

Further Studies on the Synergistic Effect of Ni(II) and Co(II) Ions on the Sulfite Induced Autoxidation of Cu(II) Penta and Hexaglycine Complexes

Luciana B. Carvalho, María V. Alipázaga, Rubén G. M. Moreno and Nina Coichev*

Instituto de Química, Universidade de São Paulo, CP 26077, 05513-970 São Paulo-SP, Brazil

A reação de autoxidação dos complexos de Cu(II)/penta e hexaglicina em pH=9 é muito lenta, apresentando um período longo de indução (aproximadamente 4 horas). A presença de S(IV) praticamente não altera a velocidade desta reação. A adição de pequenas quantidades de Ni(II) ou Co(II) aumenta significativamente a velocidade da reação e a eficiência da formação de Cu(III), diminuindo o período de indução para menos de 0,5 s. A constante de velocidade observada para a formação de Cu(III) também depende da concentração de S(IV). A discussão do mecanismo é baseada nas informações disponíveis na literatura e envolve uma cadeia de reações com formação de radicais e um ciclo de oxirredução dos íons metálicos complexados.

The autoxidation of Cu(II)/penta and hexaglycine complexes at pH = 9 is very slow showing a large induction period (about 4 h). The presence of S(IV) practically does not affect the rate of this reaction. Addition of small amounts of Ni(II) or Co(II) increases significantly the reaction rate and the effectiveness of Cu(III) formation, the induction period becomes as short as 0.5 s. The observed rate constant for Cu(III) formation also depends on the S(IV) concentration. The mechanism is discussed based on the available literature information and involves a radical chain and redox cycling of the metal ion complexes.

Keywords: cooper, nickel, cobalt, pentaglycine, hexaglycine, sulfite

Introduction

The oxidation of Cu(II)/tetraglycine complex by dissolved oxygen, at pH=9, is very slow. However, in the presence of sulfite ($(1-8) \times 10^{-5}$ mol L⁻¹) and traces of Ni(II) and Co(II) (10^{-5} mol L⁻¹), present as unavoidable impurities in the copper salts (Aldrich) and reagents, the Cu(III)/tetraglycine formation is efficient and extremely fast (the reaction is complete in 5 s).¹

The metal ions in the trivalent oxidation state react with sulfite to initiate a radical chain reaction in which sulfite is oxidized to sulfate and the metal ion is reduced to the bivalent state, with simultaneous consumption of oxygen.

The synergistic effect due to the combination of two transition metal ions on its sulfite induced autoxidation is still a challenger to be elucidated. There are some studies about synergistic effects in the absence of complexing medium, where the consumption of S(IV) (H₂SO₃, HSO₃⁻ and SO₃²⁻) were followed. However great advances were achieved in some cases, in the presence of complexing medium, where it was possible to follow the formation of

one of the metal ion, at trivalent state in large excess (10^{-4} - 10^{-3} mol L⁻¹), and the effect of the presence of the second metal ion at very low concentrations (10^{-8} - 10^{-5} mol L⁻¹).²⁻⁹

Previous work reported in the literature¹⁻¹⁰ carried out in complexing medium, using very low concentrations of S(IV) (10^{-5} mol L⁻¹) and the second metal ion (10^{-8} - 10^{-5} mol L⁻¹) showed the complexity of the systems.

In these systems: Mn(II)/Fe(III)/acetate,² Fe(II)/Mn(II)/H₂O,^{11,12} Co(II)/Mn(II)/N₃⁻,^{3,6} Ni(II)/Co(III)/cyclam or Ni(II)/Mn(III)/cyclam,⁷ Cu(II)/Ni(II)(or Fe(II)/(III), Mn(II), Cr(III))/tetraglycine,^{1,8} and Co(II)/Mn(II)/Tris,^{9,10} it was possible to follow the concentration of the metal ion (in large excess) at the 3+ state, by measuring the absorbance at a characteristic wavelength.

In fact such experiments, at low concentrations, help to understand why there are so many discrepancies on the kinetic data and mechanism proposals on this redox process, since the presence of impurities of trace metal ions are common in commercial salts and used reagents (acids, bases and buffers).

For example Cu(ClO₄)₂ salt (from Aldrich) contains Ni(II), Co(II) and Mn(II) as impurities (determined by

*e-mail: ncoichev@iq.usp.br

ICP OES technique). It is also difficult to exclude trace concentration of Fe(III) in highly purified water (10^{-9} - 10^{-8} mol L⁻¹).¹³ In some cases, synergistic effects were observed when manganese and iron ions (at very low concentrations) in acetate buffer pH 4-6 were present simultaneously.^{2,13}

In the present work we report further studies about the synergistic effect of Co(II) and Ni(II) on the sulfite induced autoxidation of Cu(II)/penta (G_5) and hexaglycine (G_6) complexes. At pH 8-9 (borate buffer) the autoxidation of these Cu(II) complexes is very slow, the Cu(III) formation is efficient and extremely fast only in the presence of small concentration of nickel and cobalt ions.

Experimental

Reagents

All reagents were of analytical grade (Merck or Sigma) and were used as received. Solutions were prepared by using deionized water purified with a Milli-Q Plus Water system (Millipore).

Stock solutions of sulfite (1.00×10^{-2} mol L⁻¹) were daily prepared by dissolving Na₂S₂O₅ salt in water previously purged with nitrogen. Water was flushed with nitrogen for at least half an hour to remove dissolved oxygen. To prepare diluted solutions of sulfite, small volumes of the stock solutions were properly added to air saturated water. The sulfite content of the stock solution was determined by iodometric titration.¹⁴

Metal ions as impurities of reagents have shown synergistic effect on the studied reaction,⁸ therefore the metal ion stock solutions of Cu(II) and Ni(II) (0.2 mol L⁻¹) were prepared from the direct reaction of Cu (wire) (99.99%) or Ni (powder) (99.99%) with double distilled nitric acid followed by standardization with EDTA by a conventional procedure.¹⁵

Co(II) (0.965 mol L⁻¹) stock solution was prepared from the direct reaction of Co(II) carbonate with perchloric acid followed by standardization with EDTA.¹⁵

The borate buffer was chosen since the Cu(II) and Cu(III) complexes are stable in this medium. Sodium tetraborate 99.998% (Aldrich) was used. In phosphate or carbonate medium the Cu(III) formation is less effective as the phosphate or carbonate anions may displace the peptide ligand.

Procedure

In the experiments freshly prepared solutions were employed. Cu(II)/ G_5 or Cu(II)/ G_6 solutions were prepared

by dissolving pentaglycine or hexaglycine in 0.1 mol L⁻¹ borate buffer solution (pH = 9.0) followed by the addition of Cu(II) solution (solutions were prepared to have 25% excess of ligand to restrain the Cu(OH)₂ precipitation). Aliquots of Co(II) or Ni(II) solutions were added to Cu(II)/ G_n ($G_n = G_5$ or G_6) solution in order to study the synergistic effect. The solutions of metal ion complex consisted of [Cu(II)] = 2.0×10^{-3} mol L⁻¹, $2.0 \times 10^{-6} \leq$ [Ni(II)] or [Co(II)] $\leq 4.0 \times 10^{-5}$ mol L⁻¹, and pH=9.0. The ionic strength, I , was adjusted in 0.2 mol L⁻¹ with NaClO₄.

An equal volume of sulfite solution ($2.0 \times 10^{-5} \leq$ [S(IV)] $\leq 14.0 \times 10^{-5}$ mol L⁻¹) was mixed with the metal ion complex solution (in borate buffer). The final concentrations after the mixture are indicated in all figures.

The kinetics were followed at 365 nm, the wavelength of maximum absorption of the Cu(III)/ G_n complexes, by using a HP8453A diode array spectrophotometer coupled to a Pro-K.2000 Stopped-Flow Mixing Accessory (Applied Photophysics). The optical path length was 0.998 cm.

In all experiments, air saturated solutions were employed for which the oxygen concentration can be considered 2.5×10^{-4} mol L⁻¹.¹⁶ A pHmeter Metrohm model 713 with a glass electrode (filled with sat. NaCl) was used in the pH measurements. The final pH was adjusted with 1.0 mol L⁻¹ NaOH or 1.0 mol L⁻¹ HClO₄ solutions. The temperature was kept at 25.0 °C.

Results and Discussion

The UV-visible spectrum of Cu(III)/ G_n in aqueous solution at pH=9.0 consists of two intense bands at 365 and 250 nm.¹⁷ At 365 nm the Cu(III)/ G_n formation can be conveniently monitored, since neither Ni(II)/Ni(III)/ G_n nor Co(II)/Co(III)/ G_n complexes interfere in the absorbance value due the low used concentrations ([Ni(II)] or [Co(II)] = 10^{-6} - 10^{-5} mol L⁻¹).

Figures 1A and 1B show the absorbance changes at 365 nm during the autoxidation of Cu(II)/ G_5 in the presence of 5.0×10^{-5} mol L⁻¹ S(IV) at pH=9.0. In the absence of Ni(II) or Co(II) ([M(II)] = zero) the reaction occurs very inefficient and slowly with induction period of 4 h. Introduction of trace amounts of Ni(II) or Co(II) affect the kinetic significantly. The Cu(III)/ G_n formation is strongly accelerated and the induction period decreases gradually (to less than 0.5 s) as the Ni(II) or Co(II) concentration increases.

The observed synergistic effect depends on the type and the concentration of the second metal ion. For instance, for a same concentration level of Ni(II) or Co(II) such as 1.0×10^{-5} mol L⁻¹ (Figure 1), the Cu(III) formation is faster in the presence of Co(II). However, in the presence

of Ni(II), a higher limit absorbance was reached (compare Figures 1A and 1B), showing that Cu(III) formation was more efficient.

The first order Cu(III) formation was calculated neglecting the induction period. It was obtained by the initial slope of $\ln(\text{Absorbance}_t - \text{Absorbance}_i)$ vs. time plots. According to the references 18 and 19, the later part of the kinetic trace (after the induction period) can exhibit the maximum rate of Cu(III) formation. In this case, any calculated rate can be subject to large error due to the interference of the autocatalytic behaviour.

Figure 1C shows that the Cu(III) formation exhibits dependence on Ni(II) and Co(II) concentrations and the slope reaches constant values at high concentrations of Ni(II) and Co(II) ions. The observed saturation can be interpreted in terms of complex formation between Ni(II) or Co(II) and sulfite,^{2,20,21} although there is no evidence from the spectrophotometric data.

The effect of sulfite concentration on the autoxidation of Cu(II)/G_n in the presence of Ni(II) or Co(II) was also investigated. Figure 2 shows typical absorbance vs. time traces for the Cu(III)/G_n formation after addition of different sulfite concentrations. The reaction is significantly faster and the induction period decreases on the increase of the Ni(II) or Co(II) (Figures 1A and 1B) and sulfite (Figures 2A and 2B) concentration. The slope is not linear with sulfite (Figure 2C), as it was obtained for Cu(II)/tetraglycine.¹ Data for sulfite concentrations smaller than 1.0×10^{-5} mol L⁻¹ would better define the intercept (in absence of sulfite) in the Figure 2C. However at such low sulfite concentration the absorbance changes were smaller with large error.

Similar experiments were carried out using G₆ as a ligand (Figure 3). It was observed that the limit absorbance at 20 s was about the same (using G₅ or G₆) for the same concentration of Ni(II) or Co(II). In the presence of Co(II), the Cu(III) formation is slightly faster in G₅ medium than G₆. (compare Figures 1 and 3), however, the opposite was observed for the synergistic effect of Ni(II).

Figures 2A and 2B shows that for a fixed concentration of Cu(II) and Ni(II) (in G₆ or G₅ medium) the limit absorbance (after 20 s) is slightly smaller and the Cu(III) formation is faster in G₆ medium for the same S(IV) concentration.

Our previous studies with tetraglycine as a ligand showed that the Cu(III)/G₄ formation is a linear function with initial sulfite concentration and can be monitored amperometric²² and spectrophotometrically^{1,8,23} at 365 nm. For analytical purposes S(IV) could be determined in wine and juices in the range of $(0.5-10) \times 10^{-5}$ mol L⁻¹ and detection limit 6.0×10^{-7} mol L⁻¹. The limit of detection (LOD) was defined as three times the standard deviation

of the linear coefficient divided by angular coefficient value.²⁴

In the present work the maximum absorbance, after 20 s, is linear with the initial S(IV) concentration which can be used for analytical purposes for S(IV) determination. Considering the data from Figures 2A and 2B, the straight line equation were $A = (0.010 \pm 0.002) + (0.096 \pm 0.001) [\text{S(IV)}]$ ($R=0.9999$, detection limit = $(6.5 \pm 0.5) \times 10^{-7}$ mol L⁻¹) and $A = (0.11 \pm 0.01) + (0.090 \pm 0.002) [\text{S(IV)}]$ ($R=0.9985$, detection limit = $(2.8 \pm 0.3) \times 10^{-6}$ mol L⁻¹) in G₅ and G₆ medium, respectively.

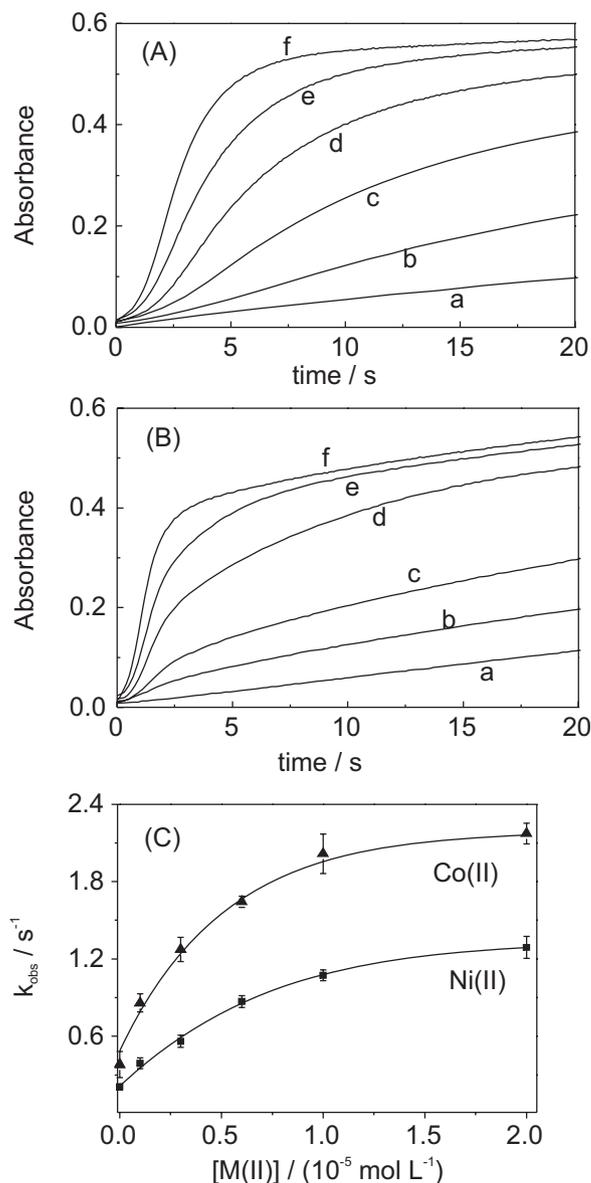


Figure 1. Synergistic effect of Ni(II) (A) and Co(II) (B) on the sulfite induced autoxidation of Cu(II)/G₅. Absorbance changes at 365 nm. k_{obs} as a function of Ni(II) or Co(II) (C). $[\text{Cu(II)/G}_5] = 1.0 \times 10^{-3}$ mol L⁻¹; $[\text{G}_5]_{\text{exc}} = 2.5 \times 10^{-4}$ mol L⁻¹; $[\text{S(IV)}] = 5.0 \times 10^{-5}$ mol L⁻¹; [borate buffer] = 0.050 mol L⁻¹ (pH=9.0); $I = 0.1$ mol L⁻¹ (NaClO₄); $T = 25.0$ °C. $[\text{Ni(II)}]$ or $[\text{Co(II)}] =$ (a) zero, (b) 1.0×10^{-6} , (c) 3.0×10^{-6} , (d) 6.0×10^{-6} , (e) 1.0×10^{-5} and (f) 2.0×10^{-5} mol L⁻¹.

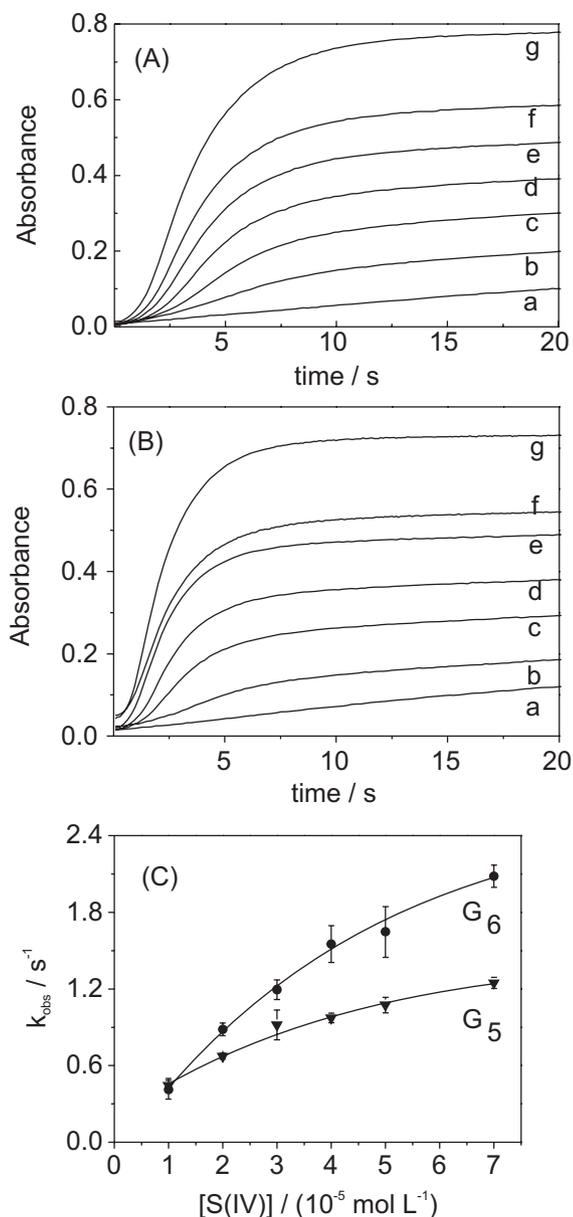
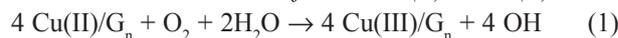


Figure 2. Effect of S(IV). Absorbances changes at 365 nm for the sulfite induced autoxidation of Cu(II)/G₅ (A) and Cu(II)/G₆ (B). k_{obs} for Cu(II)/G₅ and Cu(II)/G₆ (C). [Cu(II)/G_n] = 1.0×10^{-3} mol L⁻¹; [G_n]_{exc} = 2.5×10^{-4} mol L⁻¹; [Ni(II)] = 1.0×10^{-5} mol L⁻¹; [borate buffer] = 0.050 mol L⁻¹ (pH=9.0); I = 0.1 mol L⁻¹ (NaClO₂); T = 25.0 °C. [S(IV)] = (a) zero; (b) 1.0×10^{-5} ; (c) 2.0×10^{-5} ; (d) 3.0×10^{-5} ; (e) 4.0×10^{-5} ; (f) 5.0×10^{-5} ; (g) 7.0×10^{-5} mol L⁻¹.

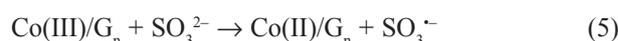
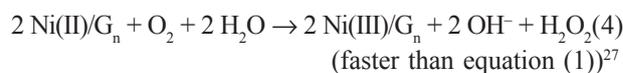
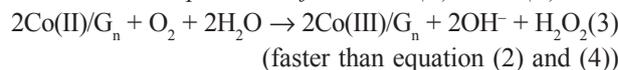
Mechanism

In the Scheme 1 the main reactions are represented. As reported before¹ the metal ion in the 3+ oxidation state is the initiator to form $SO_3^{\cdot-}$ (equations (5)-(7)). If the initiator is not initially added, it is generated by the oxidation of the metal ion complex by oxygen (equations (1), (3) and (4)). Initiation by Cu(III)/G_n as result of the spontaneous oxidation of Cu(II)/G_n by oxygen (equation (1)) or by disproportionation of Cu(II)/G_n (equation (2) suggested by Margerum's group),^{25,26} is less probable since the reactions are very slow.

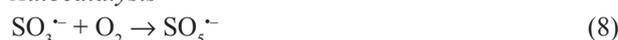
Initiation in the absence of added Ni(II) or Co(II)



Initiation in the presence of added Ni(II) or Co(II)



Autocatalysis



Scheme 1. Mechanism of the sulfite induced autoxidation of Cu(II)/G_n. Synergistic effect of Ni(II) or Co(II).

This synergistic effect was better understood by comparative studies of the reactions of Ni(II) and Co(II) penta and hexaglycine complexes. Our previous work²⁷ carried out in solutions containing each metal ion complex (Ni(II)/G_n or Co(II)/G_n) in the presence of S(IV) and oxygen (at pH=9) showed that Ni(III)/G_n formation is fast reaching a limit absorbance after 1s, followed by its decomposition via ligand oxidation. At the same experimental conditions, Co(III)/G_n formation is much slower than Ni(III)/G_n formation, after S(IV) consumption the Co(III)/G_n formation is slow due to the oxidation of Co(II)/G_n by the oxygen still remaining in solution. The Co(III)/G_n complexes seem to be stable for 20 h (the monitored time), since the absorbance at 265 nm did not decrease. In comparison, at the same pH, the autoxidation of Cu(II)/G_n in the presence of S(IV) does not occur in the first 4 h.

The synergistic effect of Ni(II) and Co(II), can be explained by the faster oxidation of Ni(II)/G_n or Co(II)/G_n

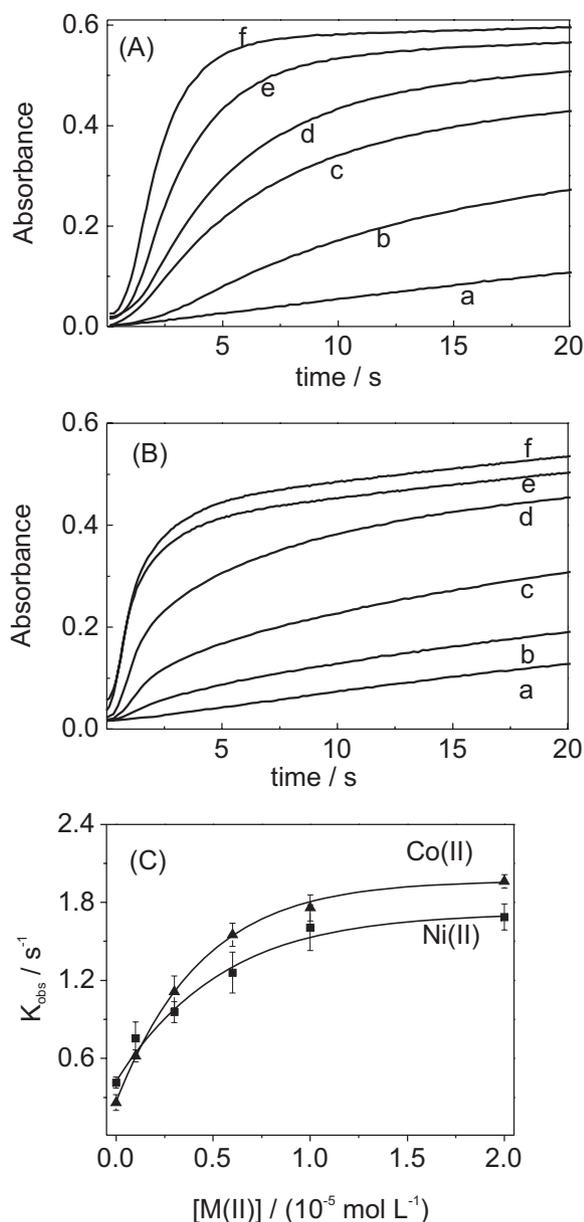


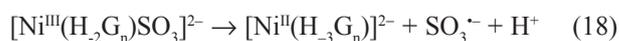
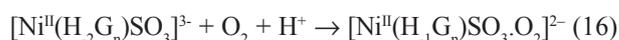
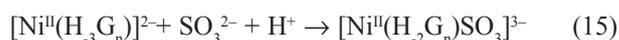
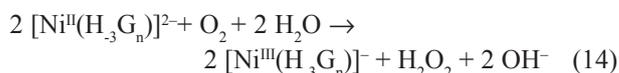
Figure 3. Synergistic effect of Ni(II) (A) and Co(II) (B) on the sulfite induced autoxidation of Cu(II)/G₆. Absorbance changes at 365 nm. k_{obs} as a function of Ni(II) or Co(II) (C). $[Cu(II)/G_6] = 1.0 \times 10^{-3} \text{ mol L}^{-1}$; $[G_6]_{exc} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$; $[S(IV)] = 5.0 \times 10^{-5} \text{ mol L}^{-1}$; $[borate \text{ buffer}] = 0.050 \text{ mol L}^{-1}$ (pH=9.0); $T = 0.1 \text{ mol L}^{-1}$ (NaClO₄); $T = 25.0 \text{ }^\circ\text{C}$. $[Ni(II)]$ or $[Co(II)] =$ (a) zero, (b) 1.0×10^{-6} , (c) 3.0×10^{-6} , (d) 6.0×10^{-6} , (e) 1.0×10^{-5} and (f) $2.0 \times 10^{-5} \text{ mol L}^{-1}$.

by oxygen (equations (3)-(4)), originating the initiator Ni(III)/G_n or Co(III)/G_n, which reacts with the sulfite to form the radical SO₃^{•-} (equations (5)-(6)). Cu(II)/G_n (in large excess, $1.0 \times 10^{-3} \text{ mol L}^{-1}$) can be oxidized by SO₅^{•-}, HSO₅⁻ and SO₄^{•-} (equations (9)-(13)). In an autocatalytic process the Cu(III)/G_n then can be reduced by SO₃²⁻ (equation (7)).

In our previous work on the systems Ni(II)/cyclam²⁸ and Mn(II)/acetate,² the oxygen consumption were followed, showing that the redox cycling depends on the

balance of sulfite and oxygen concentrations in solution. This balance could be demonstrated in the case of Fe(II)/(III)/H₂O,^{11,29} Co(II) and Mn(II) in azide medium³⁰ and Ni(II) in hydroxide medium.³¹

It is not always possible to elucidate the nature of the oxidizing metal ion species. In the case of complexes of Ni(II)/(III) and Co(II)/(III) with G₅ and G₆, there is no information in the literature. However, there are also the probability of mixed complex formation, as suggested for Ni(II)/G₄ complexes²⁰ (equations (14)-(18)).



where H_xG_n is the peptide with x deprotonated peptide nitrogen coordinated to nickel ion.

The complexity of the system does not allow a definitive assignment of the species involved. Lepentsiotis *et al.*³² suppose the formation of Ni^{III}L (SO₄^{•-}) (L=lysylglycylhistidine carboxiamide), where the SO₄^{•-} radical may coordinate to Ni^{III}L complex. Green *et al.*³³ considered the formation of reactive dimer species of Ni(II) and Ni(III)Gly₂HisGly complexes in the oxidative self-decomposition of Ni(III) complex.

Important aspects of Co(II)/Co(III) complex in the presence of oxygen need to be considered as some possible step in the oxidation. Studies³⁴ with Co(II) peptides (gly-gly, gly-ala, ala-gly and ala-ala) showed the formation of dimeric complexes with μ-superoxo bridges. In the case of Co^{II}asparagine the formation of dioxygen complex occurs prior to the oxidation of the metal center.³⁵

The pH dependence of Co^{II}G_n oxidation by oxygen (in the presence or absence of sulfite),²⁷ may be explained by the possible formation of oxygen adduct or μ-superoxo bridge. This property of Co(II)/(III) complexes may explain the different behaviour of Co^{II}G_n compared to Ni^{II}G_n in the presence of oxygen and sulfite.

Conclusions

The coordination chemistry, using proper ligands, allows the elucidation of the mechanism of S(IV) oxidation, since it is possible to follow the changes in the

oxidation state of the metal ion, which may be helpful to propose model systems. When the effect of such low concentrations of S(IV) and metal ions can be evaluated problems with collection and preservation of water, air or aerosol samples are detected.

The present work explains some reported analytical methods for sulfite, where metal ions (Cu(II), Mn(II), Fe(II) and Fe(III)) interfere in S(IV) determination.³⁶⁻³⁹

The extraction of S(IV) from samples (wine, juice, white sugar and rain water)^{8,40} is necessary prior to the analysis. This is not always possible, especially when the concentration of S(IV) is too small (10^{-8} - 10^{-6} mol L⁻¹).³⁶⁻⁴⁰

This redox cycling process of metal ion is of interest in atmospheric process,^{3,41,42} treatment of gaseous effluents to assist pollution control systems development⁴³⁻⁴⁵ and in the DNA and RNA damage by the sulfur oxy radicals.⁴⁶⁻⁴⁸

The synergistic effect due to the combination of two transition metal ion (in the 2+ oxidation state) in an autocatalytic process, with the initiator being the metal ion at trace level in the 3+ oxidation state, followed by a redox cycling, is fascinating and very complex to be fully understood. Many important aspects must be considered: the oxidation of the second metal ion (initially present or added), how faster is the reoxidation of the reduced metal ion and the stability of the metal ion complexes.

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