# Supplementary Information

## New insights on the mechanism of Oxidation of D-galacturonic acid by Hypervalent Chromium

Mangiameli, M.F.; González, J.C*.; García, S.I.; Frascaroli, M.I. ; Van Doorslaer, S. ; Salas Peregrin, J.M.; Sala, L.F.

1. Room-temperature CW-EPR spectrum

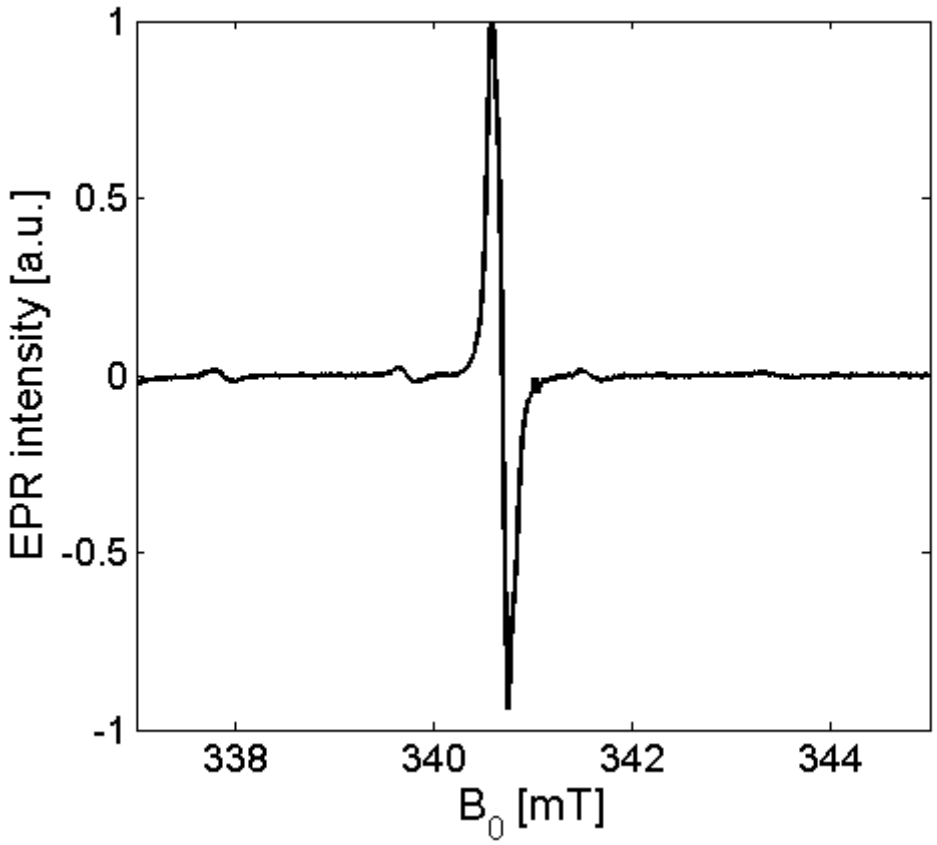



**Figure S1**. Typical room-temperature CW-EPR spectrum of $Cr^{V}$ Galur complexes formed during the oxidation of Galur with $Cr^{VI}$. The spectrum consists of a central signal flanked by four weak signals originating from the $^{53}Cr$ hyperfine interaction ($^{53}Cr$, natural abundance 9.5%). Modulation amplitude is 0.4 mT. $[Cr^{VI}]_0 = [GSH]_0 = 0.67$ mM; $[Galur]_0 = 0.33$ mM; pH =3.

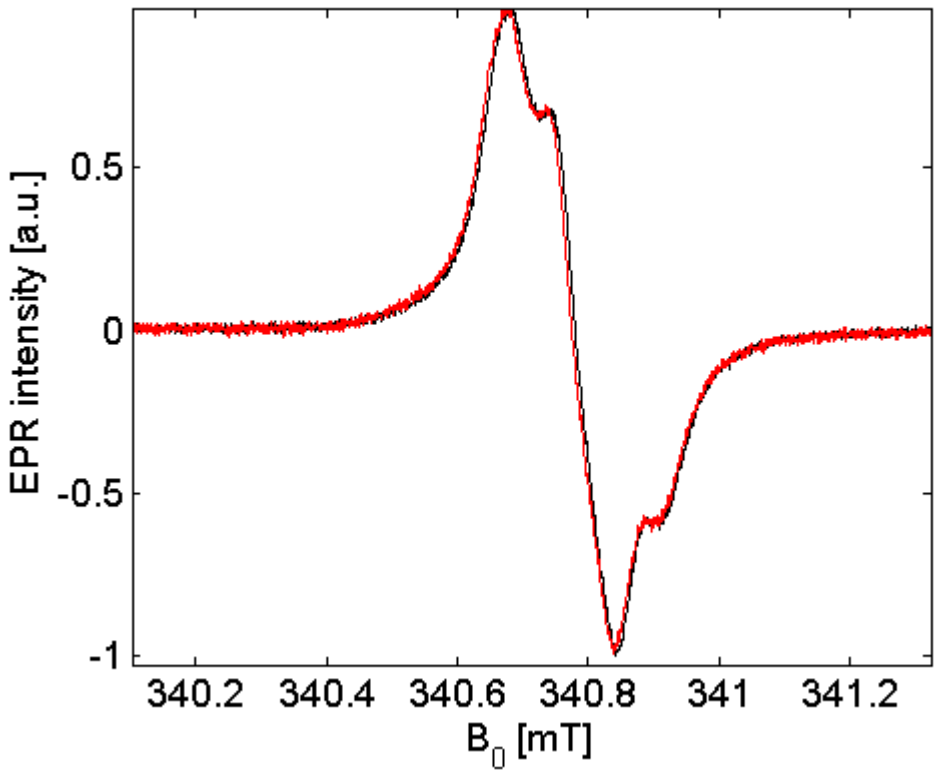


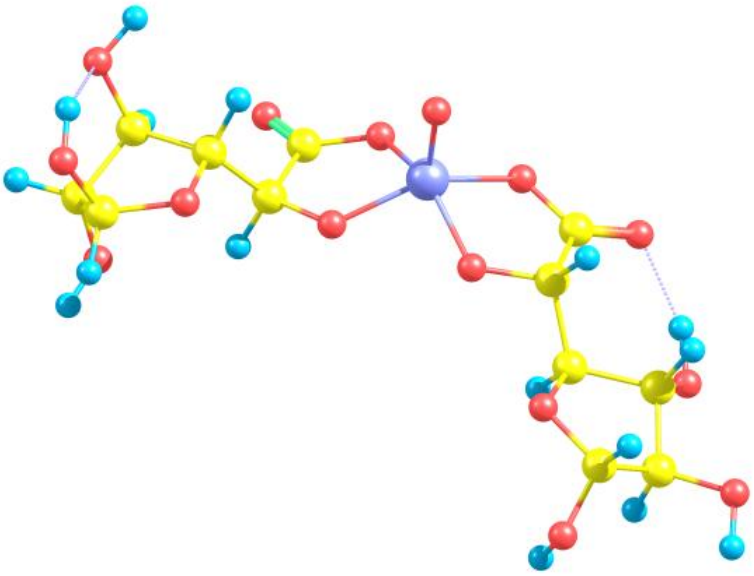

**Figure S2**. Comparison of the room-temperature CW-EPR spectra of the $Cr^{VI}$/Galur mixture at pH 3.0 in $H_2O$ (black) and in $^2H_2O$ (red). Only the central part of the spectrum is shown.$[Cr^{VI}]_0$ = $[GSH]_0$ = 0.67 mM, $[Galur]_0$ = 0.33 mM

2. DFT computations

Coordinates and total energy optimized structures:

**$[Cr^{V}O(O^{6},O^{5}$-galactofuranuronate$)_2]^-$ - structure I**

**Total Energy = -71827.13188 eV**

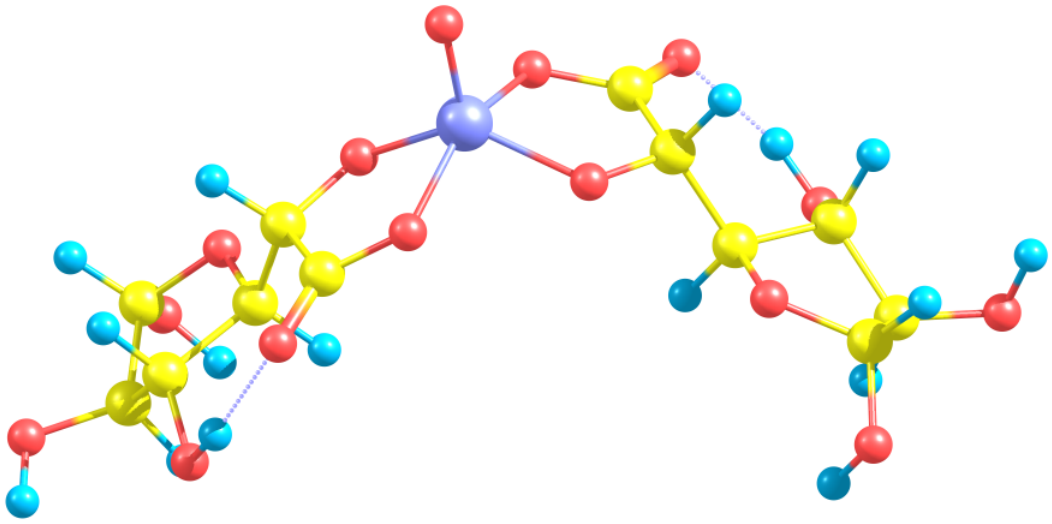


| | | | |
|---|---|---|---|
| H | -2.758510 | 0.244294 | -0.624621 |
| H | 3.386679 | -0.566586 | 1.091619 |
| O | -4.298821 | -3.573716 | -2.837159 |
| O | -4.685058 | 0.007948 | -2.050111 |
| O | -5.254168 | -3.064015 | -0.288453 |
| H | -4.963736 | -3.429862 | 0.571100 |
| C | -3.860382 | -2.253331 | -2.653754 |
| O | 4.894679 | 1.848466 | -2.845840 |
| O | 0.310965 | -2.380475 | 1.635480 |
| O | 2.855781 | 1.277031 | 3.203058 |
| C | -2.630544 | -0.263119 | 1.484441 |
| O | -1.510911 | -0.285164 | 2.197339 |
| C | -2.367444 | -0.590204 | 0.000613 |
| O | -0.975692 | -0.709975 | -0.178455 |
| O | 0.981056 | 0.162908 | 2.684635 |
| C | 2.174778 | 0.629032 | 2.398982 |
| O | 1.491391 | -0.255258 | 0.293496 |
| C | 2.619769 | 0.241348 | 0.972256 |
| Cr | 0.084104 | -0.851287 | 1.298337 |
| O | -3.730723 | -0.007542 | 1.964122 |
| C | 3.270639 | 1.389636 | 0.183570 |
| C | -3.090400 | -1.883721 | -0.452757 |
| C | 4.594074 | 1.930936 | 0.783925 |
| C | 5.292851 | 2.446545 | -0.468632 |
| C | 4.907859 | 1.392598 | -1.527591 |
| O | 3.610254 | 0.905836 | -1.128972 |
| H | 4.812901 | 3.418139 | -0.750759 |
| H | 4.343434 | 2.659097 | -2.880794 |
| H | 5.641193 | 0.554602 | -1.513004 |
| H | 5.195445 | 1.068200 | 1.169567 |
| O | -2.700898 | -2.176043 | -1.810144 |
| C | -4.636000 | -1.782960 | -0.470688 |
| C | -4.916283 | -1.384421 | -1.926684 |
| H | -5.014140 | -1.033210 | 0.255020 |
| H | -4.746285 | 0.239385 | -2.998032 |
| H | -5.946905 | -1.672994 | -2.232192 |
| H | -3.569987 | -1.858848 | -3.649836 |

| | | | |
|---|---|---|---|
| H | -4.698639 | -3.834697 | -1.969705 |
| O | 4.431807 | 2.929694 | 1.760663 |
| O | 6.683824 | 2.589880 | -0.273073 |
| H | 2.539169 | 2.229285 | 0.106071 |
| H | 3.940028 | 2.471773 | 2.493102 |
| H | 7.055998 | 2.974839 | -1.091462 |
| H | -2.764153 | -2.721043 | 0.205324 |

**$[Cr^{V}O(O^{6},O^{5}\text{-galactofuranuronate})_2]^-$ - Structure II**

**Total Energy = -71827.23735 eV**

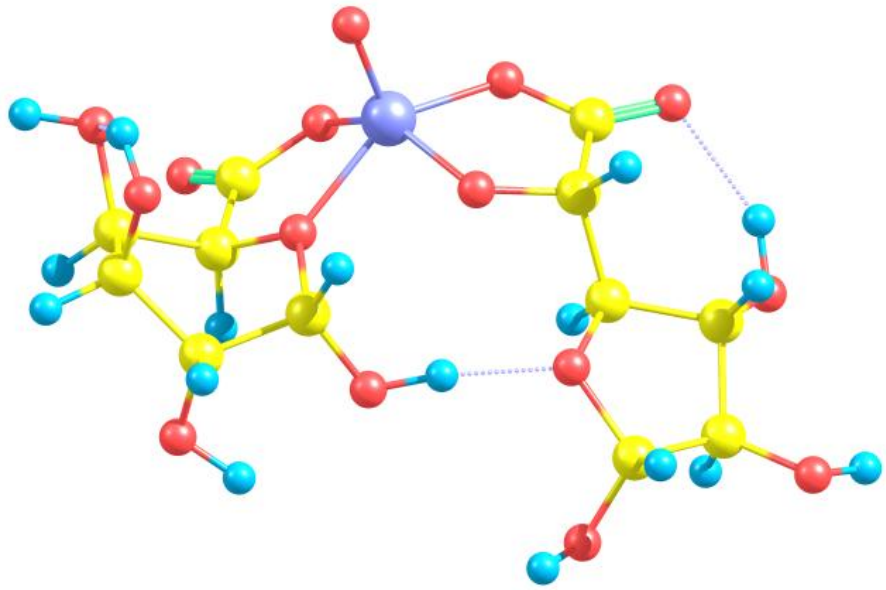


| | | | |
|---|---|---|---|
| H | 1.202239 | 1.196082 | 0.292249 |
| H | 2.361564 | 3.059852 | 2.065712 |
| O | -3.707554 | -0.940116 | 3.492891 |
| C | -5.149968 | -0.881731 | 3.458944 |
| H | 3.531464 | -0.097026 | 1.843139 |
| O | 3.009053 | 0.957365 | -2.924058 |
| O | 1.562681 | -2.783989 | 3.835509 |
| O | 2.182117 | 1.868516 | 3.360015 |
| C | -1.951467 | -2.438151 | 2.789182 |
| O | -0.976651 | -1.577729 | 3.334222 |
| C | -1.294003 | -3.229959 | 1.638892 |
| O | 0.001373 | -3.024809 | 1.573162 |
| O | 1.092718 | -0.072123 | 3.630937 |
| C | 1.893503 | 0.731308 | 2.969782 |
| O | 1.773644 | -1.150115 | 1.502608 |
| C | 2.439062 | 0.080514 | 1.681059 |
| Cr | 0.769200 | -1.817233 | 2.869956 |
| C | 2.286652 | 0.969915 | 0.436541 |
| C | 3.075141 | 2.301801 | 0.462898 |
| C | 3.231984 | 2.567015 | -1.038662 |
| C | 3.458147 | 1.150952 | -1.617788 |
| O | 2.806616 | 0.251452 | -0.697134 |
| O | 2.437201 | 3.365071 | 1.123570 |
| O | 4.197460 | 3.524917 | -1.413238 |
| H | 2.255426 | 2.949441 | -1.414134 |

| | | | |
|---|---|---|---|
| H | 2.083726 | 1.276253 | -2.979681 |
| H | 4.545073 | 0.908672 | -1.645571 |
| H | 4.094316 | 2.100454 | 0.885953 |
| O | -1.897581 | -3.988858 | 0.871801 |
| C | -3.195811 | -1.650031 | 2.351362 |
| C | -5.553933 | -1.557238 | 2.137259 |
| C | -4.386532 | -2.507505 | 1.863330 |
| H | -5.555411 | -1.456519 | 4.320921 |
| O | -5.609817 | 0.423399 | 3.635013 |
| H | -5.549344 | -0.783954 | 1.326958 |
| O | -6.820755 | -2.168996 | 2.263367 |
| O | -4.346739 | -2.900904 | 0.513175 |
| H | -4.499786 | -3.384416 | 2.550233 |
| H | -5.380563 | 0.938472 | 2.832971 |
| H | 5.060208 | 3.241668 | -1.047282 |
| H | -2.272331 | -3.185093 | 3.557447 |
| H | -2.900559 | -0.936010 | 1.544483 |
| H | -3.540108 | -3.477105 | 0.447200 |
| H | -7.032654 | -2.567508 | 1.395808 |

**[$Cr^{V}O(O^{ring},O^{6}$-galactopyranuronate)($O^{5},O^{6}$-galactofuranuronate)] – structure III**

**Total Energy = -71838.60307 eV**



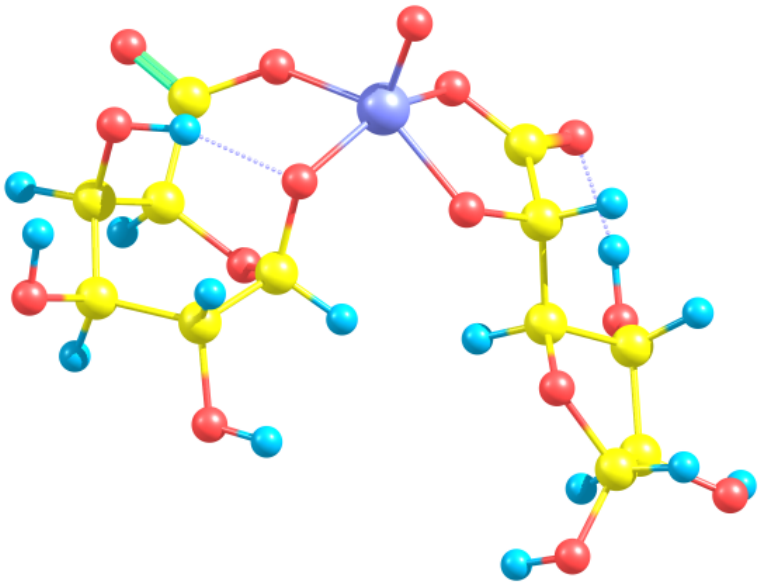
| | | | |
|---|---|---|---|
| H | -4.842822 | -1.655943 | 2.753190 |
| C | -1.169599 | -0.884391 | -0.293064 |
| H | 3.184513 | -1.258151 | 1.293382 |
| O | 2.081815 | 1.741104 | -2.616184 |
| O | -0.337949 | -2.269080 | 3.282198 |
| O | 3.536220 | 0.572941 | 3.387536 |
| C | -2.368401 | 0.737750 | 2.942869 |
| O | -1.191271 | 0.404676 | 3.482644 |
| C | -2.561189 | 0.186976 | 1.529700 |
| O | -1.352978 | -0.544348 | 1.202787 |
| O | 1.387919 | -0.084714 | 3.573859 |

| | | | |
|---|---|---|---|
| C | 2.535183 | 0.053529 | 2.909602 |
| O | 1.133368 | -1.016933 | 1.317481 |
| C | 2.419927 | -0.466385 | 1.466709 |
| Cr | -0.065733 | -0.859414 | 2.655464 |
| O | -3.197294 | 1.428861 | 3.506670 |
| C | 2.620999 | 0.677264 | 0.459771 |
| C | 4.079726 | 1.120714 | 0.244539 |
| C | 3.994089 | 1.748062 | -1.155183 |
| C | 2.928091 | 0.916274 | -1.888088 |
| O | 2.201060 | 0.199808 | -0.831474 |
| O | 4.571298 | 2.041869 | 1.188910 |
| O | 5.196798 | 1.739473 | -1.895512 |
| H | 3.587277 | 2.780678 | -1.033549 |
| H | 1.631382 | 1.201927 | -3.296867 |
| H | 3.394125 | 0.133923 | -2.524414 |
| H | 4.722430 | 0.208713 | 0.169793 |
| H | -2.654864 | 1.028582 | 0.813795 |
| C | -3.772816 | -0.739207 | 1.373128 |
| C | -3.570708 | -1.663646 | 0.112867 |
| C | -2.583428 | -1.059848 | -0.897767 |
| H | -4.668511 | -0.101622 | 1.242965 |
| O | -3.895150 | -1.565244 | 2.530966 |
| H | -0.612627 | -1.835309 | -0.232258 |
| O | -0.526824 | 0.124660 | -0.928777 |
| H | -4.556538 | -1.774851 | -0.396884 |
| O | -3.055616 | -2.915804 | 0.519800 |
| O | -3.107313 | 0.168397 | -1.365185 |
| H | -2.452171 | -1.789995 | -1.732170 |
| H | 0.475552 | 0.043446 | -0.869690 |
| H | -3.309912 | -2.974018 | 1.474903 |
| H | -2.360897 | 0.633646 | -1.803105 |
| H | 2.005736 | 1.556377 | 0.767958 |
| H | 4.525878 | 1.593121 | 2.067206 |
| H | 5.803228 | 2.377127 | -1.469520 |

**[$Cr^{V}O$(*O*$^{1}$,*O*$^{6}$- galactopyranuronate)(*O*$^{6}$,*O*$^{5}$- galactofuranuronate)]$^{-}$ – structure IVa**

***S*-chirality on $C^{1}$ center.**

**Total Energy = -71826.78924 eV**



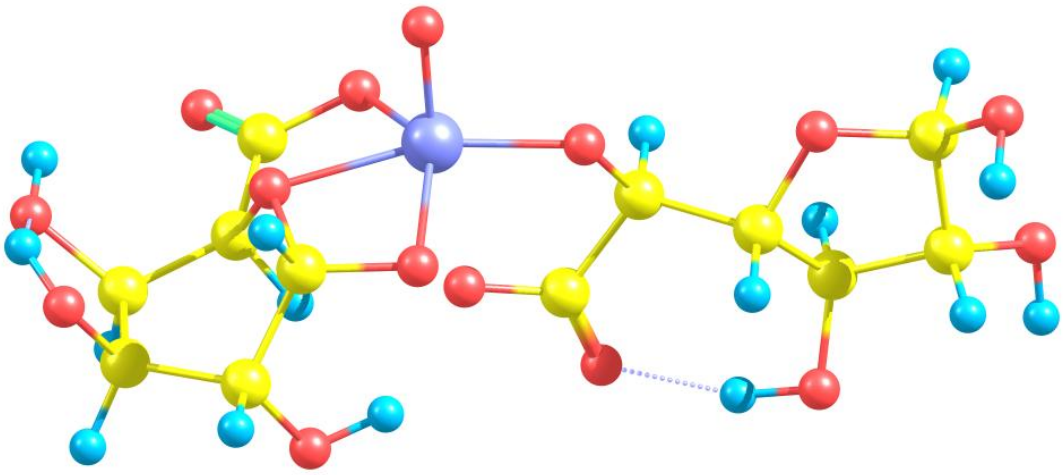
| | | | |
|---|---|---|---|
| O | -1.171500 | -0.515148 | 3.542011 |
| O | -1.635496 | 0.370228 | 0.917425 |
| H | -2.775821 | -2.236410 | 1.832398 |
| C | -1.382923 | -0.879860 | 0.265746 |
| H | 3.355739 | -1.051833 | 1.289356 |
| O | 2.844413 | 0.895833 | -3.209754 |
| O | 0.439548 | -2.801920 | 3.223790 |
| O | 3.223267 | 1.033678 | 3.180482 |
| C | -2.339443 | 0.048952 | 3.298952 |
| C | -2.741117 | 0.326437 | 1.833989 |
| O | 1.337550 | -0.161392 | 3.391468 |
| C | 2.391690 | 0.244017 | 2.720049 |
| O | 1.291241 | -1.151937 | 1.130949 |
| C | 2.458548 | -0.385679 | 1.317023 |
| Cr | 0.153400 | -1.420764 | 2.529805 |
| O | -3.110739 | 0.364103 | 4.203196 |
| C | 2.606270 | 0.662101 | 0.201602 |
| C | 3.930674 | 1.459273 | 0.215161 |
| C | 4.026848 | 1.873362 | -1.254769 |
| C | 3.488476 | 0.638828 | -1.999707 |
| O | 2.607235 | -0.018326 | -1.063629 |
| O | 3.966952 | 2.575821 | 1.070875 |
| O | 5.322892 | 2.197710 | -1.712896 |
| H | 3.311697 | 2.721410 | -1.408401 |
| H | 2.160366 | 1.579758 | -3.050792 |
| H | 4.326148 | -0.048723 | -2.251795 |
| H | 4.771935 | 0.749492 | 0.419817 |
| H | -3.174931 | 1.346978 | 1.822301 |
| C | -3.857980 | -0.675135 | 1.424276 |
| C | -3.917457 | -0.811042 | -0.105987 |
| C | -2.558058 | -1.294283 | -0.666373 |
| H | -4.825514 | -0.275383 | 1.787411 |
| O | -3.722100 | -1.974477 | 2.007032 |
| O | -1.147309 | -1.869526 | 1.227038 |
| H | -0.470949 | -0.696982 | -0.344787 |
| H | -4.112677 | 0.185400 | -0.556953 |
| O | -4.988821 | -1.666530 | -0.475138 |
| O | -2.409880 | -0.726981 | -1.961450 |
| H | -2.567223 | -2.407074 | -0.712084 |
| H | -4.936146 | -2.411082 | 0.165296 |

| | | | |
|---|---|---|---|
| H | -1.697956 | -1.213772 | -2.421403 |
| H | 1.745354 | 1.371028 | 0.266312 |
| H | 3.865740 | 2.196973 | 1.982686 |
| H | 5.608058 | 2.994877 | -1.223529 |

**[$Cr^{V}O(O^{1},O^{6}$- galactopyranuronate)($O^{6},O^{5}$- galactofuranuronate)]$^{-}$ – structure IVb**

***R*-chirality on $C^{1}$ center.**

**Total Energy = -71825.34647 eV**



| | | | |
|---|---|---|---|
| O | -2.171265 | -1.779966 | 1.140035 |
| H | -4.087216 | -1.858749 | 3.801036 |
| C | -2.461024 | -1.430282 | -0.266889 |
| H | 2.619227 | -0.002669 | 1.608528 |
| O | 5.902482 | -0.390183 | -2.033730 |
| O | 0.101919 | -3.177740 | 0.746240 |
| O | 1.133298 | 2.385308 | 1.122516 |
| C | -1.510191 | -1.159695 | 3.271123 |
| O | -0.318321 | -1.487102 | 2.800697 |
| C | -2.471276 | -0.762211 | 2.147229 |
| O | -0.220078 | 0.585661 | 1.116157 |
| C | 0.915492 | 1.161366 | 0.980389 |
| O | 1.466248 | -1.057287 | 0.248440 |
| C | 2.053292 | 0.148906 | 0.653628 |
| Cr | -0.174707 | -1.617212 | 0.814641 |
| O | -1.813043 | -1.142102 | 4.464365 |
| C | 3.052203 | 0.630334 | -0.409609 |
| C | 3.884423 | 1.876309 | -0.027688 |
| C | 5.113231 | 1.684366 | -0.918371 |
| C | 5.332385 | 0.162678 | -0.885570 |
| O | 4.033423 | -0.404501 | -0.618339 |
| O | 3.264977 | 3.115949 | -0.251343 |
| O | 6.280826 | 2.361462 | -0.499462 |
| H | 4.818462 | 1.979047 | -1.958164 |
| H | 5.395955 | -0.070779 | -2.809846 |
| H | 6.023702 | -0.105600 | -0.055812 |
| H | 4.222709 | 1.761072 | 1.035010 |
| H | -2.103711 | 0.219303 | 1.783230 |
| C | -3.971461 | -0.623638 | 2.287349 |
| C | -4.585246 | -0.595085 | 0.823061 |

| | | | |
|---|---|---|---|
| C | -3.530444 | -0.315985 | -0.294738 |
| H | -4.171609 | 0.350785 | 2.784199 |
| O | -4.606503 | -1.686725 | 2.986936 |
| H | -2.862620 | -2.366739 | -0.710048 |
| O | -1.202902 | -1.084047 | -0.734337 |
| H | -5.336842 | 0.226638 | 0.780399 |
| O | -5.185636 | -1.843680 | 0.526796 |
| O | -2.957513 | 0.971414 | -0.142085 |
| H | -4.067376 | -0.397378 | -1.268592 |
| H | -5.228695 | -2.311124 | 1.396280 |
| H | -1.991115 | 0.868135 | -0.315300 |
| H | 2.494868 | 0.836567 | -1.355476 |
| H | 2.430142 | 3.059567 | 0.301596 |
| H | 6.084528 | 3.318610 | -0.541479 |

Principal g values and dominant $^{1}H$ and $^{53}Cr$ couplings for non-exchangeable protons in structures IVa and IVb:

## a) Structure IVa

g tensor

$g_1$=-1.9755, $g_2$=1.9854, $g_z$=1.9854

Carbinolic proton on galactofuranuronate side

$A_1$=-5.93 MHz, $A_2$=0.13 MHz, $A_z$=-6.33 MHz, $\mathbf{a_{iso}}$ **= -4.04 MHz**

H on $C^1$ of galactopyranuronate

$A_1$=6.96 MHz, $A_2$=15.58 MHz, $A_z$=6.18 MHz, $\mathbf{a_{iso}}$ **= 9.57 MHz**

Cr

$A_1$=13.63 MHz, $A_2$=19.88 MHz, $A_z$=97.28 MHz, $\mathbf{a_{iso}}$ **= 43.60 MHz**

## b) Structure IVb

g tensor

$g_1$=-1.9755, $g_2$=1.9854, $g_z$=1.9854

Carbinolic proton on galactofuranuronate side

$A_1$=20.18 MHz, $A_2$=12.84 MHz, $A_z$=12.42 MHz, $\mathbf{a_{iso}}$ **= 15.15 MHz**

H on $C^1$ of galactopyranuronate

$A_1$=-4.39 MHz, $A_2$=3.20 MHz, $A_z$=-4.73 MHz, $\mathbf{a_{iso}}$ **= -1.97 MHz**

Cr

$A_1$=26.38 MHz, $A_2$=10.54 MHz, $A_z$=93.15 MHz, $\mathbf{a_{iso}}$ **= 43.36 MHz**

Table S1. Observed pseudo-first-order rate constant, $k_4$, for different [$HClO_4$] and [Galur].[a]

| [$HClO_4$]/M | 0.10 | 0.15 | 0.20 | 0.25 | 0.30 |
|---|---|---|---|---|---|
| $10^3 \times$[Galur]/M | $10^2\ k_4$[b]/$s^{-1}$ | | | | |
| 1.0 | 3.9 ± 0.20 | 3.0 ± 0.10 | 2.5 ± 0.12 | 2.3 ± 0.11 | 2.0 ± 0.10 |
| 1.5 | 5.8 ± 0.30 | 4.6 ± 0.23 | 4.0 ± 0.20 | 3.4 ± 0.17 | 3.0 ± 0.15 |
| 2.0 | 8.0 ± 0.40 | 6.0 ± 0.30 | 5.1 ± 0.25 | 4.5 ± 0.22 | 3.8 ± 0.19 |
| 3.0 | 12 ± 0.60 | 8.9 ± 0.44 | 7.4 ± 0.37 | 6.6 ± 0.33 | 6.1 ± 0.30 |
| 4.0 | 15± 0.70 | 11 ± 0.55 | 9.8 ± 0.49 | 8.6 ± 0.43 | 8.0 ± 0.40 |

[a]$T$ = 15°C; [$Cr^{IV}$]$_0$= 0.075 mM; $I$ = 1.0 M [b]Mean values from multiple determinations.

Table S2: Observed pseudo-first-order rate constants ($k_6$ and $k_5$) for different [$HClO_4$] and [Galur][a]

| [$HClO_4$]/M | 0.20 | 0.40 | 0.63 | 0.80 | 0.97 |
|---|---|---|---|---|---|
| 10×[galur]/M | $10^3\ k_6/s^{-1}$ [b] | | | | |
| 0.48 | 0.092 ± 0.010 | 0.20 ± 0.020 | 0.52 ± 0.050 | 1.0 ± 0.10 | 1.6 ± 0.20 |
| 0.96 | 0.18 ± 0.020 | 0.47 ± 0.050 | 1.1 ± 0.10 | 2.3 ± 0.20 | 3.4 ± 0.30 |
| 1.44 | 0.27± 0.030 | 0.78 ± 0.080 | 1.9 ± 0.20 | 3.6 ± 0.40 | 5.4 ± 0.50 |
| 1.92 | 0.40± 0.040 | 1.0 ± 0.10 | 2.6 ± 0.30 | 4.6 ± 0.50 | 7.1 ± 0.70 |
| 2.40 | 0.50± 0.050 | 1.2 ± 0.10 | 3.1 ± 0.30 | 5.8 ± 0.60 | 8.7 ± 0.90 |
| 3.00 | 0.54± 0.050 | 1.5 ± 0.10 | 4.0 ± 0.40 | 7.0 ± 0.70 | 10 ± 1.0 |
| 3.60 | - | - | - | 8.4 ± 0.80 | 12 ± 1.0 |
| | $10^3\ k_5/s^{-1}$ [b] | | | | |
| 0.48 | 0.26 ± 0.030 | 0.39 ± 0.040 | 0.55 ± 0.060 | 0.77 ± 0.080 | 0.95 ± 0.010 |
| 0.96 | 0.52 ± 0.050 | 0.73 ± 0.070 | 1.1 ± 0.10 | 1.5 ± 0.10 | 1.8 ± 0.20 |
| 1.44 | 0.74 ± 0.070 | 1.1 ± 0.10 | 1.6 ± 0.20 | 2.3 ± 0.20 | 2.8 ± 0.30 |
| 1.92 | 0.94 ± 0.090 | 1.4 ± 0.20 | 2.0 ± 0.20 | 3.0 ± 0.30 | 3.6 ± 0.30 |
| 2.40 | 1.1 ± 0.10 | 1.7 ± 0.20 | 2.6 ± 0.30 | 3.6 ± 0.40 | 4.5 ± 0.40 |
| 3.00 | 1.4 ± 0.20 | 2.2 ± 0.20 | 3.2 ± 0.30 | 4.5 ± 0.50 | 5.8 ± 0.60 |
| 3.60 | - | - | - | 5.4± 0.50 | 7.0 ± 0.70 |

[a] T = 33 °C; $[Cr^{VI}]_0 = 6 \times 10^{-4}$ M; I = 1.0 M. [b] Mean values from multiple determinations.