# The EPR Pattern of [CrO(*cis*-1,2-cyclopentanediolato)$_2$]$^-$ and [CrO(*trans*-1,2-cyclopentanediolato)$_2$]$^-$

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The addition of a large excess of 1,2-cyclopentanediol to a 1:1 mixture of glutathione and $Cr^{VI}$ at pH 7.5 stabilises the intermediate $Cr^V$ species formed by the one-electron reduction of $Cr^{VI}$ by glutathione. The isotropic EPR parameters ($g_{iso}$ and $A_{iso}$) of the $Cr^V$ species formed with both *cis*- and *trans*-1,2-cyclopentanediol correspond to those calculated for five-coordinate oxo-$Cr^V$ complexes with four alcoholato donors [Cr(O)(1,2-cyclopentanediolato)$_2$]$^-$. The five-coordinate oxo-$Cr^V$ species formed with both 1,2-cyclopentanediol isomers show very similar EPR superhyperfine patterns, but differ in their stability and the conditions required for their formation due to the different chelation ability of the *cis*- vs. *trans*-1,2-diolato moiety.

## Introduction

$Cr^V$ intermediates are generated in the oxidation of a number of organic substrates by $Cr^{VI}$ and are possibly linked to the formation of Cr-induced cancers.[1−2] The biological reduction of $Cr^{VI}$ to lower states has been observed with a wide variety of naturally occurring cellular reductants.[3−7] Ligands that possess two oxygen atoms able to form five-membered rings about the metal ion are effective as nonenzymatic reductants and complexation agents towards hypervalent chromium and can stabilise the labile oxidation states of chromium.[8−14] Thus, it is becoming more apparent that diol ligands may play an important role in the stabilisation of $Cr^V$ species formed during the reaction of $Cr^{VI}$ with intracellular reductants. In particular, $Cr^V$-sugar species are very stable at physiological pH values and remain in solution for between several days and several months after the initiation of the reaction.[15−24]

The most common means of characterising $Cr^V$ complexes in solution is EPR spectroscopy, where strong isotropic signals are observed at room temperature in the X-band spectra. An empirical relationship between the nature and the number of donor groups and the EPR spectral parameters of $Cr^V$ complexes has been established.[25] Five-coordinate $Cr^V$ species show higher $g_{iso}$ and lower $^{53}Cr$ $A_{iso}$ values than the corresponding six-coordinate species.[25−27] Thus, the assignment of the structures of new oxo-$Cr^V$ species in solution may be made according to the isotropic EPR parameters ($g_{iso}$ and $A_{iso}$ values) and the superhyperfine (shf) pattern of the signal.

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It has been found that the multiplicity of the EPR signal of $Cr^V$-diolato complexes is dependent upon whether the ligand is cyclically strained or not. It was observed that in $Cr^V$-diolato complexes formed with linear diols all the protons are equivalent in the isotropic EPR spectra,[28] but the strain of a six-membered ring imparts inequivalence to the magnetic environment of the protons in the second coordination sphere.[29] Thus, the signals in the EPR spectra of [CrO(*cis*-1,2-cyclohexanediolato)$_2$]$^-$ and [CrO(*trans*-1,2-cyclohexanediolato)$_2$]$^-$ exhibit a triplet and a singlet, respectively, and the difference was explained by arguing that only when the protons lie in the $Cr^V$-ligand plane is there a maximal overlap between the proton orbital and the $Cr^V$ orbital containing the unpaired electron density.[29]

In the present work we study the $Cr^V$-diolato complexes formed by reduction of $Cr^{VI}$ by glutathione (GSH) in the presence of *cis*- or *trans*-1,2-cyclopentanediol in order to extend the analysis of the EPR shf pattern to $Cr^V$-diolato species formed between $Cr^V$ and five-membered ring 1,2-diols. Our results show that [CrO(*cis*-1,2-cyclopentanediolato)$_2$]$^-$ and [CrO(*trans*-1,2-cyclopentanediolato)$_2$]$^-$ yield EPR signals of the same multiplicity, with similar shf coupling constants — an EPR pattern markedly different from that observed for $Cr^V$ complexes formed from *cis*- and *trans*-1,2-cyclohexanediol. Thus, the present results should be useful for the interpretation of the EPR spectra of the $Cr^V$ species formed in the reduction of $Cr^{VI}$ by biologically relevant substrates containing a five-membered 1,2-diolate ring.

## Results

The reaction of $Cr^{VI}$ with GSH (4.5 mM; 1:1 ratio) at pH = 7.5 affords three intermediate $Cr^V$ species with EPR signals at $g_{iso}$ = 1.9859, 1.9771 and 1.9719 [Figure 1(a)] and

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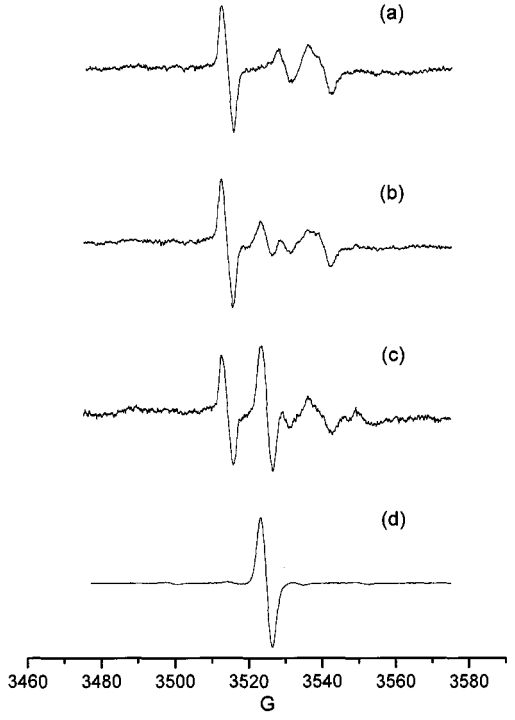



Figure 1. X-band EPR spectra of mixtures of: (a) GSH/$Cr^{VI}$ = 1:1, [$Cr^{VI}$] = 4.5 mM; (b) GSH/$Cr^{VI}$/*trans*-diol= 1:1:100, [$Cr^{VI}$] = 4.5 mM; (c) GSH/$Cr^{VI}$/*trans*-diol = 1:1:500, [$Cr^{VI}$] = 1.0 mM; (d) GSH/$Cr^{VI}$/*trans*-diol = 1:1:5000, [$Cr^{VI}$] = 1.0 mM; T = 25 °C, pH = 7.5, t = 10 min., frequency = 9.7667 GHz. mod. ampl. = 4 G

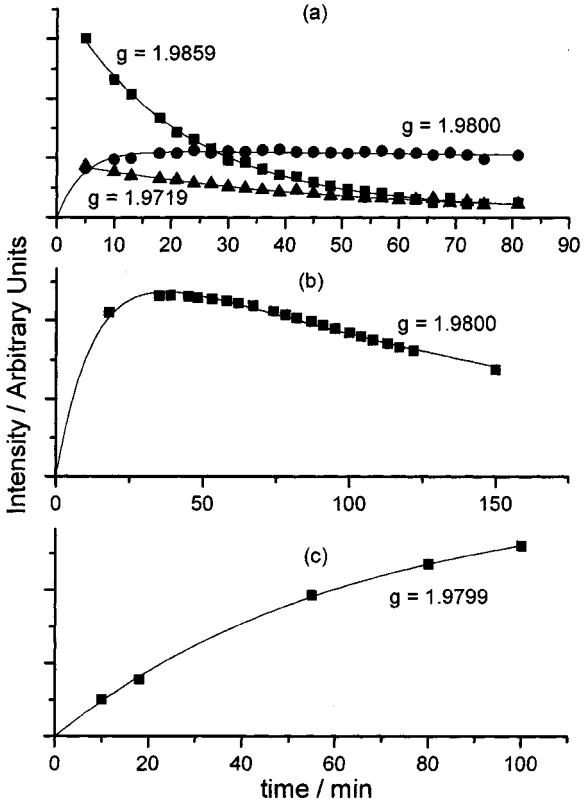



Figure 2. Time dependence of the EPR signal intensities; conditions: (a) GSH/$Cr^{VI}$/*trans*-diol = 1:1:100, [$Cr^{VI}$] = 4.5 mM; (b) GSH/$Cr^{VI}$/*trans*-diol = 1:1:5000, [$Cr^{VI}$] = 1.0 mM; (c) GSH/$Cr^{VI}$/*cis*-diol = 1:1:10000, [$Cr^{VI}$] = 0.5 mM. T = 25 °C, pH = 7.5

relative intensity 2.7:0.68:1, five minutes after the initiation of the reaction. The first signal decays twice as fast as the other two and they are no longer observed after 80 min. The same kinetic behaviour is observed for equimolar $Cr^{VI}$/GSH mixtures down to 0.5 mM.

When the same reaction is performed in the presence of a 100-fold excess of 1,2-*trans*-cyclopentanediol, the three signals attributed to the $Cr^{V}$-GSH intermediate species again decay with time and disappear 80 min. after mixing, while a fourth signal appears at $g_{iso}$ = 1.9800 [Figure 1(b)]. This new signal reaches its maximum intensity 30 min. after mixing and decays slowly. The time-dependent variation of the intensity of this signal together with those corresponding to the decay of the $Cr^{V}$-GSH species at $g_{iso}$ = 1.9859 and 1.9719 are shown in Figure 2(a).

In the presence of a 500-fold excess of *trans*-1,2-cyclopentanediol over the GSH/$Cr^{VI}$ mixture, the EPR spectra are immediately dominated by the $Cr^{V}$ signal at $g_{iso}$ = 1.9800 [Figure 1(c)]. Under these conditions, this signal partially resolves into its components when the modulation amplitude is reduced to 0.4 G.

When the reaction is followed using a much larger *trans*-1,2-cyclopentanediol/$Cr^{VI}$ ratio (5000:1), only the signal at $g_{iso}$ = 1.9800 is observed [Figure 1(d)]. Under these conditions, this signal reaches its maximum intensity 40 min. after mixing and then decays slowly; the time-dependent trace shown in Figure 2(b). In this case, when the modulation amplitude is lowered to 0.4 G, the shf splitting of the signal resolves.

In the presence of excess *cis*-1,2-cyclopentanediol, a 100:1:1 diol/$Cr^{VI}$/GSH ratio is enough to afford a $Cr^{V}$ signal at $g_{iso}$ = 1.9799 as the only EPR feature in the spectrum. In this case a 500-fold excess of *cis*-1.2-cyclopentanediol is not enough to resolve the EPR signal [Figure 3(a)], but when a much larger excess (5000−10000:1:1 diol/$Cr^{VI}$/GSH) is used the multiplet resolves well [Figure 3(b)]. Under the last conditions, the rate of decay of the $Cr^{V}$ signal is extremely slow and the signal intensity increases continuously for several hours [Figure 2(c)].

## Discussion

It is well known that five-membered $Cr^{V}$ chelates are the most stable and that the $CrO^{3+}$ ion shows a marked preference for binding to *cis*- rather than *trans*-diol groups of cyclic diols.[15,21−24,30−32] Several observations confirm the expected higher ability of the *cis* vs. the *trans* isomer of 1,2-cyclopentanediol for binding $Cr^{V}$: the receiver gain required to observe the $Cr^{V}$-diolato signal is 1000 times higher for the *trans* than for the *cis* isomer; the excess of diol needed for the complete replacement of GSH in the $Cr^{V}$ coordination sphere is much larger for the *trans* (5000:1) than for the *cis* (100:1) isomer; under the same experimental conditions, the rate of decay of the $Cr^{V}$ signal is much faster for the *trans* than for the *cis* isomer of 1,2-cyclopentanediol.

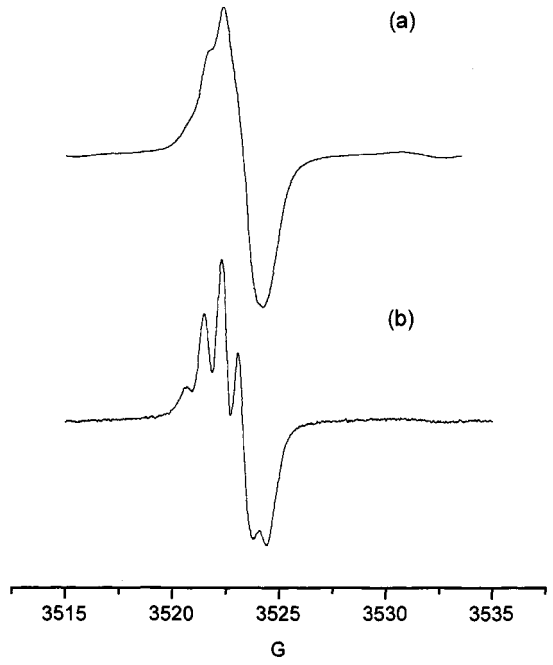



Figure 3. X-band EPR spectra of mixtures of: (a) GSH/Cr$^{VI}$/*cis*-diol = 1:1:500, [Cr$^{VI}$] = 1.0 mM; (b) GSH/Cr$^{VI}$/*cis*-diol = 1:1:10000, [Cr$^{VI}$] = 0.5 mM; T = 25 °C, pH = 7.5, t = 15 min., frequency = 9.7634 GHz. mod. ampl. = 0.04 G

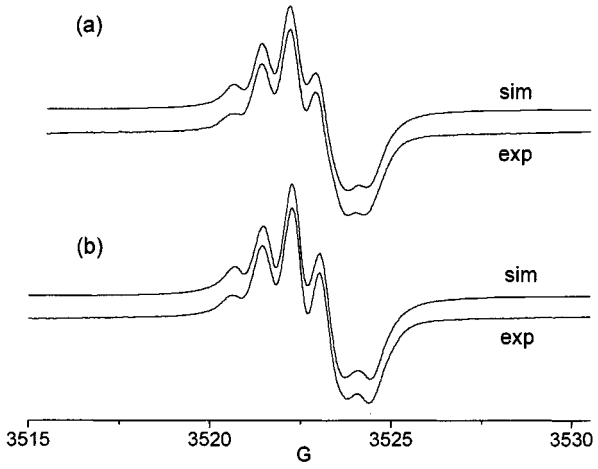



Figure 4. Experimental and simulated X-band EPR spectra of mixtures of: (a) GSH/Cr$^{VI}$/*trans*-diol = 1:1:5000, [Cr$^{VI}$] = 1.0 mM, frequency = 9.7620 GHz., mod. ampl. = 0.4 G; (b) GSH/Cr$^{VI}$/*cis*-diol = 1:1:5000, [Cr$^{VI}$] = 0.5 mM, frequency = 9.7634 GHz., mod. ampl. = 0.4 G

We used the isotropic EPR parameters $g_{iso}$ and $A_{iso}$ to estimate the coordination number and the nature of the donor groups of the Cr$^V$ species formed in the reaction of Cr$^{VI}$ with GSH in the presence of either excess *cis* or *trans* 1,2-cyclopentanediol, according to a described empirical method.[25−27] The EPR spectra were found to be composed of two Cr$^V$ species (the signals were deconvoluted by fitting the spectra by Lorentzian derivatives). The best fit of the whole set of EPR spectra of Cr$^V$ species formed with either the *cis* or *trans* isomer and different diol-to-Cr$^{VI}$ ratios affords the spectral parameters listed in Table 1; the goodness-of-fit is shown in Figure 4. The spectral parameters for each Cr$^V$ species listed in Table 1 are consistent within all simulation, with maximum deviations in the $g_{iso}$ and $^1$H $a_{iso}$ values being ±0.0001 units and ±0.02 × 10$^{-4}$ cm$^{-1}$, respectively. When setting all equivalent protons or pairs of equivalent protons to fit spectra, the spectral parameters were not consistent for all the simulated spectra even when some individual spectra showed a good correlation.

The $g_{iso}$ and $A_{iso}$ values of the Cr$^V$ species formed with the two isomers correspond to those calculated for five-coordinate oxo-Cr$^V$ complexes with four alcoholato donors.[25] In the presence of a large excess of either *cis*- or *trans*-1,2-cyclopentanediol, the EPR signal is a composite of two oxo-Cr$^V$-(diolato)$_2$ species with four (two from each chelate ring) and three carbinolic protons coupled to the Cr$^V$ electronic spin, respectively (Table 1). In our simulations, we included values for $^1$H $a_{iso}$ only where the $^1$H $a_{iso}$ value is greater than the line width (LW) of the Cr$^V$ species, since the signal is not significantly affected when the $^1$H $a_{iso}$ value is ≤ LW. Thus, the fourth carbinolic proton of the second component should be very weakly coupled to the Cr$^V$ electronic spin resulting in a $^1$H $a_{iso}$ < LW. The values of $^1$H $a_{iso}$ of 0.41 × 10$^{-4}$ and 0.47 × 10$^{-4}$ cm$^{-1}$ found for the second component of the EPR signals are just inside the lower simulation limit.

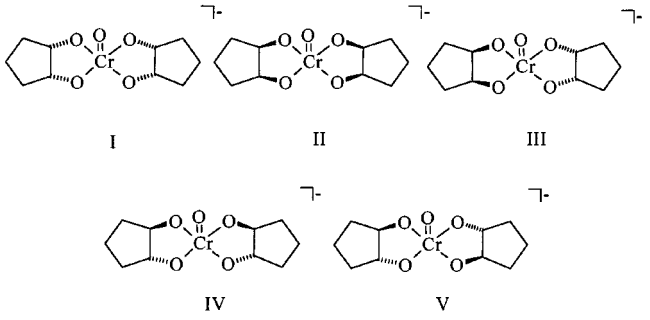
For the two protons lying in the Cr$^V$-ligand plane in [CrO(*cis*-1,2-cyclohexanediolato)$_2$]$^-$, the observed $^1$H$_{eq}$ $a_{iso}$ is approximately 0.9 × 10$^{-4}$ cm$^{-1}$.[29] Measurements of isotropic and anisotropic $^1$H ENDOR spectra of a series of oxo-Cr$^V$-diolato$_2$ complexes formed with linear diols showed that the shf coupling constants $^1$H$_{eq}$ $a_{iso}$ and $^1$H$_{ax}$ $a_{iso}$ are equal to 0.81 and 0.37 × 10$^{-4}$ cm$^{-1}$, respectively.[33] This gives us an idea of the values of $^1$H $a_{iso}$ corresponding

Table 1. EPR spectral parameters

| Cr$^V$ species | $g_{iso}$ | $^{53}$Cr $A_{iso}$/10$^4$ cm$^{-1}$ | $a_H$/10$^4$cm$^{-1}$ |
|---|---|---|---|
| [Cr(O)(*cis*-1,2-cyclopentanediolato)$_2$]$^-$ | 1.9803 | 15.9 | 0.84, 0.81,0.74, 0.64 |
| | 1.9798 | | 0.76, 0.65, 0.41 |
| [Cr(O)(*trans*-1,2-cyclopentanediolato)$_2$]$^-$ | 1.9804 | 15.9 | 0.84, 0.76, 0.72, 0.62 |
| | 1.9799 | | 0.75, 0.64, 0.47 |

to the maximal and minimal overlap between the proton orbital and the $Cr^V$ orbital containing the unpaired electron density in oxo-$Cr^V$-diolato$_2$ systems. Accordingly, in the present case, for the $Cr^V$ species at $g_{iso}$ = 1.9798/9 it is possible to differentiate two carbinolic protons with shf coupling constants intermediate between those corresponding to "pseudo-axial" and "pseudo-equatorial" protons, and two carbinolic protons close to the "pseudo-axial" orientation. While for the $Cr^V$ species at $g_{iso}$ = 1.9803/4, two carbinolic protons lie near the $Cr^V$-ligand plane and the two others form larger angles with the $Cr^V$-ligand plane.

The two components can be attributed to two geometric isomers of the $[Cr^V(O)(diolato)_2]^-$ moiety (Scheme 1).[29] Three different geometric isomers (I−III) are possible for $[Cr^V(O)(cis\text{-}1,2\text{-cyclopentanediolato})_2]^-$, whereas only two (IV−V) can exist for $[Cr^V(O)(trans\text{-}1,2\text{-cyclopentanediolato})_2]^-$. However, in both cases only two species are required to simulate the EPR signal. It seems reasonable to assume that the angles between the carbinolic protons and the $Cr^V$-ligand plane in two of the geometric isomers of $[Cr^V(O)(cis\text{-}1,2\text{-cyclopentanediolato})_2]^-$ are very similar, so we cannot distinguish between them (this should be the case for isomers I and II).




Scheme 1

For the largest diol/$Cr^{VI}$ ratio used in this work the $g_{quint}$/$g_{quart}$ ratios are 1:1.5 and 1:2.3 for $Cr^V$ species formed with the *cis* and *trans* isomers, respectively, and are independent of the reaction time.

The shf EPR pattern observed for the $[Cr^V(O)(diolato)_2]^-$ species formed with *cis*- and *trans*-1,2-cyclopentanediol is clearly different from that reported for oxo-$Cr^V$-(diolato)$_2$ species formed with *cis*- and *trans*-1,2-cyclohexanediol. In the case of 1,2-cyclohexanediol, the *trans* isomer affords a singlet, while the *cis* isomer affords two triplets corresponding to two geometric isomers of $[Cr^V(O)(cis\text{-}1,2\text{-cyclohexanediolato})_2]^-$, each with two equivalent $H_{eq}$ coupled to the $Cr^V$ electronic spin. It seems evident that the $[Cr^V(O)(1,2\text{-cyclohexanediolato})_2]^-$ system differentiates the axially and equatorially disposed carbinolic protons, and, consequently, the resulting shf coupling corresponds to the maximal and minimal values expected for the $^1H$ coupled to the $Cr^V$ electronic spin.

The situation is different for the oxo-$Cr^V$-(diolato)$_2$ species formed with *cis*- and *trans*-1,2-cyclopentanediol. The EPR spectra of $[Cr^V(O)(1,2\text{-cyclopentanediolato})_2]^-$ formed with both the *cis* and *trans* isomers show the same EPR spectral pattern corresponding to two $Cr^V$ components split by nonequivalent carbinolic protons coupled to the $Cr^V$ electronic spin: one $Cr^V$ component with two "pseudo-equatorial" protons [$^1H$ $a_{iso}$ = 0.84, 0.81 × $10^{-4}$ $cm^{-1}$ (*cis*-diolate) and 0.84, 0.76 × $10^{-4}$ $cm^{-1}$ (*trans*-diolate)] and two protons disposed at angles in between the "pseudo-axial/equatorial" orientations, and a second $Cr^V$ species with two "pseudo-axial" protons [$^1H$ $a_{iso}$ = 0.41, < LW (*cis*-diolate) and 0.47, < LW (*trans*-diolate)], and two protons protruding at intermediate angles. Thus, the strained bi-cycle arising from the two fused five-membered rings in $[Cr^V(O)(1,2\text{-cyclopentanediolato})_2]^-$ yields isotropic EPR spectra corresponding to the average conformations of two geometric isomers in which all the carbinolic protons are inequivalent.

## Conclusions

Our results show that, as expected, *cis*-1,2-cyclopentanediol possesses a higher ability for binding $Cr^V$ than *trans*-1,2-cyclopentanediol, and that the EPR spectra of $Cr^V$-(diolato)$_2$ species formed with either the *trans* or *cis* isomer of 1,2-cyclopentanediol exhibit a very similar EPR pattern. For both the *cis* and *trans* isomers, the EPR signal is a composite of two oxo-$Cr^V$-(diolato)$_2$ species split by four and three (the fourth $^1H$ $a_{iso}$ is less than the line width) carbinolic protons coupled to the electronic spin, respectively. This new information on the spectral pattern of the EPR signal of $Cr^V$ chelates formed with the *cis* and *trans* isomers of five-membered ring 1,2-diols should be useful in the interpretation of the EPR spectra of the $Cr^V$ species formed in the reduction of $Cr^{VI}$ by NAD(P)H[4] and nucleotides[34] by $Cr^V$ binding to the *cis*-1,2-diolato moiety of the ribose ring and confirm the previous interpretation of the EPR spectra of $Cr^V$-furanosic sugar species.[21]

## Experimental Section

**Materials:** *cis*-1,2-Cyclopentanediol (Aldrich grade), *trans*-1,2-cyclopentanediol (Aldrich grade), sodium dichromate (Mallinckrodt) and GSH (Sigma grade) were used without further purification. Water was purified by deionisation, followed by double distillation from a potassium permanganate solution. The pH of the solutions was adjusted by addition of 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES).

**Warning:** Chromic acids are toxic and carcinogenic.

**Methods: EPR Measurements:** The EPR spectra were performed on a Bruker ESP 300 E spectrometer. The microwave frequency was generated with a Bruker 04 ER (9−10 GHz) and measured with a Racal−Dana frequency meter. The magnetic field was measured with a Bruker NMR probe gaussmeter. All of the EPR experiments were carried out at room temperature. In a typical experiment, 10μL of an aqueous solution of $Cr^{VI}$ (0.1 M) was added to a mixture of 10μL GSH (0.1 M), 0.5030 g diol and 1 mL HEPES (0.1 M) and immediately transferred to a flat quartz cell. The EPR spectra were simulated with a program for the automatic computer simulation of EPR spectra,[35] using 100% Lorentzian lineshapes.

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