimised structures of $[Ru_2(CYM)_2(Cys\text{-}2H)(Cys\text{-}H)]^+$. The calculations were perfomed at the B3LYP-D3/6-31G**:SDD(Ru) level of theory using Gaussian 16 workpackage.

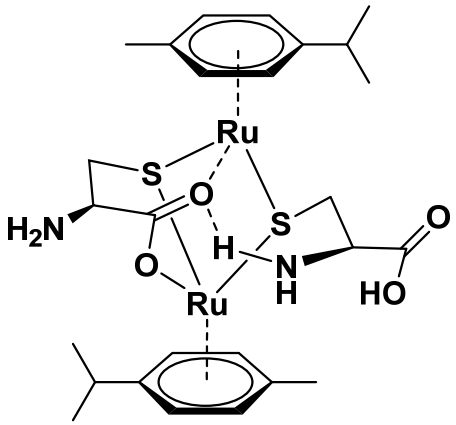
A (Cys3)



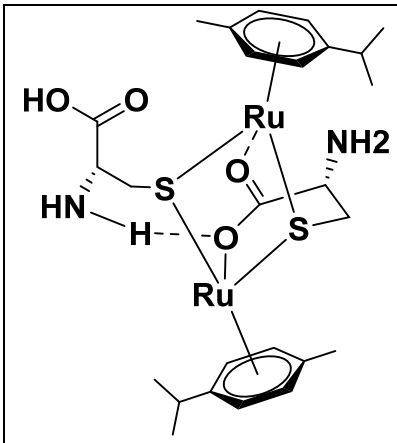
Charge = 1 Multiplicity = 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.687857	0.016618	-1.212205
2	6	0	-3.669362	-1.408458	-1.046909
3	6	0	-3.706092	-1.981558	0.241901
4	6	0	-3.836293	-1.100738	1.374990
5	6	0	-3.910564	0.293977	1.200234
6	6	0	-3.816440	0.895233	-0.103680
7	44	0	-2.060340	-0.426316	0.178255
8	16	0	-0.646508	1.327061	1.111453
9	6	0	-0.267855	0.830702	2.856176
10	6	0	-0.084614	-0.699497	3.050761
11	7	0	0.894423	-0.921267	4.100032
12	6	0	-3.542727	-3.459278	0.462538
13	6	0	-3.857123	2.406003	-0.239636
14	6	0	-3.069233	2.936570	-1.444117
15	44	0	1.426933	0.713902	-0.062729
16	8	0	2.643632	-1.305423	-3.207856
17	6	0	2.261909	-2.070796	-2.344359
18	6	0	0.825450	-2.629410	-2.301041
19	6	0	-0.176645	-1.522504	-2.648851
20	16	0	-0.383585	-0.055213	-1.523226
21	6	0	3.060640	1.861092	0.970438
22	6	0	3.706053	0.811743	0.255732
23	6	0	3.434655	0.674548	-1.133612
24	6	0	2.521944	1.540354	-1.788863
25	6	0	1.877414	2.611413	-1.099280
26	6	0	2.166322	2.739319	0.294280
27	6	0	4.663626	-0.171712	0.898539
28	6	0	4.414680	-0.419938	2.389592
29	6	0	0.910929	3.530789	-1.793947
30	8	0	1.394412	-1.127755	1.182176
31	6	0	0.241382	-1.300744	1.672784
32	8	0	-0.703864	-1.901358	1.049654
33	6	0	6.104210	0.323716	0.640819
34	8	0	3.036500	-2.516127	-1.357531
35	1	0	0.784023	-3.334805	-3.142319
36	6	0	-5.326205	2.873492	-0.272612
37	1	0	-3.540254	-2.046503	-1.914660
38	1	0	-3.549022	0.427094	-2.205272
39	1	0	-3.949259	0.938626	2.073314
40	1	0	-3.387966	2.808096	0.667421
41	1	0	-3.818947	-1.519669	2.375667
42	1	0	4.525931	-1.119913	0.366480
43	1	0	3.395730	-0.779068	2.545881
44	1	0	5.106866	-1.184052	2.753945
45	1	0	4.583521	0.479309	2.992568
46	1	0	6.820999	-0.403916	1.032148
47	1	0	6.284270	1.280960	1.142118
48	1	0	6.301340	0.453553	-0.427433
49	1	0	3.206691	1.971139	2.037790
50	1	0	1.629483	3.487850	0.869990
51	1	0	2.269428	1.332501	-2.823726
52	1	0	0.378356	3.000688	-2.587316
53	1	0	0.175124	3.930015	-1.091354

	54 1 0 1.447485 4.373528 -2.244021 55 1 0 3.870751 -0.142218 -1.691960 56 1 0 -4.467056 -3.884630 0.867914 57 1 0 -3.304572 -3.977656 -0.468764 58 1 0 -2.736917 -3.642206 1.179222 59 1 0 -3.022886 4.028242 -1.400464 60 1 0 -2.048232 2.545565 -1.457714 61 1 0 -3.550755 2.674063 -2.392335 62 1 0 -5.879532 2.533194 0.608376 63 1 0 -5.373588 3.965960 -0.300978 64 1 0 -5.835680 2.489256 -1.162845 65 1 0 0.659921 1.346099 3.118084 66 1 0 -1.057770 1.212075 3.507354 67 1 0 -1.038305 -1.133394 3.364321 68 1 0 0.934010 -1.901688 4.364391 69 1 0 1.820990 -0.655114 3.777294 70 1 0 -1.179994 -1.943909 -2.745523 71 1 0 0.119671 -1.092892 -3.608003 72 1 0 2.421307 -3.081151 -0.812490 73 7 0 0.630876 -3.371749 -1.060289 74 1 0 0.148691 -2.823751 -0.344823 75 1 0 0.135757 -4.243813 -1.204828 --- Low frequencies --- -6.9918 -3.9681 -0.0016 -0.0015 -0.0014 5.1207 Low frequencies --- 14.9252 22.8554 33.2855 Zero-point correction= 0.625056 (Hartree/Particle) Thermal correction to Energy= 0.665197 Thermal correction to Enthalpy= 0.666142 Thermal correction to Gibbs Free Energy= 0.554193 Sum of electronic and zero-point Energies= -2410.411735 Sum of electronic and thermal Energies= -2410.371594 Sum of electronic and thermal Enthalpies= -2410.370650 Sum of electronic and thermal Free Energies= -2410.482599
B (Cys1)  	Charge = 1 Multiplicity = 1 Standard orientation: --- Center Atomic Atomic Coordinates (Angstroms) Number Number Type X Y Z --- 1 6 0 3.767140 -0.889043 -0.251657 2 6 0 3.915209 -0.407673 1.096750 3 6 0 3.842731 0.964196 1.397962 4 6 0 3.652826 1.942994 0.356990 5 6 0 3.559861 1.491502 -0.976936 6 6 0 3.591087 0.087984 -1.270219 7 44 0 2.022427 0.375022 0.216794 8 16 0 0.336879 0.056084 -1.488095 9 6 0 -0.090167 1.556235 -2.485169 10 6 0 -0.420814 2.916821 -1.853504 11 6 0 -1.799177 3.026778 -1.196006 12 8 0 -2.758120 2.330830 -1.864243 13 6 0 3.501256 3.394559 0.712121 14 6 0 3.816199 -2.381570 -0.522769 15 6 0 2.981846 -2.817839 -1.733743 16 8 0 0.752518 1.693682 1.456634 17 6 0 -0.379512 1.158374 1.688770 18 6 0 -0.511987 0.415780 3.016990 19 7 0 -1.894979 0.029242 3.283391 20 8 0 -1.331886 1.120202 0.857261 21 44 0 -1.414285 -0.844712 -0.092587 22 16 0 0.633879 -1.420234 1.130631 23 6 0 0.386109 -0.849318 2.887281 24 6 0 -1.815475 -2.954640 -0.630524 25 6 0 -2.438274 -2.676551 0.633780 26 6 0 -3.343224 -1.608493 0.784782 27 6 0 -3.723727 -0.796731 -0.339746 28 6 0 -3.109946 -1.050567 -1.583817 29 6 0 -2.142256 -2.099617 -1.716783 30 6 0 -0.831724 -4.082397 -0.781889

	31 6 0 -4.801673 0.262359 -0.205626 32 6 0 -4.589016 1.242691 0.958608 33 6 0 -6.166569 -0.450383 -0.091481 34 6 0 5.286463 -2.825090 -0.660868 35 7 0 0.653881 3.434016 -1.025232 36 8 0 -2.051237 3.742408 -0.255532 37 1 0 -0.515702 3.580518 -2.728863 38 1 0 3.343918 2.204891 -1.763742 39 1 0 3.409216 -0.233563 -2.288860 40 1 0 3.992663 -1.129122 1.905111 41 1 0 3.391651 -2.867783 0.365059 42 1 0 3.857789 1.291204 2.432328 43 1 0 -4.805997 0.828763 -1.143945 44 1 0 -3.626913 1.753633 0.890501 45 1 0 -5.387989 1.990436 0.957906 46 1 0 -4.639327 0.724247 1.921990 47 1 0 -6.972525 0.288911 -0.067118 48 1 0 -6.222438 -1.039071 0.830399 49 1 0 -6.343801 -1.122357 -0.936592 50 1 0 -3.710001 -1.370596 1.774293 51 1 0 -2.138358 -3.245999 1.507780 52 1 0 -1.623940 -2.227557 -2.661760 53 1 0 -0.156287 -3.905002 -1.622069 54 1 0 -0.230405 -4.200911 0.122731 55 1 0 -1.367019 -5.021029 -0.964679 56 1 0 -3.322590 -0.404187 -2.427856 57 1 0 4.482813 3.821185 0.948140 58 1 0 3.057569 3.950785 -0.114351 59 1 0 2.860670 3.504270 1.591572 60 1 0 2.954622 -3.909924 -1.786671 61 1 0 1.956142 -2.445035 -1.666264 62 1 0 3.414034 -2.461128 -2.674862 63 1 0 5.874978 -2.555669 0.221829 64 1 0 5.344146 -3.910128 -0.788167 65 1 0 5.751958 -2.356333 -1.534573 66 1 0 -0.069799 -1.673098 3.441969 67 1 0 1.388392 -0.666016 3.280108 68 1 0 -0.072297 1.062537 3.791224 69 1 0 -2.028048 -0.115757 4.280444 70 1 0 -2.521696 0.774163 2.992980 71 1 0 0.791515 1.697047 -3.115897 72 1 0 -0.917463 1.236439 -3.122195 73 1 0 0.654502 2.924836 -0.141268 74 1 0 0.428449 4.395168 -0.777822 75 1 0 -3.598394 2.562050 -1.434380 --- Low frequencies --- -5.7868 -0.0008 -0.0006 0.0005 4.5637 6.7313 Low frequencies --- 23.7977 27.3928 38.5098 Zero-point correction= 0.624823 (Hartree/Particle) Thermal correction to Energy= 0.664954 Thermal correction to Enthalpy= 0.665898 Thermal correction to Gibbs Free Energy= 0.555365 Sum of electronic and zero-point Energies= -2410.408407 Sum of electronic and thermal Energies= -2410.368276 Sum of electronic and thermal Enthalpies= -2410.367332 Sum of electronic and thermal Free Energies= -2410.477865
C (Cys6)	Charge = 1 Multiplicity = 1 Standard orientation: --- Center Atomic Atomic Coordinates (Angstroms) Number Number Type X Y Z --- 1 6 0 -2.236446 -2.221052 -1.586280 2 6 0 -3.028523 -2.151650 -0.391307 3 6 0 -3.673938 -0.953677 -0.028560 4 6 0 -3.531172 0.180746 -0.911083 5 6 0 -2.828473 0.082032 -2.128608 6 6 0 -2.152081 -1.131835 -2.493990 7 44 0 -1.470128 -0.509347 -0.476018



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10	8	0	0.671840	1.141354	1.768375
11	44	0	2.026049	0.166282	0.375524
12	16	0	0.441853	0.648771	-1.374297
13	6	0	0.288341	2.428046	-1.867045
14	6	0	-0.325578	3.476403	-0.928544
15	7	0	0.421041	3.618430	0.299826
16	6	0	-4.437817	-0.766340	1.268664
17	6	0	-5.921331	-0.473405	0.956677
18	6	0	-1.359465	-1.225775	-3.767632
19	6	0	3.706516	0.295616	-1.015785
20	6	0	3.676391	1.521684	-0.270947
21	6	0	3.663268	1.506282	1.141173
22	6	0	3.751226	0.228509	1.803736
23	6	0	3.818629	-0.969522	1.067004
24	6	0	3.772274	-0.968705	-0.371937
25	6	0	3.485600	2.772661	1.930088
26	6	0	3.793832	-2.285244	-1.126392
27	6	0	5.254513	-2.744740	-1.307344
28	16	0	0.485860	-1.760042	0.386779
29	6	0	0.018325	-2.055113	2.159769
30	6	0	-0.110110	-0.764490	3.023746
31	7	0	-1.166289	-0.954039	4.008215
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34	8	0	-2.430992	3.243068	0.303480
35	8	0	-2.481260	3.261612	-1.953000
36	6	0	-4.317838	-1.943445	2.243016
37	1	0	-0.247674	4.416511	-1.497037
38	1	0	3.556324	2.465323	-0.791838
39	1	0	3.605506	0.339532	-2.093670
40	1	0	3.814085	-1.919792	1.592543
41	1	0	3.279755	-3.013650	-0.486353
42	1	0	3.688827	0.190807	2.886173
43	1	0	-4.000619	0.123139	1.741148
44	1	0	-3.278485	-2.188436	2.479252
45	1	0	-4.820181	-1.697278	3.182440
46	1	0	-4.798667	-2.844203	1.845562
47	1	0	-6.463645	-0.272817	1.884875
48	1	0	-6.392913	-1.332219	0.467363
49	1	0	-6.042248	0.397254	0.305739
50	1	0	-3.049324	-3.007400	0.271884
51	1	0	-1.670947	-3.124291	-1.792300
52	1	0	-2.703443	0.967050	-2.742415
53	1	0	-0.878427	-0.273080	-4.001483
54	1	0	-0.581426	-1.988979	-3.690967
55	1	0	-2.021724	-1.491169	-4.599413
56	1	0	-3.921375	1.140028	-0.590496
57	1	0	4.464113	3.208354	2.162390
58	1	0	2.895000	3.494997	1.361109
59	1	0	2.966218	2.570415	2.869494
60	1	0	2.983278	-3.246620	-2.885444
61	1	0	2.034170	-1.846115	-2.345180
62	1	0	3.572059	-1.618181	-3.201534
63	1	0	5.776363	-2.821839	-0.348278
64	1	0	5.284641	-3.726397	-1.789117
65	1	0	5.807155	-2.040468	-1.938516
66	1	0	-0.945928	-2.567261	2.134401
67	1	0	0.749336	-2.740012	2.595883
68	1	0	0.835606	-0.588746	3.542606
69	1	0	-1.083409	-0.269600	4.755143
70	1	0	-2.066443	-0.795992	3.561083
71	1	0	1.316490	2.728712	-2.083503
72	1	0	-0.267037	2.409011	-2.807452
73	1	0	0.343703	2.765690	0.856255
74	1	0	0.017281	4.366318	0.857824
75	1	0	-3.433883	3.306990	-1.764990

Low frequencies --- -4.8667 -3.3099 -0.0015 -0.0007 0.0000 2.6795

Low frequencies --- 24.0300 27.1582 34.7419
Zero-point correction= 0.624753 (Hartree/Particle)
Thermal correction to Energy= 0.665102
Thermal correction to Enthalpy= 0.666046
Thermal correction to Gibbs Free Energy= 0.553963
Sum of electronic and zero-point Energies= -2410.403688
Sum of electronic and thermal Energies= -2410.363339
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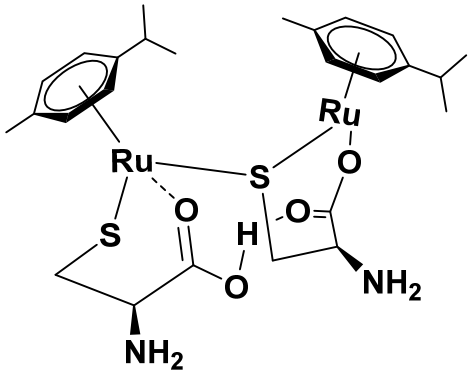
Sum of electronic and thermal Free Energies= -2410.474478

D (Cys5)



Charge = 1 Multiplicity = 1

Standard orientation:

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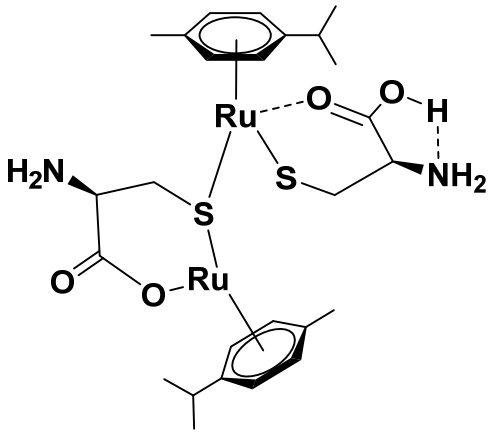
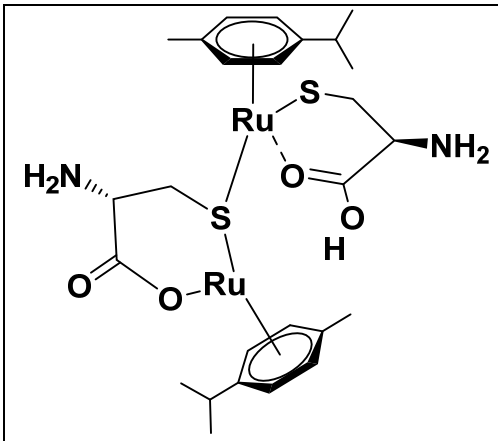
2	6	0	2.685127	-1.637420	-1.957738
3	6	0	3.169319	-0.322487	-2.233930
4	6	0	3.809376	0.450151	-1.218752
5	6	0	4.022529	-0.054962	0.109954
6	6	0	3.480342	-1.320127	0.394289
7	44	0	1.824690	-0.070991	-0.550723
8	8	0	1.413434	1.508827	0.641116
9	6	0	0.607107	2.515481	0.491160
10	8	0	0.164141	3.124897	1.476244
11	6	0	2.005933	-2.445501	-3.029743
12	6	0	4.699540	0.819887	1.146222
13	6	0	6.220829	0.566125	1.101037
14	16	0	-0.162117	0.248865	-1.758657
15	6	0	-0.536621	2.069155	-1.799648
16	6	0	0.321479	3.012609	-0.943680
17	7	0	1.549329	3.351662	-1.666897
18	44	0	-1.647839	-0.736749	-0.085128
19	16	0	-3.416596	-0.036841	-1.560179
20	6	0	-4.543132	0.698719	-0.300922
21	6	0	-1.252447	-1.662696	1.991550
22	6	0	-0.263246	-2.164076	1.121171
23	6	0	-0.642223	-2.702405	-0.155191
24	6	0	-1.994364	-2.893148	-0.536535
25	6	0	-2.990359	-2.449961	0.395915
26	6	0	-2.629846	-1.830709	1.608443
27	6	0	-0.942643	-0.982994	3.311850
28	6	0	-1.138546	-2.001419	4.455334
29	6	0	-2.380122	-3.508554	-1.852154
30	8	0	-1.863554	1.184236	0.799792
31	6	0	-2.699151	2.112885	0.782905
32	6	0	-4.108680	2.083930	0.181604
33	1	0	-4.777760	2.401233	0.993927
34	6	0	0.439947	-0.325627	3.369682
35	6	0	4.130525	0.647322	2.560677
36	1	0	-4.036229	-2.504689	0.112950
37	1	0	-3.405347	-1.435328	2.256529
38	1	0	0.781656	-2.078653	1.385850
39	1	0	-1.692359	-0.189650	3.428282
40	1	0	0.129848	-2.977545	-0.862553
41	1	0	4.515120	1.857524	0.840997
42	1	0	4.344891	-0.347084	2.968016
43	1	0	4.597774	1.373218	3.231495
44	1	0	3.051489	0.817195	2.570565
45	1	0	6.732283	1.245262	1.788873
46	1	0	6.631371	0.725677	0.098835
47	1	0	6.451604	-0.460697	1.404112
48	1	0	4.137990	1.457875	-1.453349
49	1	0	3.008767	0.113556	-3.215203
50	1	0	2.361574	-3.034207	-0.341657
51	1	0	1.536942	-3.344072	-2.622030
52	1	0	1.242036	-1.850220	-3.538779
53	1	0	2.740819	-2.764975	-3.776047
54	1	0	3.512446	-1.708917	1.405492
55	1	0	-2.657479	-4.559149	-1.710974

	56 1 0 -3.233132 -2.978108 -2.282934 57 1 0 -1.551771 -3.464226 -2.563648 58 1 0 0.554882 0.198503 4.322479 59 1 0 1.243375 -1.070343 3.318336 60 1 0 0.575524 0.400931 2.566325 61 1 0 -0.407674 -2.813765 4.378903 62 1 0 -0.998210 -1.509015 5.421657 63 1 0 -2.139537 -2.443996 4.442517 64 1 0 -0.401996 2.366899 -2.842152 65 1 0 -1.594545 2.148227 -1.562106 66 1 0 -0.253264 3.937514 -0.828187 67 1 0 2.088784 4.043158 -1.151722 68 1 0 2.129401 2.523422 -1.761838 69 7 0 -4.242482 3.054912 -0.900688 70 1 0 -3.908562 3.972632 -0.624576 71 1 0 -3.736878 2.742062 -1.725493 72 8 0 -2.378416 3.282545 1.270092 73 1 0 -5.522057 0.811508 -0.775008 74 1 0 -4.655736 0.015217 0.546022 75 1 0 -1.375131 3.318334 1.460853 --- Low frequencies --- -3.6722 -1.3118 0.0011 0.0012 0.0014 5.9417 Low frequencies --- 19.3365 28.8707 34.9809 Zero-point correction= 0.624392 (Hartree/Particle) Thermal correction to Energy= 0.664399 Thermal correction to Enthalpy= 0.665343 Thermal correction to Gibbs Free Energy= 0.553988 Sum of electronic and zero-point Energies= -2410.377872 Sum of electronic and thermal Energies= -2410.337865 Sum of electronic and thermal Enthalpies= -2410.336921 Sum of electronic and thermal Free Energies= -2410.448276
E (Cys4)  	Charge = 1 Multiplicity = 1 Standard orientation: --- Center Atomic Atomic Coordinates (Angstroms) Number Number Type X Y Z --- 1 6 0 3.363774 1.719151 0.425304 2 6 0 3.080473 1.679317 -0.966373 3 6 0 3.380747 0.528350 -1.767719 4 6 0 3.891278 -0.644342 -1.178471 5 6 0 4.161387 -0.616242 0.238196 6 6 0 3.947642 0.540836 1.009673 7 44 0 2.039576 0.004021 -0.013067 8 16 0 0.816442 0.325957 2.027637 9 6 0 4.078994 -1.919774 -1.950378 10 6 0 3.101486 2.938032 1.289716 11 6 0 1.890627 3.760240 0.832660 12 16 0 0.083159 0.495145 -1.425919 13 6 0 0.007105 -0.783934 -2.764027 14 6 0 -0.346977 -2.209675 -2.327241 15 7 0 -0.745219 -2.960349 -3.521744 16 44 0 -2.168314 0.511880 -0.680599 17 8 0 -2.409332 -1.378645 -1.279081 18 6 0 -1.415730 -2.270088 -1.226887 19 8 0 -1.401152 -3.156930 -0.384059 20 6 0 -2.365839 2.741660 -0.702361 21 6 0 -3.452146 2.097375 -1.380736 22 6 0 -4.315939 1.167905 -0.716529 23 6 0 -4.036627 0.732095 0.594333 24 6 0 -2.860675 1.279594 1.219680 25 6 0 -2.088174 2.313451 0.618532 26 6 0 -1.502147 3.748987 -1.407691 27 6 0 -4.884134 -0.325388 1.275630 28 6 0 -4.062689 -1.506944 1.820263 29 6 0 -5.724079 0.339525 2.384707 30 8 0 1.525618 -2.147374 0.070817 31 6 0 1.349518 -2.738635 1.141972 32 6 0 0.225412 -2.459738 2.136453 33 6 0 4.380427 3.796694 1.354296

	34 1 0 4.480489 -1.532029 0.726795 35 1 0 4.111128 0.507227 2.081643 36 1 0 2.581688 2.517985 -1.436596 37 1 0 2.886457 2.563734 2.298399 38 1 0 3.112990 0.531061 -2.818977 39 1 0 -5.567981 -0.719885 0.514916 40 1 0 -3.403601 -1.190487 2.636165 41 1 0 -4.742235 -2.259481 2.230738 42 1 0 -3.458190 -1.973298 1.037878 43 1 0 -6.386673 -0.398692 2.845449 44 1 0 -6.340932 1.154182 1.993239 45 1 0 -5.079370 0.748422 3.171046 46 1 0 -5.113297 0.693425 -1.279749 47 1 0 -3.627089 2.325923 -2.427808 48 1 0 -1.196520 2.656569 1.130826 49 1 0 -0.488148 3.748698 -1.003704 50 1 0 -1.444583 3.535378 -2.477904 51 1 0 -1.924238 4.752192 -1.280553 52 1 0 -2.538583 0.895643 2.180443 53 1 0 5.145406 -2.150973 -2.046700 54 1 0 3.595341 -2.748062 -1.424657 55 1 0 3.650356 -1.846327 -2.952475 56 1 0 1.670039 4.537822 1.568975 57 1 0 2.075240 4.262537 -0.123345 58 1 0 1.012567 3.117206 0.731252 59 1 0 4.634589 4.189456 0.363788 60 1 0 4.231474 4.645610 2.027906 61 1 0 5.235542 3.219929 1.720103 62 1 0 -0.742372 -0.413398 -3.469861 63 1 0 0.971572 -0.785369 -3.277250 64 1 0 0.535506 -2.692169 -1.907526 65 1 0 -0.828968 -3.949583 -3.301981 66 1 0 -1.656633 -2.646781 -3.850309 67 8 0 2.145329 -3.720955 1.495889 68 1 0 1.870508 -3.919736 2.436148 69 1 0 -0.555563 -3.173365 1.838465 70 7 0 0.737994 -2.860443 3.452589 71 6 0 -0.377878 -1.057980 2.010643 72 1 0 -0.977675 -1.021370 1.098813 73 1 0 -1.061023 -0.915425 2.853747 74 1 0 1.225804 -2.077764 3.887305 75 1 0 -0.010305 -3.152117 4.072863 --- Low frequencies --- -2.5970 -0.0010 0.0002 0.0009 3.7594 7.7714 Low frequencies --- 21.5046 29.8071 34.6574 Zero-point correction= 0.624567 (Hartree/Particle) Thermal correction to Energy= 0.665150 Thermal correction to Enthalpy= 0.666094 Thermal correction to Gibbs Free Energy= 0.552370 Sum of electronic and zero-point Energies= -2410.373850 Sum of electronic and thermal Energies= -2410.333267 Sum of electronic and thermal Enthalpies= -2410.332323 Sum of electronic and thermal Free Energies= -2410.446047
F (Cys2)	Charge = 1 Multiplicity = 1 Standard orientation: --- Center Atomic Atomic Coordinates (Angstroms) Number Number Type X Y Z --- 1 6 0 2.066277 -1.555137 -2.315782 2 6 0 3.040718 -0.527930 -2.551566 3 6 0 4.042666 -0.216382 -1.576037 4 6 0 4.024779 -0.801886 -0.294579 5 6 0 2.951365 -1.718178 -0.017845 6 6 0 2.048643 -2.149260 -1.031126 7 44 0 1.966808 0.083399 -0.795864 8 8 0 2.359057 1.965527 -0.274706 9 6 0 1.685333 3.083444 -0.001899 10 8 0 2.224374 3.997961 0.593793



11	6	0	5.025011	-0.406593	0.776923
12	6	0	5.848545	-1.637085	1.201959
13	6	0	1.057455	-1.918769	-3.368079
14	16	0	-0.285363	0.574105	-1.328749
15	44	0	-2.093317	0.204063	0.338210
16	6	0	-3.670599	0.018915	-1.313782
17	6	0	-3.436670	1.383016	-0.967799
18	6	0	-3.552020	1.869289	0.364817
19	6	0	-3.929385	0.910780	1.368105
20	6	0	-4.103887	-0.449485	1.047860
21	6	0	-3.948476	-0.927079	-0.304124
22	6	0	-3.310043	3.312676	0.712711
23	6	0	-4.091410	-2.411319	-0.583051
24	6	0	-5.580944	-2.748621	-0.800144
25	6	0	-0.186451	2.391724	-1.631369
26	6	0	0.201086	3.210464	-0.404367
27	7	0	-0.236934	4.596298	-0.582603
28	16	0	-0.889664	0.995391	2.221719
29	6	0	0.603952	-0.023601	2.326967
30	6	0	0.352353	-1.510172	2.631685
31	7	0	1.611758	-2.179667	2.974584
32	6	0	-0.323463	-2.229003	1.478228
33	8	0	-1.116995	-1.754935	0.665665
34	8	0	-0.035061	-3.531405	1.424915
35	6	0	-3.226490	-2.903952	-1.751691
36	6	0	4.351677	0.269876	1.984723
37	1	0	-0.404583	-1.552828	3.437509
38	1	0	-3.973002	1.223652	2.406422
39	1	0	-4.292727	-1.163299	1.843503
40	1	0	-3.511295	-0.297058	-2.336771
41	1	0	-3.755225	-2.928428	0.325451
42	1	0	-3.124123	2.071118	-1.745121
43	1	0	5.705598	0.322766	0.322479
44	1	0	3.655239	-0.417991	2.474051
45	1	0	5.112153	0.556422	2.717067
46	1	0	3.806936	1.165955	1.676425
47	1	0	6.619934	-1.340785	1.918474
48	1	0	6.342095	-2.110347	0.347407
49	1	0	5.212579	-2.386160	1.686969
50	1	0	4.741437	0.588365	-1.782695
51	1	0	3.029413	0.008437	-3.495131
52	1	0	1.268514	-2.858112	-0.781124
53	1	0	0.136467	-2.297264	-2.918091
54	1	0	0.800946	-1.051847	-3.981133
55	1	0	1.470027	-2.694631	-4.022785
56	1	0	2.808190	-2.084490	0.997431
57	1	0	-4.257582	3.863209	0.685416
58	1	0	-2.897378	3.400892	1.721402
59	1	0	-2.611027	3.791226	0.020010
60	1	0	-3.277578	-3.994958	-1.815940
61	1	0	-3.579792	-2.512244	-2.711007
62	1	0	-2.181835	-2.605854	-1.621504
63	1	0	-5.962925	-2.248618	-1.696249
64	1	0	-5.709736	-3.826981	-0.931976
65	1	0	-6.193481	-2.434678	0.050512
66	1	0	0.524733	2.527089	-2.452697
67	1	0	-1.164692	2.722065	-1.983952
68	1	0	-0.348722	2.809517	0.453158
69	1	0	0.087268	5.124522	0.226095
70	1	0	0.257304	5.009800	-1.373064
71	1	0	1.210371	0.391245	3.138159
72	1	0	1.214711	0.060857	1.411458
73	1	0	2.010210	-1.728375	3.793655
74	1	0	1.453572	-3.153453	3.220092
75	1	0	-0.570059	-3.936989	0.719737

Low frequencies --- 0.0004 0.0009 0.0019 1.4989 4.6953 7.8766

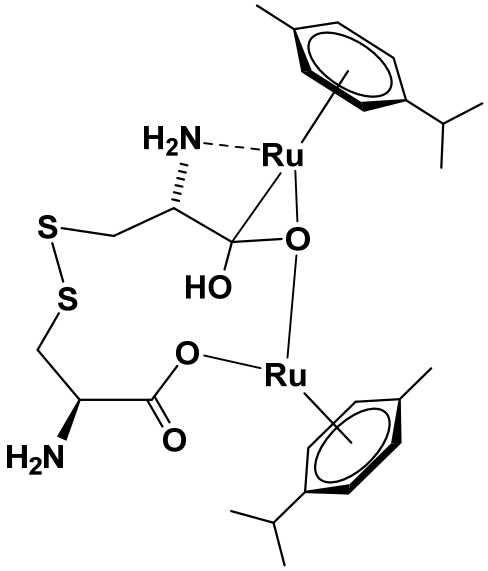
Low frequencies --- 18.0633 19.1549 25.7330

Zero-point correction= 0.624051 (Hartree/Particle)

Thermal correction to Energy= 0.664609

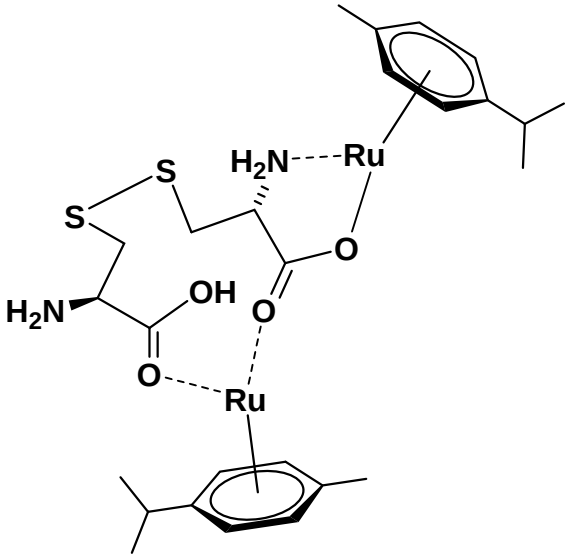
Thermal correction to Enthalpy= 0.665553
Thermal correction to Gibbs Free Energy= 0.551501
Sum of electronic and zero-point Energies= -2410.363853
Sum of electronic and thermal Energies= -2410.323296
Sum of electronic and thermal Enthalpies= -2410.322352
Sum of electronic and thermal Free Energies= -2410.436404

G (oxCys6)



Charge = 1 Multiplicity = 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	1.838865	-1.357150	-0.270396
2	6	0	3.016674	-3.034018	0.584603
3	6	0	3.509642	-2.725696	-0.716891
4	6	0	4.042231	-1.441751	-1.066070
5	6	0	3.951470	-0.379070	-0.151089
6	6	0	3.385282	-0.653216	1.144527
7	6	0	2.956278	-1.951286	1.517570
8	6	0	2.575095	-4.423289	0.961776
9	6	0	4.420376	1.026886	-0.484298
10	6	0	3.933807	1.512222	-1.858269
11	6	0	5.954731	1.111807	-0.366985
12	6	0	-0.088722	-1.285812	0.360831
13	8	0	0.235113	0.001358	-0.083578
14	8	0	-0.521194	-1.376707	1.653559
15	44	0	-0.850943	1.676241	-0.103003
16	6	0	-1.199661	3.112364	-1.727708
17	6	0	-1.989795	3.528633	-0.615011
18	6	0	-1.409087	3.670880	0.664077
19	6	0	-0.008530	3.439122	0.878077
20	6	0	0.805870	3.143805	-0.257995
21	6	0	0.214698	2.951740	-1.526361
22	6	0	-1.832589	2.846857	-3.063793
23	6	0	0.567425	3.523519	2.279496
24	6	0	1.144840	4.936980	2.499649
25	6	0	1.608404	2.433825	2.578274
26	8	0	-2.401121	0.418871	0.366999
27	6	0	-3.614802	0.574311	-0.128392
28	8	0	-3.890851	1.297874	-1.078819
29	6	0	-4.730455	-0.166245	0.626133
30	1	0	-4.946318	0.503457	1.485482
31	7	0	-5.860182	-0.366807	-0.267975
32	1	0	-6.720444	-0.513219	0.249883
33	1	0	-5.969885	0.434685	-0.880963
34	7	0	0.368147	-1.991645	-1.765540
35	1	0	0.200561	-1.275501	-2.470166
36	1	0	0.510046	-2.874262	-2.250860
37	6	0	-0.769026	-2.058039	-0.765383
38	1	0	-1.664611	-1.556362	-1.148935
39	6	0	-1.083072	-3.520844	-0.472965
40	1	0	-3.065303	3.578537	-0.727967
41	1	0	0.825994	2.597200	-2.350263
42	1	0	1.855898	2.912996	-0.125960
43	1	0	-2.047825	3.857231	1.521575
44	1	0	-0.271063	3.383707	2.972905
45	1	0	3.989817	1.690135	0.277765
46	1	0	2.848980	1.396997	-1.949751
47	1	0	4.194351	2.565334	-2.003543
48	1	0	4.398876	0.949024	-2.673579
49	1	0	6.295761	2.137441	-0.537967
50	1	0	6.434243	0.466554	-1.110480
51	1	0	6.297486	0.798391	0.623584
52	1	0	4.427553	-1.280953	-2.065762
53	1	0	3.494674	-3.505448	-1.473359
54	1	0	2.514133	-2.108781	2.496298
55	1	0	1.755064	-4.392289	1.684149
56	1	0	2.245939	-4.987494	0.084762
57	1	0	3.406099	-4.973626	1.418021
58	1	0	3.263624	0.162171	1.848782

	59 1 0 -1.966050 3.795190 -3.598011 60 1 0 -1.202271 2.199087 -3.678669 61 1 0 -2.807535 2.375893 -2.928490 62 1 0 1.885940 2.469932 3.635377 63 1 0 1.218037 1.436526 2.354023 64 1 0 2.525580 2.587300 1.998898 65 1 0 0.392305 5.712217 2.327366 66 1 0 1.507896 5.037150 3.526492 67 1 0 1.986213 5.122352 1.823069 68 1 0 -1.434723 -1.041070 1.674124 69 16 0 -2.482292 -3.881920 0.670723 70 1 0 -1.284877 -4.034741 -1.419236 71 1 0 -0.223365 -4.005076 0.004440 72 6 0 -4.315974 -1.510293 1.220046 73 1 0 -3.402960 -1.434418 1.809788 74 1 0 -5.108267 -1.877259 1.878207 75 16 0 -4.082093 -2.777542 -0.119802 --- Low frequencies --- -6.1012 -4.2446 0.0007 0.0008 0.0012 1.8745 Low frequencies --- 13.4987 18.8828 28.0495 Zero-point correction= 0.623386 (Hartree/Particle) Thermal correction to Energy= 0.663472 Thermal correction to Enthalpy= 0.664416 Thermal correction to Gibbs Free Energy= 0.550645 Sum of electronic and zero-point Energies= -2410.307906 Sum of electronic and thermal Energies= -2410.267821 Sum of electronic and thermal Enthalpies= -2410.266876 Sum of electronic and thermal Free Energies= -2410.380648
H (oxCys2)  	Charge = 1 Multiplicity = 1 Standard orientation: --- Center Atomic Atomic Coordinates (Angstroms) Number Number Type X Y Z --- 1 44 0 2.370714 0.663782 0.667699 2 6 0 3.744162 2.403852 1.241515 3 6 0 4.487975 1.202324 1.045359 4 6 0 4.430599 0.455435 -0.170191 5 6 0 3.581065 0.856314 -1.237246 6 6 0 2.782293 2.022664 -1.017138 7 6 0 2.861301 2.778434 0.187984 8 6 0 3.882321 3.227242 2.492866 9 6 0 3.503191 0.111153 -2.557381 10 6 0 3.567049 -1.415135 -2.404833 11 6 0 4.604490 0.625293 -3.506918 12 8 0 0.303828 0.697331 0.827313 13 6 0 -0.265074 -0.272658 1.467181 14 8 0 -1.502615 -0.333789 1.693988 15 6 0 0.639071 -1.461061 1.757843 16 7 0 2.006273 -0.974217 2.072452 17 44 0 -2.618747 0.389865 0.047700 18 6 0 -3.017652 2.576953 -0.141179 19 6 0 -3.626296 2.051578 1.043043 20 6 0 -4.553542 0.968391 1.010131 21 6 0 -4.858071 0.318808 -0.216561 22 6 0 -4.217440 0.819073 -1.398061 23 6 0 -3.347139 1.943625 -1.375571 24 6 0 -5.794555 -0.856383 -0.284358 25 6 0 -2.072143 3.763032 -0.063316 26 6 0 -0.786392 3.574247 -0.883988 27 6 0 -2.824589 5.043318 -0.478091 28 8 0 -1.914602 -1.356113 -1.010328 29 6 0 -0.827763 -1.715203 -1.473486 30 8 0 0.251762 -0.937527 -1.519087 31 6 0 -0.589189 -3.107351 -2.051033 32 7 0 0.118471 -3.107939 -3.321705 33 1 0 0.997623 -2.603141 -3.253427 34 1 0 -0.435660 -2.685491 -4.060430 35 1 0 -1.579376 -3.548393 -2.199859 36 1 0 0.116980 -0.101068 -1.020990

	37 1 0 2.664034 -1.748769 1.999142 38 1 0 2.052054 -0.641933 3.037029 39 6 0 0.076149 -2.537919 2.681492 40 16 0 0.500045 -4.238915 2.091089 41 1 0 -4.962741 0.585439 1.939832 42 1 0 -4.371073 0.293721 -2.336016 43 1 0 -2.880734 2.270041 -2.298288 44 1 0 -3.336098 2.463458 2.004697 45 1 0 -1.778655 3.863867 0.989068 46 1 0 2.529087 0.358382 -2.999821 47 1 0 2.808642 -1.764067 -1.697867 48 1 0 3.400793 -1.896835 -3.374161 49 1 0 4.547948 -1.749781 -2.051547 50 1 0 4.520794 0.145318 -4.487081 51 1 0 5.597574 0.400386 -3.103437 52 1 0 4.535446 1.707824 -3.649844 53 1 0 5.016151 -0.453037 -0.252939 54 1 0 5.112847 0.833905 1.854202 55 1 0 2.205953 3.634210 0.317217 56 1 0 2.952089 3.751713 2.727019 57 1 0 4.154937 2.605792 3.350265 58 1 0 4.669589 3.980640 2.366148 59 1 0 2.066115 2.322596 -1.776652 60 1 0 -6.804055 -0.519319 -0.548729 61 1 0 -5.471352 -1.572360 -1.044777 62 1 0 -5.850384 -1.374389 0.676123 63 1 0 -0.129839 4.439811 -0.746054 64 1 0 -0.254924 2.674939 -0.563187 65 1 0 -0.996269 3.499703 -1.956775 66 1 0 -3.722183 5.195086 0.128911 67 1 0 -2.180418 5.919997 -0.359085 68 1 0 -3.131560 4.989739 -1.528363 69 1 0 0.739274 -1.888475 0.752594 70 1 0 0.481790 -2.458263 3.696642 71 1 0 -1.009981 -2.451386 2.740012 72 6 0 0.209682 -3.985399 -1.053560 73 1 0 0.474300 -4.902261 -1.583794 74 1 0 1.135164 -3.488032 -0.750214 75 16 0 -0.780521 -4.434705 0.453259 --- Low frequencies --- -3.0528 -1.2633 -0.0007 0.0006 0.0015 4.4401 Low frequencies --- 6.9032 14.7277 25.6349 Zero-point correction= 0.622303 (Hartree/Particle) Thermal correction to Energy= 0.663244 Thermal correction to Enthalpy= 0.664188 Thermal correction to Gibbs Free Energy= 0.546680 Sum of electronic and zero-point Energies= -2410.276564 Sum of electronic and thermal Energies= -2410.235624 Sum of electronic and thermal Enthalpies= -2410.234680 Sum of electronic and thermal Free Energies= -2410.352188