

Photochemical transformation of iminodiacetic acid induced by complexation with copper(II) in aqueous solution

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Abstract

The photodegradation of copper(II) iminodiacetate (CuIDA) was studied at 20 °C using monochromatic excitation at various pH values. The 1:1 complex between copper(II) and iminodiacetic acid was present under our experimental conditions. The initial quantum yield of CuIDA transformation, determined by high performance liquid chromatography (HPLC), was low and independent of pH. A redox process was observed giving rise to Cu^I, HCHO, CO₂ and glycine. In the presence of oxygen, the immediate re-oxidation of copper(I) into copper(II) occurred, giving a very interesting catalytic aspect to the system. In neutral solution, copper(II) was complexed by glycine (the main photoproduct of CuIDA transformation) and the photodegradation continued, to give Cu^I, NH₄⁺, CO₂ and HCHO.

Keywords: Photodegradation; Copper complex; Iminodiacetic acid; Aqueous solution

1. Introduction

Aminopolycarboxylic acids are strong complexing agents with divalent or trivalent metal cations and are therefore widely used in the detergent industry as substitutes for phosphates [1–3]. Nitrilotriacetic acid (NTA) strongly complexes with iron and copper and stabilizes the higher valence states of the metals [4]. The complexation of NTA with transition metals, such as iron(III) or copper(II), leads to the onset of absorption in the near-UV and visible region and, as a result, iron(III) and copper(II) nitrilotriacetate can undergo phototransformation on excitation by solar light. General studies on NTA degradation, photoinduced by complexation with a metal, e.g. iron(III) [5–7] or copper(II) [8], have been described including our previous work [9,10]. The major photoproducts are the reduced metal, iminodiacetic acid (IDA), CO₂ and formaldehyde. We subsequently studied the transformation of IDA photosensitized by iron(III) and copper(II). We have previously reported the photochemical behaviour of iron(III) iminodiacetate (FeIDA) [11] and, in this paper, the phototransformation of the copper(II) salt (CuIDA) is described. In order to elucidate the

complete mechanism, we decided to investigate the photochemical behaviour of CuIDA in dilute aqueous solution at different pH values with and without oxygen using different monochromatic excitation wavelengths, i.e. the work was not limited to the pH values (5.5 < pH < 7.5) or excitation wavelengths ($\lambda > 295$ nm) usually found in the environment.

2. Experimental details

2.1. Materials

IDA and glycine were purchased from Fluka and were used without further purification. CuCl₂ (anhydrous) was obtained from Merck. Chromotropic acid sodium salt dihydrate was a Fluka product used after recrystallization from water.

The solutions of CuCl₂–IDA were deaerated by bubbling with argon for 30 min at room temperature. The pH was adjusted with NaOH and controlled with an Orion pH meter to ± 0.02 pH unit. The ionic strength was not controlled. The solutions were unbuffered to avoid the complexation of copper(II) by the buffer. The solutions were not very stable and a weak change in the UV–visible spectrum of the solution could be

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observed after 1 week; freshly prepared solutions were used in all cases.

2.2. Apparatus and procedure

A low-pressure Hg lamp was used for irradiation at 254 nm and a high-pressure Hg lamp with a Bausch and Lomb monochromator was used for irradiation at 296 nm (and 313 nm). The beam was parallel and the reactor was a square quartz cell with a path length of 1 cm. The light intensity was measured by ferrioxalate actinometry. UV-visible spectra were recorded on a Cary 3 double-beam spectrophotometer.

High performance liquid chromatography (HPLC) experiments were carried out using a Waters 540 chromatograph equipped with a diode array detector (Waters 990), with a mixture of 500 cm³ sodium acetate (0.03 mol dm⁻³) and 100 cm³ CH₃CN as eluent. The flow rate was 1 cm³ min⁻¹ and the column was a Beckman ultrasphere ODS (length, 25 cm).

Electron spin resonance (ESR) spectra were recorded on a Bruker ER 200 D spectrometer at 9.30 and 9.50 GHz with a modulation field of 100 kHz. A xenon mercury Hanovia lamp was used for irradiation in the ESR spectrometer cavity. DPPH was used as internal standard.

HCHO formation was measured by colorimetry with chromotropic acid as described by Bricker and Johnson [12].

3. Results

3.1. Characterization of CuIDA in solution

The solution was prepared by the addition of an aqueous solution of CuCl₂ to a solution of IDA in order to obtain a 1:1 stoichiometry. The mixture was stirred for 30 min. The UV-visible spectrum of the stoichiometric mixture of CuCl₂ ([CuCl₂] = 4 × 10⁻⁴ mol dm⁻³, pH 4.50) and IDA ([IDA] = 4 × 10⁻⁴ mol dm⁻³, pH 3.05), whose final pH was 3.50, presented a maximum at 236 nm and a weak absorption near the visible domain. The UV spectrum was not strongly modified when the pH was varied from 3.50 to 7.00.

To assess the stoichiometry of the copper(II) salt in aqueous solution, we measured the absorbance at 236 nm as a function of the ligand to metal ratio. As shown in Fig. 1, the 1:1 complex, CuIDA, was present under our experimental conditions.

To estimate the percentage of copper(II) complexed by IDA, we must consider our pH domain and the pK_a values of IDA (pK₁ = 2.58 and pK₂ = 9.33) [4].

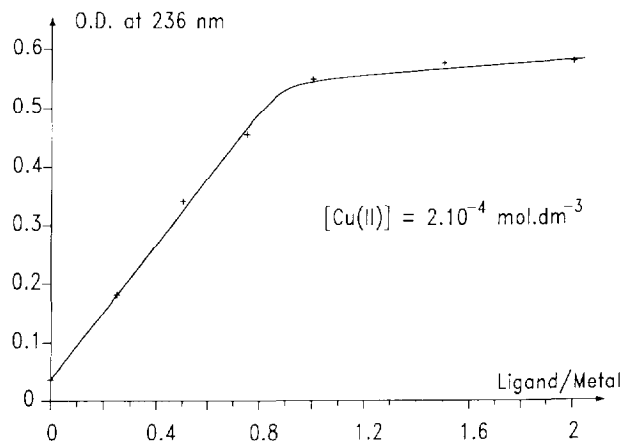
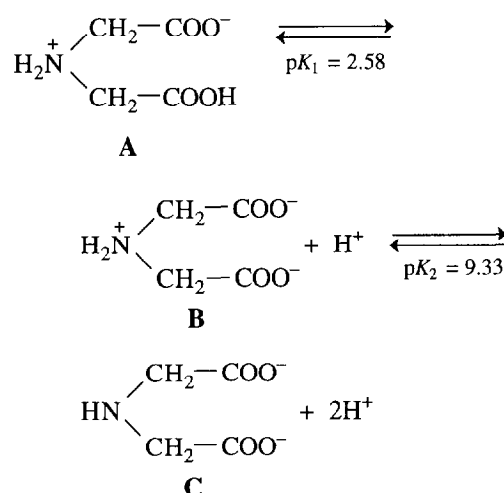
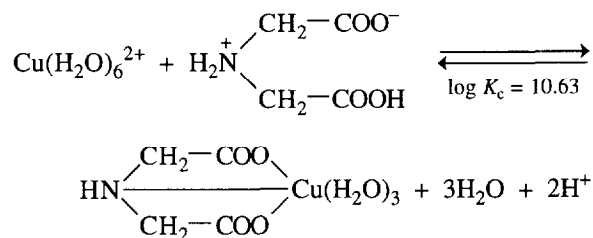


Fig. 1. Evolution of the optical density (OD) at 236 nm as a function of the ligand to metal ratio (*L/M*).



The major species is the deprotonated form B. By taking into account the complexation constant of copper(II) by IDA (*K_c*) [4]



it appears that copper(II) is mainly complexed by IDA [13,14]. At low concentrations of copper(II), no 1:2 complex is formed. Chaberek and Martell [13] reported similar results.

This was further confirmed by comparison of the titration of a CuIDA solution and IDA solution alone by sodium hydroxide. The titration curves showed that the equivalence point was reached for two equivalents of sodium hydroxide for the mixture copper(II)-IDA, whereas it was reached for only one equivalent of NaOH (Fig. 2) for IDA alone. The difference between

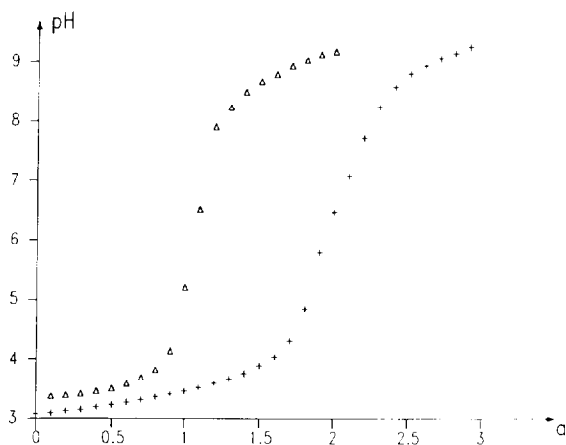


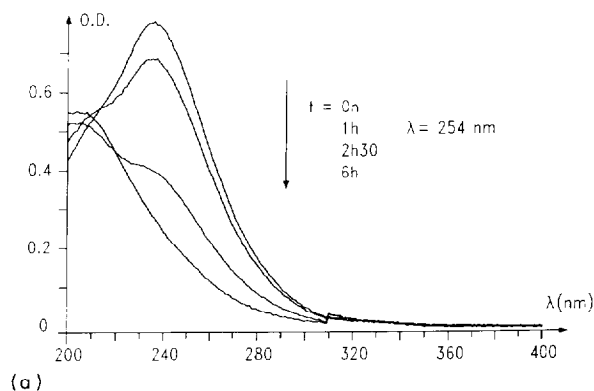
Fig. 2. Titration curves of iminodiacetic acid (IDA) (5×10^{-4} mol dm^{-3}) and $\text{CuCl}_2 + \text{IDA}$ (5×10^{-4} mol dm^{-3}), where a is the number of moles of base per mole of acid: Δ , titration of an IDA solution by NaOH; +, titration of a CuIDA solution by NaOH.

these two titration curves is due to the chelation of copper(II) by IDA.

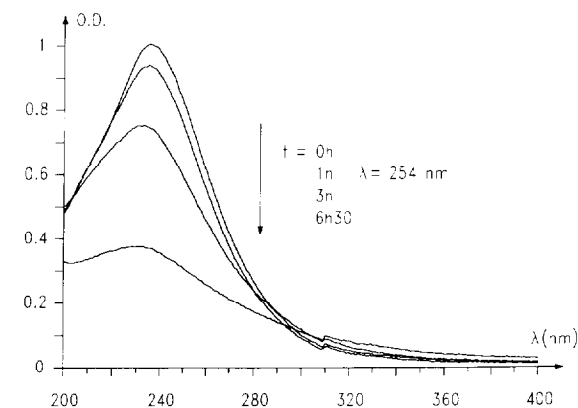
3.2. Photochemical behaviour of CuIDA

On irradiation, the spectral changes in the UV–visible spectrum of CuIDA were similar irrespective of the irradiation wavelength. However, the evolution was very slow for irradiations at $\lambda = 313$ and 296 nm ($\epsilon_{313} = 60$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ and $\epsilon_{296} = 200$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$). Therefore most of the experiments were performed at 254 nm ($\epsilon_{254} = 2500$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$). A continuous decrease was observed for the entire spectrum in aerated solution. Fig. 3 shows the spectral evolution of CuIDA (3×10^{-4} mol dm^{-3}) at pH 3.50 and pH 6.50. In degassed solution, together with the decrease, a continuous absorption was observed, reflecting the presence of a colloidal suspension. When opened to the air, the suspension quickly disappeared. The UV absorption of the solution so obtained was dependent on the pH. In acidic medium, the optical density decreased when opened to the air, whereas it increased again in neutral solution.

The quantum yields of CuIDA transformation were determined by HPLC. At 254 nm, the quantum yield was low ($\phi = 0.012$) and independent of pH. Due to the very low values of the molar extinction coefficients and the low concentrations used in this work, it was impossible to determine the initial quantum yield with precision for irradiation at longer wavelengths (296 and 313 nm). However, they appeared to be of the same order of magnitude. The presence of oxygen did not affect the initial rate significantly. The only difference was the immediate re-oxidation of copper(I) into copper(II) in the presence of oxygen. The primary mechanism was not affected by oxygen (see later).



(a)



(b)

Fig. 3. Spectral evolution of an aerated solution of CuIDA (3×10^{-4} mol dm^{-3}) on irradiation at 254 nm: (A) pH 3.50; (B) pH 6.50.

The treatment by chromotropic acid of a CuIDA solution irradiated in the presence or absence of oxygen, in acidic or neutral conditions, revealed the formation of formaldehyde. However, the amount of HCHO formed was dependent on the pH of the solution.

In acidic medium (pH 3.50), the complete transformation of CuIDA led to the formation of HCHO with a ratio of 1:1. In contrast, in neutral solution, the reaction continued and stopped when two equivalents of HCHO were formed. The results are summarized in Table 1. The initial concentration of CuIDA was 3.00×10^{-4} mol dm^{-3} .

We checked that there was no subsequent photo-reaction between copper(II) and formaldehyde.

3.3. ESR spectroscopy

A four-line signal at $g = 2.1424$ with a total width equal to 220 G ($a = 60$ G) was observed for a solution of CuIDA (5×10^{-4} mol dm^{-3}) at room temperature (Fig. 4). This four-line signal is characteristic of complexation between copper(II) ($I = 3/2$) and the ligand IDA [15].

On irradiation, we observed a decrease in the copper(II) signal in the CuIDA complex, which con-

Table 1
Photochemical transformation of CuIDA ($[\text{CuIDA}]_0 = 3 \times 10^{-4} \text{ mol dm}^{-3}$)

pH	CuIDA disappeared (HPLC) (mol dm^{-3})	HCHO formed (mol dm^{-3})	Irradiation time
Acid (pH 3.50)	0.53×10^{-4}	0.55×10^{-4}	40 min
	1.45×10^{-4}	1.20×10^{-4}	2 h
	3.00×10^{-4}	2.60×10^{-4}	3 h 20 min
Neutral (pH 6.50)	1.50×10^{-4}	2.60×10^{-4}	2 h
	2.70×10^{-4}	4.20×10^{-4}	5 h
	3.00×10^{-4}	5.20×10^{-4}	6 h
	3.00×10^{-4}	6.00×10^{-4}	8 h

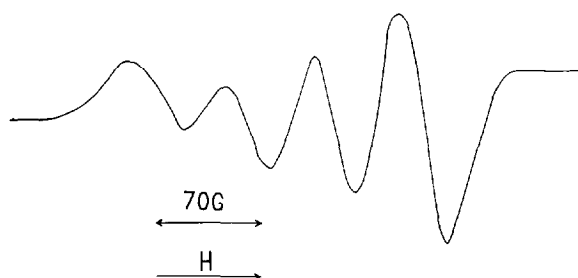


Fig. 4. ESR spectrum of a solution of CuIDA ($5 \times 10^{-4} \text{ mol dm}^{-3}$).

Table 2
Photochemical transformation of Cu-glycine ($[\text{CuCl}_2] = [\text{glycine}] = 3 \times 10^{-4} \text{ mol dm}^{-3}$)

pH	HCHO formed (mol dm^{-3})
4.0	0.615×10^{-4}
4.9	1.05×10^{-4}
5.9	1.75×10^{-4}
6.9	2.80×10^{-4}

firmed the oxidoreduction reaction between copper(II) and IDA leading to copper(I).

3.4. Study of the Cu-glycine complex

Because of the complexation of copper(II) (arising from copper(I) oxidation) with the photoproducts, mainly glycine, we prolonged the study to the copper(II)-glycine system. However, the work was restricted to the experimental conditions relevant to the copper(II)-IDA system. Further information on the copper(II)-glycine system is given in Ref. [16].

The UV-visible spectrum of a stoichiometric mixture of CuCl_2 and glycine presents a maximum at 236 nm and is strongly dependent on pH. Fig. 5 shows the variation of the optical density at 236 nm as a function of pH. At $\text{pH} < 3.0$, complexation is almost negligible,

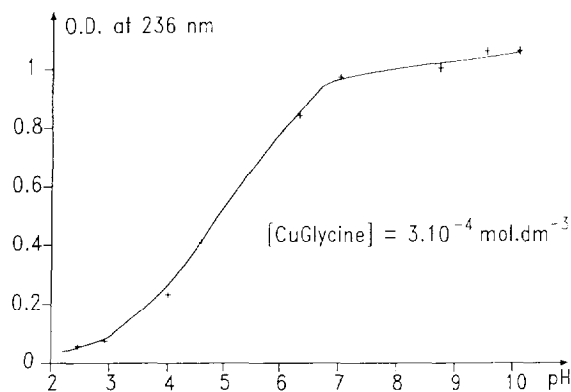


Fig. 5. Evolution of the optical density (OD) at 236 nm of an aqueous solution of CuCl_2 -glycine ($3 \times 10^{-4} \text{ mol dm}^{-3}$) as a function of pH.

whereas at $\text{pH} > 7.0$, complexation between copper(II) and glycine is important.

On irradiation at 254 nm, the absorbance at 236 nm of an aerated Cu-glycine mixture continuously decreases. In degassed solution, as for CuIDA, continuous absorption is observed reflecting the presence of a colloidal suspension; it disappears very rapidly on contact with air.

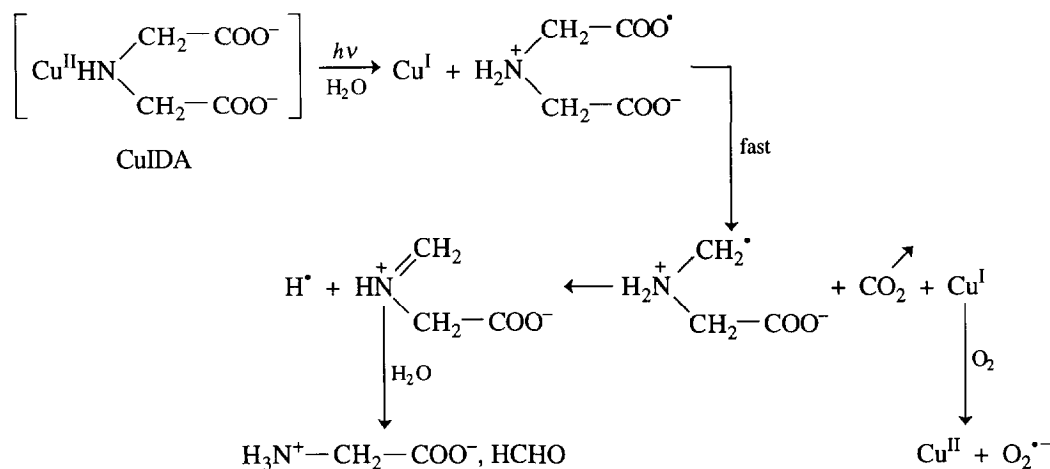
The treatment by chromotropic acid of an irradiated Cu-glycine solution reveals the formation of formaldehyde. The formation of HCHO is strongly dependent on the pH of the starting solution. The results are listed in Table 2 for four solutions ($[\text{glycine}] = [\text{Cu}^{II}] = 3 \times 10^{-4} \text{ mol dm}^{-3}$) in the presence of oxygen at different pH values after irradiation at 254 nm until total disappearance of the complex between copper(II) and glycine was obtained.

In acidic medium, no HCHO formation is observed, whereas at pH 7, the complete disappearance of the complex between copper(II) and glycine corresponds to the formation of $3 \times 10^{-4} \text{ mol dm}^{-3}$ of HCHO. These results are in agreement with the evolution of the complexation between copper(II) and glycine as a function of pH. Without any complexation with copper(II), the phototransformation of glycine is not effective.

4. Discussion

On irradiation at 254, 296 or 313 nm, an aqueous solution of CuIDA undergoes a photo-oxidoreduction reaction giving rise to the reduced metal and the oxidized ligand. It is worth noting that the redox process is observed in acidic and neutral solution. The quantum yield of disappearance of CuIDA is around 10^{-2} . The formation of HCHO is efficient in this system.

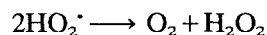
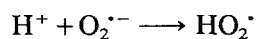
In acidic medium ($\text{pH} \approx 3.0$), the 1:1 stoichiometry between the formation of HCHO and the phototransformation of CuIDA complies with a mechanism involving charge transfer between copper(II) and the carboxylate group (Scheme 1).



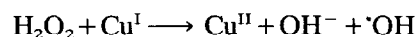
Scheme 1.

The first step is charge transfer leading to copper(I) and a carboxyl radical. The carboxyl radical undergoes a very fast decarboxylation giving rise to R-CH₂[•] [17]. This unstable radical gives the aldimine by loss of H[•], and by reaction with a water molecule, leads to the formation of formaldehyde and glycine. We obtain the ratio 1:1 between the formation of HCHO and the disappearance of CuIDA. In the presence of oxygen, copper(I) is immediately re-oxidized into copper(II). However, in this pH domain, the complexation between copper(II) and glycine is negligible and the reaction stops.

The fast re-oxidation of copper(I) is mainly due to the reaction with oxygen. An oxidation process involving O₂^{•-} and its conjugated form can also be put forward

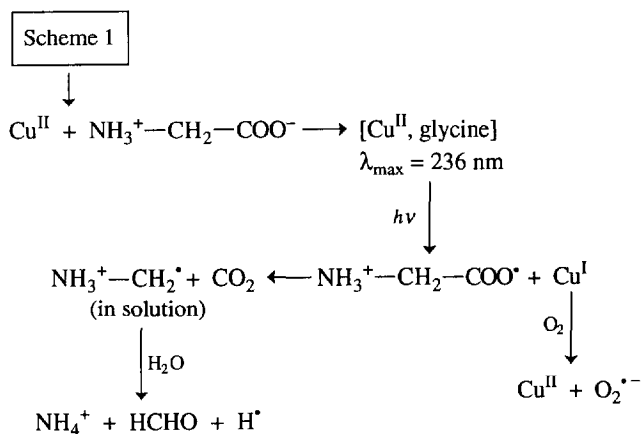


H₂O₂ can then react with Cu^I in a Fenton-like reaction giving rise to copper(II) [18]



However, the stoichiometric ratio between HCHO formation and CuIDA disappearance implies that the above-mentioned mechanism giving rise to the oxidative species [•]OH is of minor importance. Moffet and Zika [18] reported the same conclusion regarding the re-oxidation of copper(I) in surface waters.

In neutral medium, the first part of the mechanism is similar to that observed in acidic medium. However, under these conditions, copper(II) is complexed by glycine giving rise to absorption up to 320 nm and the photoreaction can proceed. This phenomenon accounts for the increase in absorbance when an irradiated solution is opened to the air. A subsequent photo-oxidoreduction then occurs and we again observe the reduction of copper(II) to copper(I) and the formation of HCHO (Scheme 1 + Scheme 2).



Scheme 2.

The complexation between copper(II) and glycine accounts for the 2:1 stoichiometry between the formation of HCHO and the phototransformation of CuIDA obtained in neutral medium. So, the re-oxidation of copper(I) into copper(II) in the presence of oxygen permits the total degradation of IDA.

4.1. Estimation of the half-life of CuIDA in the environment

The half-life of IDA on irradiation by solar light in the presence of copper(II) can be evaluated according to [19]

$$\tau_{1/2} = \frac{\ln 2}{2300 \int_{\lambda_1}^{\lambda_2} \phi(\lambda) I_0(\lambda) \epsilon(\lambda) d\lambda}$$

where $\tau_{1/2}$ is the half-life (s), ϕ is the quantum yield of CuIDA disappearance on excitation at λ , ϵ is the molar extinction coefficient at λ (l mol⁻¹ cm⁻¹) and

I_0 is the intensity of sunlight at λ (einstein cm^{-2}). A half-life of approximately 50 h was calculated using the solar irradiation intensities reported by Franck and Klöpfer [20].

5. Conclusions

On photodegradation of CuIDA, a redox phenomenon is observed giving rise to the oxidized ligand and copper(I) which is spontaneously re-oxidized into copper(II) in the presence of oxygen. In acidic solution, the complexation between copper(II) and glycine is negligible and the reaction stops. However, in neutral solution, the photodegradation of IDA is complete since copper(II) is complexed by glycine and undergoes a subsequent photoredox process. Despite the limited overlap between sunlight and the CuIDA spectrum, the catalytic aspect related to copper makes the photodegradation process efficient in natural conditions.

References

- [1] R.H. Nuttall and D.M. Stalker, *Talanta*, **24** (1977) 355.
- [2] G. Anderegg, *Inorg. Chim. Acta*, **121** (1986) 229.
- [3] H.B. Lockhart and R.V. Blakeley, *Environ. Lett.*, **9** (1975) 19.
- [4] L.G. Sillen and A.E. Martell, *Stability Constants of Metal-Ion Complexes*, Special Publications 17 and 25, Chemical Society, London, 1964.
- [5] T. Trott, R. Hanwood and C.H. Langford, *Environ. Sci. Technol.*, **6** (1972) 367.
- [6] R. Stolzberg and D. Hume, *Environ. Sci. Technol.*, **9** (1975) 654.
- [7] A. Svenson, L. Kas and H. Bjorndol, *Chemosphere*, **18** (1989) 1805.
- [8] C.H. Langford, H. Wingham and V.S. Sasti, *Environ. Sci. Technol.*, **7** (1973) 820.
- [9] S.L. Andrianirinaharivelo, J.F. Pilichowski and M. Bolte, *Transition Met. Chem.*, **18** (1993) 37.
- [10] S.L. Andrianirinaharivelo and M. Bolte, *J. Photochem. Photobiol. A: Chem.*, **73** (1993) 213.
- [11] S.L. Andrianirinaharivelo and M. Bolte, *Chemosphere*, **24** (1992) 953.
- [12] C.E. Bricker and H.R. Johnson, *Ind. Eng. Chem. Anal. Ed.*, **17** (1945) 400.
- [13] S. Chaberek, Jr. and A.E. Martell, *J. Am. Chem. Soc.*, **74** (1952) 5052.
- [14] A.E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, Prentice-Hall, New York, 1957.
- [15] (a) P. Laubry, G. Mousset, P. Martinet, M. Tissier, C. Tissier and J. Juillard, *J. Chem. Soc., Faraday Trans. 1*, **84** (9) (1988) 3175.
(b) M.F. Colombo, L. Austrilino, O.R. Nascimento, E.E. Castellano and M. Tabak, *Can. J. Chem.*, **65** (1987) 821.
(c) A. Rossi, M. Ptak, P. Grenouillet and R.P. Martin, *J. Chim. Phys.*, **10** (1974) 1371.
- [16] P. Natarajan and G. Ferraudi, *Inorg. Chem.*, **20** (1981) 3708.
- [17] J.K. Kochi, *Organometallic Mechanism and Catalysis*, Academic Press, New York, 1978, p. 99.
- [18] J.W. Moffet and R.G. Zika, *Mar. Chem.*, **13** (1983) 239.
- [19] European Chemical Industry Ecology and Toxicology Centre (ECETOC), B63 The phototransformation of chemicals in water: results of a ring test, *Technical Report 12*, Brussels, 1984.
- [20] R. Franck and W. Klöpfer, *Chemosphere*, **17** (1988) 985.