



*Dedicated to Professor Ionel Haiduc  
on the occasion of his 75<sup>th</sup> anniversary*

## KINETICS OF REDUCTION OF COBALAMIN BY SULFOXYLATE IN AQUEOUS SOLUTIONS

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The kinetics of individual stages of reductive interaction of hydroxocobalamin with sulfoxylate in aqueous solutions, (Co(III)→Co(II) and Co(II)→Co(I)), have been investigated spectrophotometrically. The rate-limiting step in both reactions is the formation of intermediate complexes of sulfoxylate with Cbl(III) and Cbl(II), respectively. It is shown that Cbl(I) is capable of reducing the sulfur dioxide anion-radical SO<sub>2</sub><sup>-</sup> – a product of one-electron oxidation of sulfoxylate. Computational density functional theory (DFT) data are shown in an attempt to explore the feasibility of such a complex.

### INTRODUCTION

Super-reduced cobalamin, Cbl(I), may be obtained via two-electron reduction of the stable Co(III) form (Cbl(III)) (vitamin B<sub>12</sub>) or by a one-electron reduction of the Cbl(II) form. Cbl(I) plays an important role in processes occurring in the human body, as intermediates in the catalytic cycle of methionine synthase.<sup>1,2</sup> Cbl(I) exhibits extremely strong nucleophilic properties (its nucleophilicity by Swain-Scott is  $\approx 10.7$ )<sup>3</sup>, so it is often called a supernucleophile. The interaction of Cbl(I) with halogenated alkanes<sup>4,5</sup> (including polyhalogenated compounds),<sup>6-8</sup> N<sub>2</sub>O,<sup>9</sup> NO, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>,<sup>10-12</sup> sucralose<sup>13</sup>, oxiranes (epoxides)<sup>14</sup> has been studied. For the reduction of Cbl(III) or Cbl(II) to Cbl(I) one can use zinc,<sup>15</sup> Ti(III) citrate,<sup>2</sup> sodium borohydride.<sup>13</sup> We have found, however, that the interaction of hydroxocobalamin HOCbl(III) with a known sulfur-containing

reducing agent – sodium dithionite – does not result in reduction to Cbl(I), but rather to a six-coordinated Cbl(II) with the anion-radical SO<sub>2</sub><sup>-</sup> (the product of monomerization of the dimeric structure of dithionite, S<sub>2</sub>O<sub>4</sub><sup>2-</sup>).<sup>16</sup> It was previously shown that highly reduced forms of tetrapyrrole metal complexes can be obtained using as reducing another sulfur compound – thiourea dioxide (NH<sub>2</sub>)<sub>2</sub>CSO<sub>2</sub> (TDO).<sup>17-20</sup> However, the kinetics of interaction of the reactive product of its decomposition in aqueous solutions – sulfoxylate SO<sub>2</sub>H<sup>-</sup> (SO<sub>2</sub><sup>2-</sup>) – with cobalamin has not been studied. In this paper we investigate the interaction of sulfoxylate with hydroxocobalamin HOCbl(III).

### MATERIALS AND METHODS

**Materials.** Hydroxocobalamin hydrochloride (HOCbl,  $\geq 98$  %), thiourea dioxide, ascorbic acid (AA), sodium dithionite (85 %), and sodium sulfite

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were from Sigma-Aldrich and were used without further purification. Distilled water was used for the preparation of solutions. Argon was used in all anaerobic procedures.

**Instrumentation.** All kinetic studies were carried out under anaerobic conditions in the UV and visible regions of the spectrum on a spectrophotometer Specord M40, equipped with a water thermostat LT 100 ( $\pm 0.1$  °C), in a sealed quartz cell with a 1 cm optical path length. Investigations on the kinetics of fast reactions were performed on a SX 18MV stopped-flow spectrophotometer, Applied Photophysics.

**Kinetic measurements.** Sulfoxylate solutions  $\text{SO}_2\text{H}^-$  ( $\text{SO}_2^{2-}$ ) were prepared by dissolving TDO in 0,1 M NaOH under anaerobic conditions and incubating for 4 hours.<sup>21</sup> The use of aged solutions of TDO allows to remove an influence of rate-limiting stage of decomposition of TDO and study reactions between different forms of cobalamins and sulfoxylate directly. It is established that the only nitrogen-containing breakdown product of TDO in highly alkaline environments – urea<sup>22</sup> – does not affect the rates of the processes studied in here. Kinetic measurements on the reduction of Cbl(III)OH to Cbl(II) were performed by following the decrease in absorbance at 535 nm, corresponding to an absorption maximum of the initial form of hydroxocobalamin. The kinetics of formation of Cbl(I) cobalamin were monitored using the increase in absorbance at 387 nm, which corresponds to the absorption maximum of Cbl(I). In the presence of dithionite the kinetics of Cbl(I) were monitored by the decrease in absorbance at 460 nm. The reduction of cobalamin was only studied under alkaline conditions, as in acidic media Cbl(I) is known to react with  $\text{H}^+$ ;<sup>4</sup> furthermore, acidic media decrease the stability of sulfoxylate.<sup>23</sup>

**Computations.** The models consisted of corrin rings without any lateral substituents, ligated axially as indicated in text; the  $\text{B}_{12}$ -derived axial base ligand was modeled as a benzimidazole. Models were subjected to full geometry optimizations unless otherwise specified. Geometries were optimized for each spin state without any geometrical constraints, with the BP86 functional, which uses the gradient-corrected exchange functional proposed by Becke, the correlation functional by Perdew, and the 6-31G\*\*, as implemented in Spartan.<sup>24</sup> For the SCF calculations, a fine grid was used, and the convergence criteria were set to  $10^{-6}$  (for the root-mean square of electron density) and  $10^{-8}$  (energy), respectively. For geometry optimization, convergence criteria were set to 0.001 au (maximum gradient criterion) and 0.0003 (maximum

displacement criterion). Charges and spin densities were derived from Mulliken population analyses after DFT geometry optimization.

## RESULTS AND DISCUSSION

It was found that the reduction of hydroxocobalamin by sulfoxylate (Sulf) is a two-stage process. In the first stage, a rapid reduction of the original form of HOCbl(III) to Cbl(II) is seen. The color of the solution changes from red to yellow, and the electronic absorption spectrum develops absorption maxima at 385 and 452 nm (Fig. 1).

The spectrum of the product formed at the end of the first stage of reduction with sulfoxylate differs from that of the well-known pentacoordinated Co(II) cobalamin ( $\text{B}_{12r}$ ) obtainable for example using ascorbic acid. Instead, this new spectrum corresponds to the one measured for the hexacoordinated complex of Cbl(II) with the anion-radical  $\text{SO}_2^-$ , which was previously described in the interaction of hydroxocobalamin with dithionite.<sup>16</sup>

The kinetics of the first stage of reduction of hydroxocobalamin with excess sulfoxylate can be described as first order (Fig. 2 (a)). In this work we obtained the values of the observed rate constants in the temperature range 5...35 °C (Fig. 2 (b)).

The plots shown in Fig. 2 (b) show that the reaction order is 1 with respect to sulfoxylate. From the temperature dependence of this first part of reduction the following Eyring activation parameters were calculated:  $\Delta H^\ddagger_1 = 42 \pm 2$  kJ/mol;  $\Delta S^\ddagger_1 = -41 \pm 2$  J/(mol·K).

The second stage of the reduction proceeds much more slowly than the first. The electronic spectrum develops absorption maxima at 387, 455, 548, 685 nm (Fig. 1), and the color of the solution changes from yellow to light gray. According to the literature,<sup>15</sup> this spectrum corresponds to Cbl(I) ( $\text{B}_{12s}$ ). Though Cbl(III) could undergo self-reduction in strongly alkaline solutions<sup>25,26</sup> this reaction proceeds much slower than reduction by sulfoxylate in 0.1 M NaOH. A typical kinetic curve for the accumulation of Cbl(I) is shown in Fig. 3 (a). Its linearization in the coordinates  $\ln(A_\infty - A)$  versus time ( $A_\infty$  – final absorbance at a given wavelength) indicates a first-order reaction with respect to cobalamin. The kinetic curves display lag times, distinctly longer than the first stage of reduction which occurred within a few seconds. The observed rate constant for the reduction of  $\text{B}_{12r-s}$  to  $\text{B}_{12s}$  is linearly dependent on the concentration of sulfoxylate (Fig. 3 (b)). At low concentrations of sulfoxylate ( $\leq 2.5 \cdot 10^{-4}$  M) Cbl(I) is not obtained.

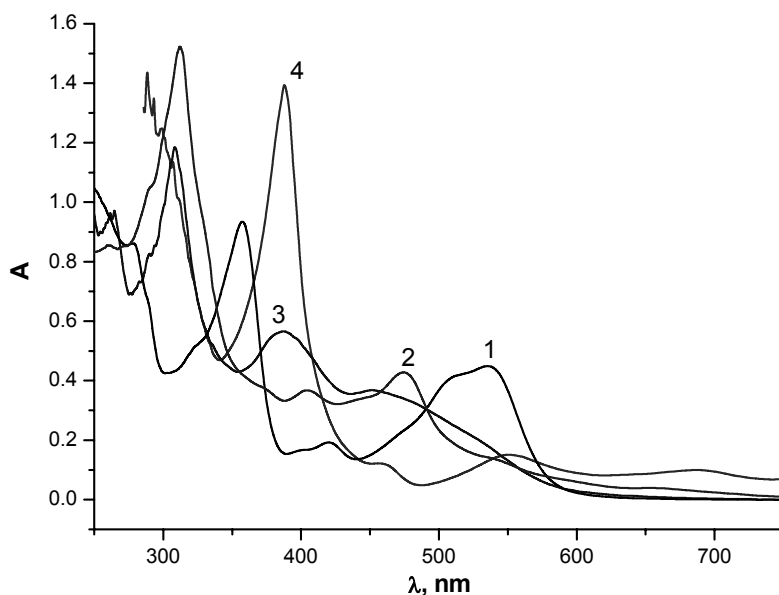


Fig. 1 – UV-vis spectra of the various forms of Cbl: 1 – HO-Cbl(III); 2 – Cbl(II), obtained by reduction with ascorbic acid (AA); 3 – Cbl(II), obtained by reduction with sulfhydryl; 4 – Cbl(I). [Cbl] =  $5 \cdot 10^{-5}$  M, [AA] =  $5 \cdot 10^{-3}$  M, [Sulf] =  $[\text{SO}_2^{2-}] + [\text{SO}_2\text{H}^-] = 5 \cdot 10^{-3}$  M, 0.1 M NaOH, 25 °C, anaerobic conditions.

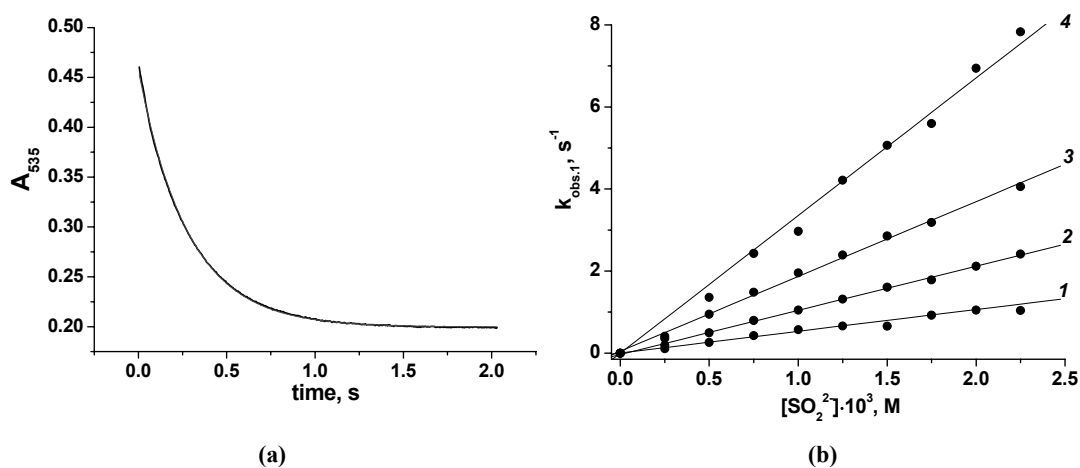


Fig. 2 – A typical kinetic curve of the reduction of HO-Cbl(III) by sulfhydryl ( $2.25 \cdot 10^{-3}$  M) at 25 °C (a) and the dependence of the observed rate constants on [Sulf] at different temperatures, °C: 1 – 5; 2 – 15; 3 – 25; 4 – 35 (b). Conditions: [Cbl] =  $5 \cdot 10^{-5}$  M; 0.1 M NaOH.

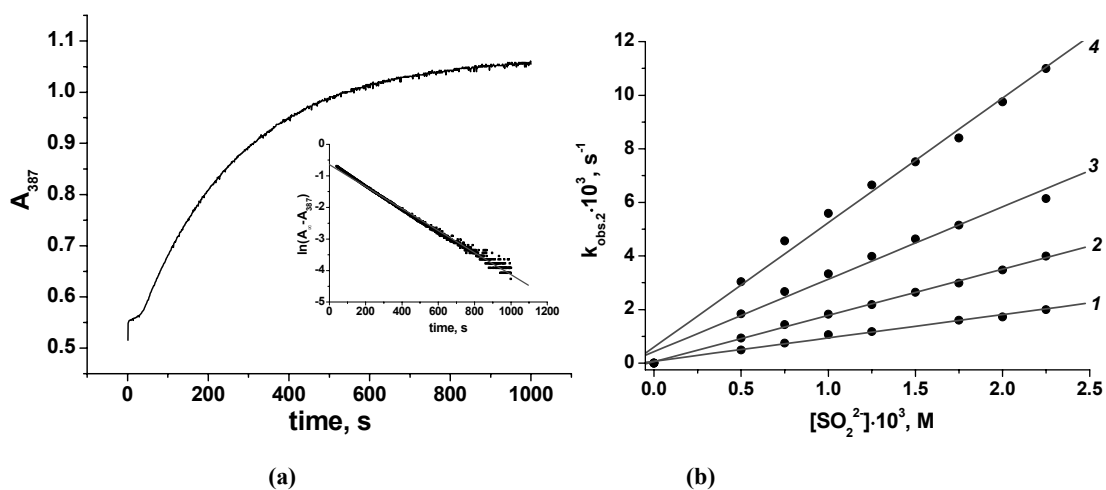


Fig. 3 – A typical kinetic curve for the reduction of B<sub>12r-s</sub> by sulfhydryl ( $1 \cdot 10^{-3}$  M) at 25 °C (a) and the dependence of the observed rate constants for the reduction of B<sub>12r-s</sub> on [Sulf] at °C: 1 – 5; 2 – 15; 3 – 25; 4 – 35 (b). Conditions: [Cbl] =  $5 \cdot 10^{-5}$  M; 0.1 M NaOH.

Addition of 0.05 M  $S_2O_4^{2-}$  to a solution of Cbl(I) leads to a rapid change of color of the solution from gray to yellow, and spectrum is identical with the spectrum of 3 in Fig. 1. Increasing the concentration of added dithionite reduces the degree of reduction of Cbl(II) to Cbl(I)

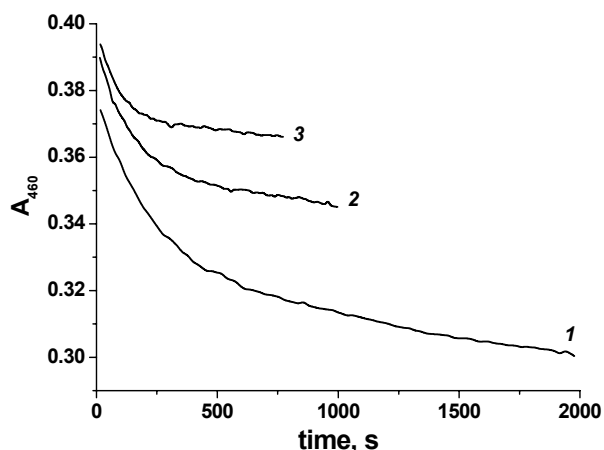
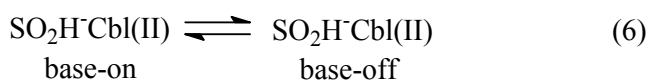
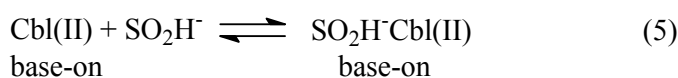
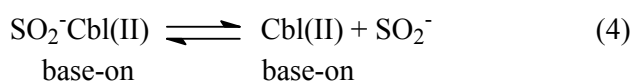
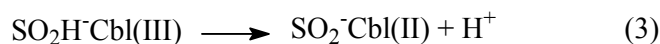
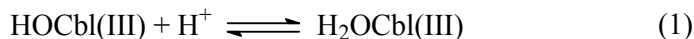


Fig. 4 – Kinetic curves of the reduction of  $B_{12r-s}$  by sulfoxylate in the presence of varying concentrations of  $S_2O_4^{2-}$ : 1.7 (1), 3.3 (2), 5 (3) mM. Conditions:  $[Cbl] = 5 \cdot 10^{-5}$  M,  $[Sulf] = 1 \cdot 10^{-3}$  M, 0.1 M NaOH, 25 °C.

It can be assumed that the introduction of dithionite leads to oxidation of Cbl(I) to Cbl(II), and that the oxidizer is actually dithionite or radical anion  $SO_2^-$ , since sulfite, present as contaminant in commercial dithionite, does not oxidize Cbl(I) at concentrations up to 0.1 M (0.1 M NaOH). The induction period on the kinetic curves for the reduction of  $B_{12r-s}$  with sulfoxylate (Fig. 3 (a)) is proposed to be due to the occurrence of a redox cycle involving Cbl(I), Cbl(II),  $SO_2H^-$  ( $SO_2^{2-}$ )



(Fig. 4). At higher concentrations of dithionite ( $[S_2O_4^{2-}] > 0.05$  M) Cbl(I) is no longer observed. The dependence of the observed rate constant for the second stage ( $k_{obs,2}$ ) on  $[Sulf]$  in the presence of  $S_2O_4^{2-}$  clearly intersects the y-axis (Fig. 5), indicating that a reversible process is involved.

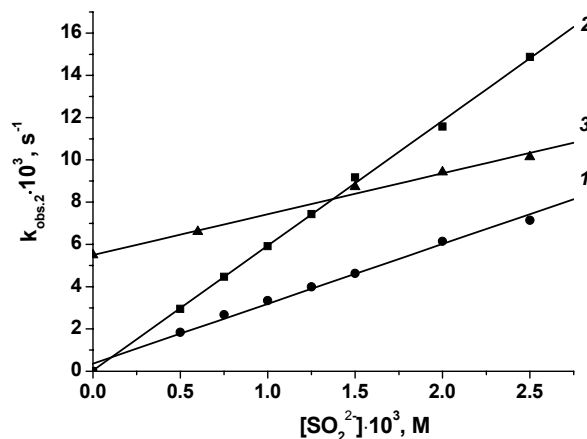
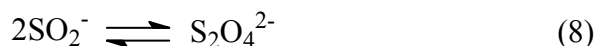
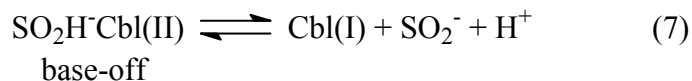


Fig. 5 – Dependence of  $k_{obs,2}$  on  $[Sulf]$  for the accumulation of Cbl(I) during the reaction between sulfoxylate and  $B_{12r-s}$ , as obtained after the first stage of reduction of Cbl(III)OH, (1),  $B_{12r}$ , obtained by the use of ascorbic acid, (2), and  $B_{12r-s}$  in the presence of 3.3 mM  $S_2O_4^{2-}$  (3). Conditions:  $[Cbl] = 5 \cdot 10^{-5}$  M, 0.1 M NaOH, 25 °C.

and  $SO_2^-$ . It is important to note that upon addition of dithionite to a solution of Cbl(I), obtained by reduction of Cbl(III) with sodium borohydride,  $B_{12r-s}$  is formed. The reduction of  $B_{12r-s}$  to  $B_{12s}$  is characterized by the following activation parameters:  $\Delta H^\ddagger_2 = 37 \pm 2$  kJ/mol,  $\Delta S^\ddagger_2 = -114 \pm 2$  J/(mol·K).

Based on the above data we can propose the following scheme of reactions occurring during the production of Cbl(I) ( $B_{12s}$ ) from Cbl(III):



In this scheme terms “base-on” and “base-off” mean complexes with or without bound Co-dimethylbenzimidazole, respectively. The negative entropies of activation for both steps of the reduction show that the overall rates are being determined by the reactions of formation of intermediate complexes 2 and 5 which proceeds more slowly than any other reactions. These are associative processes, including some inherent sterical impediments – especially in the case of 2. Obviously, the intermediate complex with sulfoxylate is less stable than the complex with the sulfur dioxide anion-radical, and cannot be observed in the spectra. According to data of Liptak and Brunold,<sup>15</sup> the conversion of 5-coordinate Cbl(II) to 4-coordinate Cbl(I) is energetically accessible via formation of a 4-coordinate Cbl(II) intermediate, but not a 5-coordinate Cbl(I) intermediate. Consequently, removal of  $\text{SO}_2^-$  should proceed simultaneously with inner-sphere electron transfer from sulfoxylate to Co(II). On the contrary, the back reaction – oxidation of Cbl(I) by the sulfur dioxide anion-radical should proceed as an outer-sphere process. Thus, oxidation of Cbl(I) could be a very convenient example for study of Marcus model. Surprisingly, this possibility is considered very rarely, with a report by Balasubramanian and Gould<sup>11</sup> worth mentioning as an exception. However, oxidation of Cbl(I) in the presence of thiourea dioxide (sulfoxylate) is complicated by formation of the complex between Cbl(II) and  $\text{SO}_2^-$ . It should be also noted that with an excess of sulfoxylate and in the absence of added dithionite the oxidation reaction of Cbl(I) can be neglected. These interpretations are also supported by the fact that the absorption maxima corresponding to Cbl(I) are independent of the method for producing this superreduced cobalamin (using excess borohydride or sulfoxylate).

Density functional calculations were undertaken in order to explore possible structures for the newly-detected  $\text{B}_{12r-s}$  species, cf. Fig. 6. While the experimental data suggests a six-coordinate metal in this form of cobalamin, Fig. 6 also lists some 5- and 4-coordinate structures which mostly serve as references. The possibility of dithionite/sulfoxylate-derived ligands binding to

reduced  $\text{B}_{12}$  forms is examined – with ligands  $\text{SO}_2^{2-}$ ,  $\text{SO}_2$ ,  $\text{SO}_2\text{H}^-$  and  $\text{SO}_3\text{H}^-$ ; hydroxide, amino and aqua ligands are also considered. Attempts to model a Co(II) base-on center with a sulfoxylate  $\text{SO}_2^{2-}$  ligand failed to yield a stable minimum, as the base dissociated from the metal. On the other hand, a protonated sulfoxylate did lead to a stable base-on six-coordinate complex; interestingly, the spin density in this complex was located almost mostly on the macrocycle, cf. Fig. 6. Another structure considered was the base-on Co(II)-hydroxo. While this was found to be a local minimum, the spin density was, as in the case of the Co(II)-sulfoxylate base-on adduct, found to be localized mainly on the macrocycle. By contrast, the Co(II)-aqua base-on model featured cobalt-localized spin density quite similar to what was seen for the reference 5-coordinate base-on Co(II) model. Last but not least, an adduct of sulfur dioxide,  $\text{SO}_2$ , was examined; this species features an electronic structure reasonably close to that of the base-off.

The unusual electronic structures seen in the hydroxide- and sulfoxylate-bound Co(II) base-on models are to our knowledge without precedent for cobalamin and with no experimental proof to support them. The common element in these structures appears to be the strongly-interacting axial ligands. One may raise the question, whether sulfoxylate or hydroxide alone are responsible for this phenomenon. Fig. 6 shows that hydroxide alone in a base-off model does not lead to any unusual structure. Thus, strong axial ligation per se, and not the particular identity of the hydroxide ligand, are responsible for the unusual electronic structure in the base-on Co(II)-hydroxide model. On the other hand, sulfoxylate, but not its protonated version or sulfur dioxide, does in fact induce delocalization of the spin density from the cobalt onto the macrocycle in a base-off Co(II) model, as shown in Fig. 6. This last structure deserves further attention, as it may also be interpreted to arise from reaction of base-off Co(I) with dithionite in the form of  $\text{SO}_2^-$  radicals. While a base-off 5-coordinated form of this nature is not expected to be stable at the high pH values employed in our work, previously known data do show a remarkable species resulted from dithionite

treatment of B<sub>12</sub> under acidic conditions. This species features an unusual EPR spectrum, very different from typical B<sub>12</sub> forms, with less cobalt-like features. Previous computational studies have examined 4-coordinate Co(II) as well as 5-coordinate Co(II)-aqua or Co(II)-base-on comparatively, asserting that the total absence of an axial ligand would indeed be responsible for the drastic change in EPR spectrum, from a cobalt-like one to a distinctly more isotropic one. Our computational data now shows an alternative explanation for the unusual EPR spectrum of dithionite-treated B<sub>12</sub> under acidic conditions: a strongly-interacting ligand, such as SO<sub>2</sub><sup>-</sup>, would actually induce a drastic qualitative change in electronic structure, much more dramatic than those seen upon going from aqua base-off to four-coordinate Co(II). While Brunold and co-workers<sup>27</sup> have shown with theoretical methods that in principle the latter two structures (which with their methods are described very similarly to what is shown in Fig. 6) are different enough to yield dramatically different EPR spectra, the alternative proposed here by us may deserve further attention in the future. It may be noted that other sulfur ligands besides SO<sub>2</sub><sup>-</sup>, such as sulfite or SO<sub>2</sub>, also delocalize a large amount of spin density in the 5-coordinated models of Fig. 6, and may be

expected to exhibit interesting EPR properties by comparison with typical B<sub>12</sub> adducts.

To conclude, we have shown here experimental data according to which the intermediate reaction product of hydroxocobalamin with the two sulfur-containing reducing agents – sulfoxylate and dithionite – is the relatively stable six-coordinated complex B<sub>12r-s</sub>. This complex is the final product of the interaction of cobalamin and dithionite. In case of the sulfoxylate further reduction occurs from B<sub>12r-s</sub> to form B<sub>12s</sub>. Some considerations on the possible electronic structure of reduced cobalamins were made based on computational DFT results; among other things, these data suggest that the sulfoxylate adduct of cobalamin is likely to be monoprotonated at one of the oxygen atoms.

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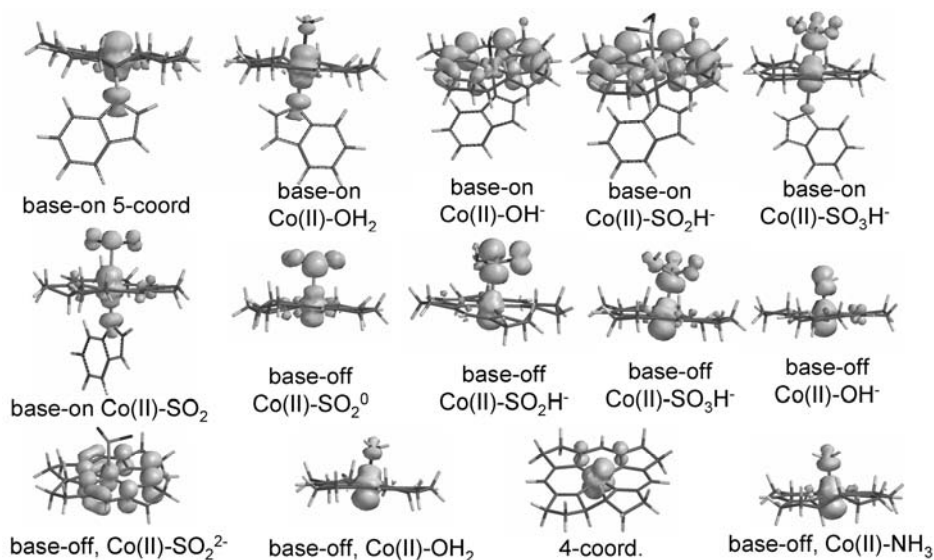


Fig. 6 – DFT-derived geometries and spin densities for putative structures corresponding to the newly-detected B<sub>12r-s</sub>.

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