



An absorption spectroscopic investigation of the interaction of lac dyes with metal ions

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Abstract

As part of an investigation on mordants and lac dyeing of silk and cotton, UV–VIS spectroscopic studies were carried out on the effect of pH and metal ions on Thai lac dye extracted from stick lac from the Rain tree in northeast Thailand. These results were compared with those from commercial lac dye (Wako Company), and from laccic acids A and B. It was shown that increasing the metal ion concentration caused a bathochromic shift of the lac dye absorption bands in the visible region in both the laccic acids A and B and the dyes. Also when the pH of the lac dye solution was increased from 2.5 to 11, a substantial bathochromic shift of the lac dye visible absorption band was observed in both Wako and Thai lac dyes. At alkaline pH, the phenolic hydroxyl (and carboxylic acid groups) in lac dye molecules is deprotonated, resulting in a pronounced bathochromic shift. The study also indicated that when the concentration of metal salts increased within the range of concentrations studied, the intensity of the long wavelength absorption band of laccic acid A, laccic acid B and commercial lac dye increased accordingly.

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1. Introduction

Lac, a natural resin of insect origin, is used extensively for natural food additives, cosmetics and as a colourant for silk and cotton dyeing. Lac dye, which is the soluble part of stick lac, is composed

mainly of two major anthraquinone-based components: laccic acids A and B [1–7]; the minor components, laccic acids C, D and E, have also been isolated [8,9] (Fig. 1). The UV–VIS spectrum of laccic acid A is very similar to the spectrum of crude laccic acid in ethanol [2], with absorption maxima for laccic acid A reported at 290, 340, 500 and 530 nm in this solvent [2]; in water, λ_{\max} values were reported at 292 and 490 nm and at 500 nm in acetone for this acid (referred to as laccic acid (I)) [10].

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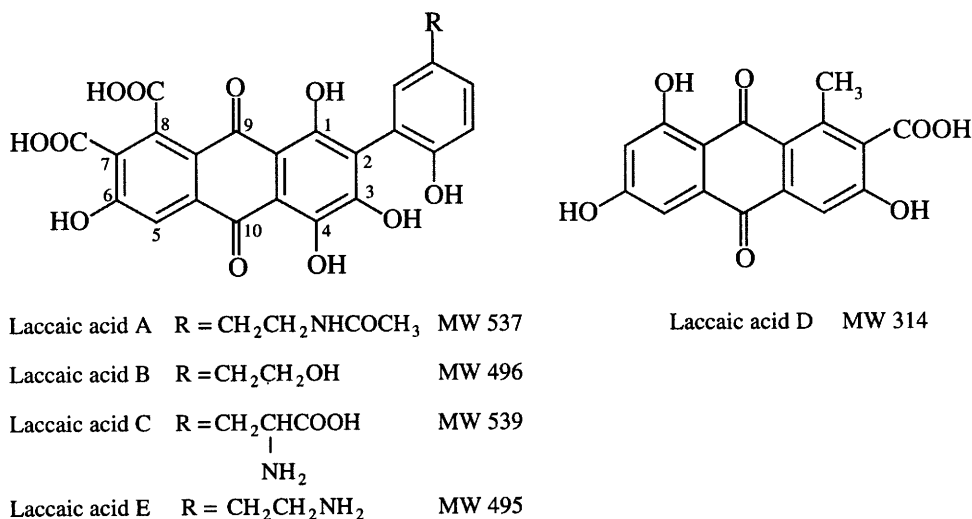


Fig. 1. Chemical structures of laccaic acids.

For generations, villagers in northeast Thailand have used lac dyes extracted from stick lac formed on the Rain tree, *Samanea saman* (Jacq.) Merr. (*Pithecolobium saman*, Mimosaceae) for textile dyeing [11]. As part of the dyeing process with lac dye on cotton and silk, alum, potassium dichromate, stannous chloride and copper sulfate have been used as mordants to improve colour fastness. While metal ion mordants have also been used by others in dyeing with lac dyes [12–14], there have not been any reports on specific spectroscopic studies involving these components. In an effort to gain a greater understanding of the action of these mordants, and with a view ultimately to improving the reliability and quality of the dyeing process, a systematic study of the interaction of lac dyes and laccaic acids with selected metal ions was undertaken. In particular, metal ion and pH effects on the visible absorption spectra of Thai lac dye extracted from stick lac from the Rain tree in northeast Thailand were investigated and comparative studies done with commercial lac dye (Wako Company) and laccaic acids A and B in order to ascertain if the Thai lac dye had any distinctively different characteristics. The results of this study are reported in this paper.

2. Experimental

2.1. Chemicals

Laccaic acid A [124-04791], laccaic acid B [127-04801], and lac dye [124-04012] were purchased from the Wako Company (Osaka, Japan). For simplicity, the last compound is referred to as Wako lac dye. Analytical grade metal ion salts, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (alum) were purchased from the Merck Co., Ltd.

2.2. Extraction of lac dye

Stick lac (500.48 g) collected from Rain trees in northeast Thailand (Nakhon Ratchasima Province) was powdered in a grinding mill and finely ground (18 mesh). The powdered material was extracted with deionized water (1.5 L) at 60 °C for 1 h. The aqueous solution was filtered and then concentrated under reduced pressure (rotary evaporator) to give a crude lac dye extract (38.33 g), which was then used without further purification. This extract is referred to as Thai lac dye.

2.3. Methods

2.3.1. Measurement of pH and spectra

The influence of pH on the visible absorption spectra of Wako lac dye and Thai lac dye was determined using 3% (v/v) acetic acid solution in the pH range 2.5–4.5, and 0.5 M sodium hydroxide solution in the pH range 5.0–11.0. The pH values were measured using a pH meter (Mettler Delta 320, UK). The UV–VIS spectra were recorded using a Cary 1E UV–VIS spectrophotometer. This instrument was used for all UV–VIS absorption spectra in this work.

2.3.2. Metal ion effects

2.3.2.1. Effect of metal ion concentration on laccaic acid A and laccaic acid B visible absorption spectra in deionized water. The final concentration of laccaic acids A and B in the measured aqueous solutions (deionized water) was 9.31×10^{-5} and 1.05×10^{-4} M, respectively. The final concentrations of metal ions in the laccaic acids A and B solution varied as follows: 5.0×10^{-5} , 2.0×10^{-4} , 5.0×10^{-4} , 2.0×10^{-3} , 5.0×10^{-3} , 7.0×10^{-3} , 1.0×10^{-2} , 1.5×10^{-2} , 2.0×10^{-2} , 2.5×10^{-2} , 3.0×10^{-2} , 3.5×10^{-2} , and 4.0×10^{-2} M. The pH of the final solution in each case was measured using a pH meter.

2.3.2.2. Alum solution studies on the visible absorption spectra of Wako lac dye and Thai lac dye. Wako and Thai lac dye solutions were freshly prepared prior to each determination. Wako lac dye (1.0364 g) was partially dissolved in deionized water, the mixture filtered, and the filtrate diluted to 500 mL with deionized water in a 500 mL volumetric flask. The Thai lac dye solution was prepared by treating the dye (0.5024 g) with deionized water (400 mL). This solution was filtered and the filtrate diluted to 500 mL with deionized water in a 500 mL volumetric flask. Into two series of twelve 10 mL volumetric flasks was added 0.50 mL of each lac dye solution. To the flasks, was added successively, 0.10, 0.50, 1.00, 1.50, 2.00, 2.50, 3.00, 4.00, 5.00, 6.00, 7.00, and 8.00 mL of aqueous 5×10^{-2} M $KAl(SO_4)_2 \cdot 12H_2O$ (alum). Each flask was then

diluted to the mark with deionized water and the solutions allowed to stand for 30 min. After complex formation was complete, the absorption spectra and the changes in absorbance at 537 nm were recorded on a Cary 1E UV–VIS spectrophotometer against deionized water as the blank and using quartz cells. The final concentrations of the alum solution in this experiment were as follows: 5.0×10^{-4} , 2.5×10^{-3} , 5.0×10^{-3} , 7.5×10^{-3} , 1.0×10^{-2} , 1.25×10^{-2} , 1.5×10^{-2} , 2.0×10^{-2} , 2.5×10^{-2} , 3.0×10^{-2} , 3.5×10^{-2} , and 4.0×10^{-2} M.

2.3.2.3. Nickel (II) ion solution studies on the visible absorption spectra of Wako lac dye and Thai lac dye. Lac dye solutions were prepared as noted in Section 2.3.2.2. Into each series of twelve 10 mL volumetric flasks was added 0.50 mL of lac dye solution. To the flasks, was then added consecutively, 0.10, 0.50, 1.00, 1.50, 2.00, 2.50, 3.00, 4.00, 5.00, 6.00, 7.00, and 8.00 mL of aqueous 5×10^{-2} M $Ni(NO_3)_2 \cdot 6H_2O$. Each flask was diluted to the mark with deionized water and the solutions then kept at room temperature for 30 min. After complex formation was complete, the absorption spectra and the changes in absorbance at 562 nm were recorded on a Cary 1E UV–VIS spectrophotometer against deionized water as the blank and using quartz cells. The final concentrations of nickel (II) solution in this experiment were as follows: 5.0×10^{-4} , 2.5×10^{-3} , 5.0×10^{-3} , 7.5×10^{-3} , 1.0×10^{-2} , 1.25×10^{-2} , 1.5×10^{-2} , 2.0×10^{-2} , 2.5×10^{-2} , 3.0×10^{-2} , 3.5×10^{-2} , and 4.0×10^{-2} M.

2.3.3. Determination of the mole ratio for the nickel (II) ion–laccaic acid A complex

The continuous variation (Job's) method was used to determine stoichiometry [15]. A series of aqueous solutions were prepared by mixing 5×10^{-4} M laccaic acid A and 5×10^{-4} M $Ni(NO_3)_2 \cdot 6H_2O$ and diluting to 5.00 mL with ethanol. The pH of each solution was measured, and the pH range observed was 2.8–4.2. The mixtures were allowed to stand at room temperature for at least 30 min and the changes in absorbance at λ_{max} of the longest wavelength absorption band were then measured.

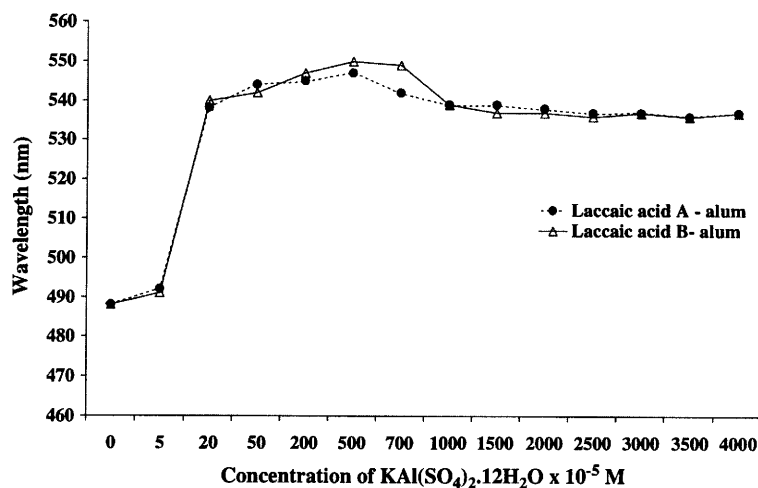


Fig. 3. The effect of alum concentrations on the most intense visible absorption band of laccaic acids A and B.

the bands absorbing at the longest wavelengths, and these changes were characteristic of the metal ion. With aluminum (III) ions, the λ_{\max} value of the long wavelength absorption band was observed at 537 nm and with nickel (II) ions, two bands at λ_{\max} values of approximately 523 and 562 nm were observed. In the absence of metal ions, Thai lac dye itself had a long wavelength absorption maximum at 487 nm.

Metal ions also caused a bathochromic shift of the long wavelength absorption bands of laccaic acids A and B themselves with increasing ion concentrations, for example with alum (Fig. 3). It was also observed that there was little change in pH (ca 4.0) over alum concentration ranges of 5.0×10^{-5} M to 4.0×10^{-2} M (Table 1). It is probable that the bathochromic shift observed with laccaic acids A and B, as with other dyes [20], occurs as a result of coordination by the lone pair

electrons on the N or O donor atoms with the aluminum ion site, thus stabilizing the excited state relative to the ground state leading to longer wavelength absorption maxima [19,20] (Tables 2 and 3). In addition, an increase of the absorption intensity within the range of alum concentration was observed as shown in Table 4. This behaviour of laccaic acids is similar to the other dyes [20] where the increased absorption intensity plateaued at higher concentrations.

The effect of varying alum concentrations on Thai lac dye compared to Wako lac dye absorption spectra is presented in Fig. 4, and a similar bathochromic shift of the lac dye band was observed as for the laccaic acids. This result is consistent with these acids being the major components of the dyes. A greater absorbance difference between the dyes was observed on monitoring at λ 537 nm (Table 3). It is apparent

Table 1
Changes in pH of solutions of laccaic acids with alum and nickel (II) ion

Solution	Laccaic acid concentration (M)	Ion concentration (M)	pH
Laccaic acid A-alum	9.31×10^{-5}	5.0×10^{-5} – 4.0×10^{-2}	4.45–3.90
Laccaic acid B-alum	1.05×10^{-4}	5.0×10^{-5} – 4.0×10^{-2}	4.58–3.97
Laccaic acid A-Ni(II)	9.31×10^{-5}	5.0×10^{-5} – 4.0×10^{-2}	4.90–4.44
Laccaic acid B-Ni(II)	1.05×10^{-4}	5.0×10^{-5} – 4.0×10^{-2}	5.00–4.37

Table 2
Changes in pH of solutions of Wako lac dye and Thai lac dye with alum and nickel (II) ion

Solution	Lac dye concentration (ppm)	Ion concentration (M)	pH
Wako lac dye–alum	49	5.0×10^{-4} – 4.0×10^{-2}	3.73–3.32
Thai lac dye–alum	50	5.0×10^{-5} – 4.0×10^{-2}	4.10–3.37
Wako lac dye–Ni(II)	49	5.0×10^{-5} – 4.0×10^{-2}	4.39–4.02
Thai lac dye–Ni(II)	50	5.0×10^{-5} – 4.0×10^{-2}	5.63–5.12

that Thai lac dye, which was not as pure as Wako lac dye, absorbed less strongly. Furthermore, the pH of the Thai lac dye solution was consistently higher than Wako lac dye at all alum concentrations (Table 2).

The results of the study of nickel (II) ion effects on the visible spectra (λ_{\max}) of laccaic acids A and B and the lac dyes are presented in Figs. 5 and 6 which indicated the larger bathochromic shift of laccaic acids A and B as the metal ion concentration increased. This behaviour was also observed in Wako lac dye and Thai lac dye. The higher metal ion concentration presumably results in stronger interaction with the dyes stabilizing the excited state and leading to a lower energy separation from the ground state. When the concentration of nickel (II) ions increased within the range of concentrations studied, the intensity of the long wavelength absorption band of laccaic

acids A and B and Wako lac dye increased except in the case of Thai lac dye which was not much affected as shown in Tables 3 and 4. The different behaviour of Thai lac dye from laccaic acids A and B and Wako lac dye, was consistent with the lower purity of Thai lac dye hence the lower absorption. The similar pattern of behaviour of laccaic acids A and B and the lac dyes again indicated similar chromophores for these substances. These visible absorbance results differ in some respects from the interactions of other dyes with metal ions [20] where the increased absorption intensity plateaued at higher concentrations.

3.3. Nickel (II)–laccaic acid A complex

The mole ratio of nickel (II):laccaic acid A as determined by Job's method (Fig. 7) was 1:1 and it

Table 3
Absorbance value dependence of Thai lac dye and Wako lac dye on concentrations of alum at $\lambda = 537$ nm and nickel (II) ion at $\lambda = 562$ nm

Alum concentrations $\times 10^{-4}$ (M)	Absorbance of Thai lac dye–alum	Absorbance of Wako lac dye–alum	Ni(II) ion concentrations $\times 10^{-4}$ (M)	Absorbance of Thai lac dye–Ni(II)	Absorbance of Wako lac dye–Ni(II)
0	0.1085	0.3068	0	0.0503	0.0633
5	0.2470	0.7192	5	0.2253	0.1968
25	0.2737	0.8502	25	0.2467	0.3626
50	0.2906	0.8966	50	0.2407	0.4451
75	0.2890	0.9064	75	0.2444	0.4933
100	0.2918	0.9412	100	0.2502	0.5041
125	0.2908	0.9479	125	0.2540	0.5404
150	0.3037	0.9548	150	0.2651	0.6035
200	0.2989	0.9421	200	0.2715	0.6870
250	0.3004	0.9917	250	0.2672	0.6837
300	0.3022	0.9726	300	0.2655	0.7694
350	0.3090	1.0245	350	0.2723	0.7521
400	0.3139	1.0382	400	0.2724	0.7373

Table 4

Absorbance value dependence of laccaic acids A and B on concentrations of alum at $\lambda = 537$ nm and nickel (II) ion at $\lambda = 562$ nm

Alum concentrations $\times 10^{-5}$ (M)	Absorbance of laccaic acid A–alum	Absorbance of laccaic acid B–alum	Ni(II) ion concentrations $\times 10^{-5}$ (M)	Absorbance of laccaic acid A–Ni(II)	Absorbance of laccaic acid B–Ni(II)
0	0.4621	0.4386	0	0.1257	0.1123
5	0.6526	0.6011	5	0.2022	0.1313
20	0.9887	1.0098	20	0.2598	0.2821
50	1.0025	1.1130	50	0.3866	0.2991
200	1.1789	1.2335	200	0.5222	0.5230
500	1.3032	1.3727	500	0.6424	0.7365
700	1.2960	1.4284	700	0.7620	0.7689
1000	1.3832	1.4615	1000	0.8140	0.8004
1500	1.4121	1.4547	1500	0.8655	0.8784
2000	1.4371	1.4916	2000	0.9090	1.0428
2500	1.4639	1.5357	2500	1.0254	0.9936
3000	1.4880	1.5156	3000	0.9979	1.0056
3500	1.5205	1.5034	3500	1.0526	1.0272
4000	1.4927	1.5391	4000	1.0771	1.0807

is likely that the rest of the coordination sites of nickel (II) ion would be occupied by solvent molecules. Computer-based molecular modelling studies using the Spartan '02 computer program (AM1/PM3; '02 Linux/Unix) were then undertaken to assess possible structures for this 1:1 nickel (II)–laccaic acid A complex. In the modelling process, water was included as a ligand, and the phenolic and carboxylic acid groups were not ionized since in the experimental study the solution

was in the pH range 2.8–4.2. The complex shown in Fig. 8 was the one with the lowest heat of formation (-195 kJ/mol) and it incorporated the quinone carbonyl oxygen and the phenolic group as ligands and four water ligands in the octahedral complex. Interestingly, the complex structure was also stabilized by hydrogen bonding interactions with the carboxylic acid functionality, and a phenolic group and the acetamide carbonyl group in the aryl substituent. These interactions, together

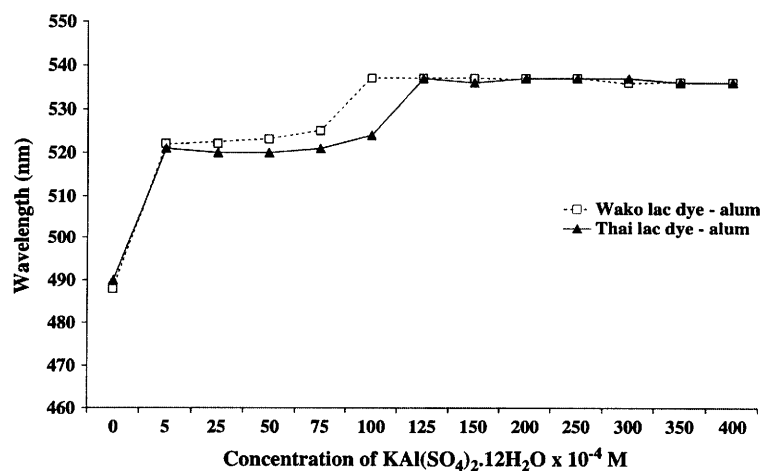


Fig. 4. The effect of alum concentrations on the most intense visible absorption band of Wako and Thai lac dye.

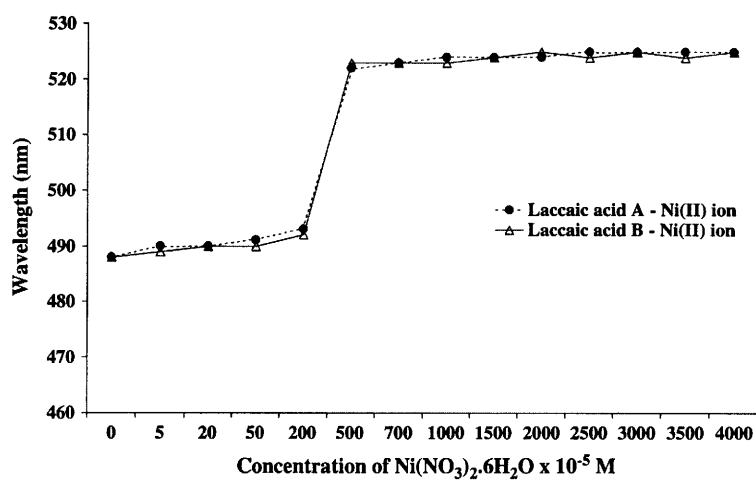


Fig. 5. The effect of nickel (II) ion concentrations on the visible absorption band of laccaic acids A and B.

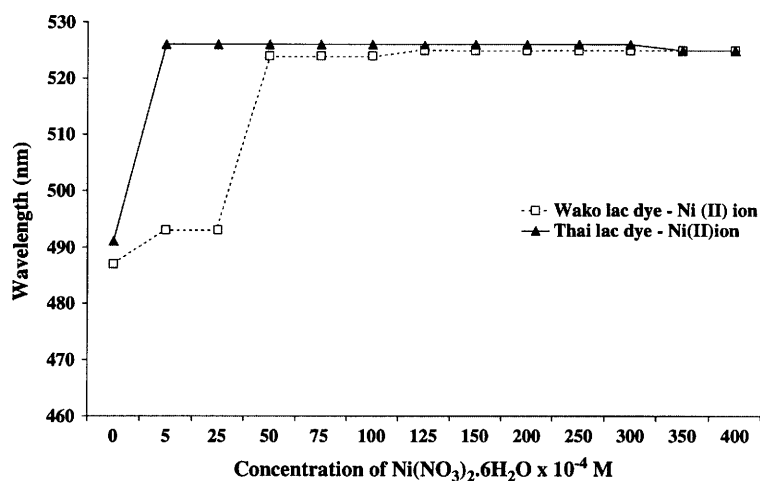


Fig. 6. The effect of nickel (II) ion concentrations on the visible absorption band of Wako lac dye and Thai lac dye.

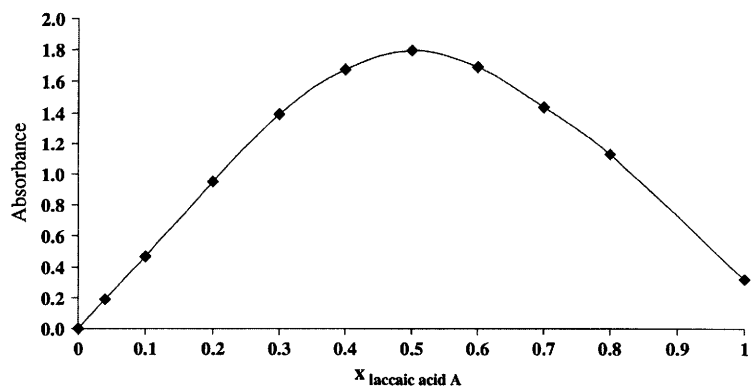


Fig. 7. Determination of the mole ratio for nickel (II) ion-laccaic acid A complex in ethanol.

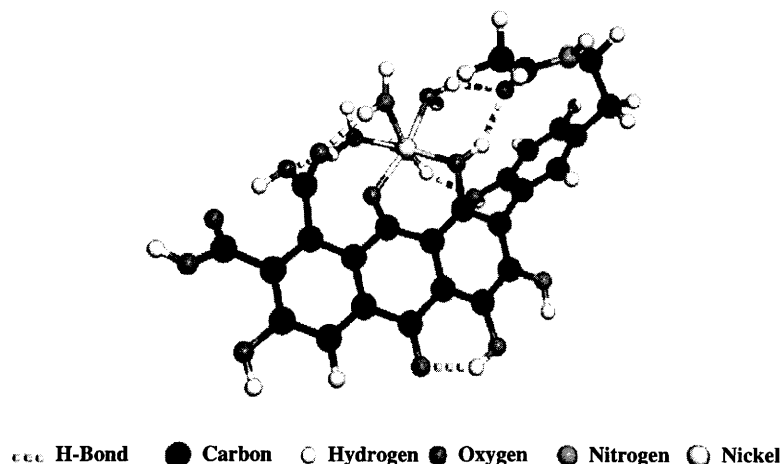


Fig. 8. The proposed structure of nickel (II) ion–laccaic acid A complex from computer-based modelling (Spartan '02 Linux/Unix; PM3).

with increased electron density at the quinone carbonyl oxygen from lone pair electron delocalization from the phenolic groups at positions 3 and 6, presumably account for this preference for nickel ion complex formation at the position proposed. In support of the latter point, an electrostatic potential map (Spartan program, AM1) of laccaic acid A confirmed higher negative potential at the 9-quinone carbonyl oxygen group compared with the potential at the other quinone group.

4. Conclusions

When the pH of the lac dye solution was increased from 2.5 to 11, a substantial bathochromic shift of the lac dye visible absorption band was observed in both Wako and Thai lac dyes. Also increasing the metal ion concentration, for both alum and nickel (II) ion, caused a bathochromic shift of the visible absorption bands in both dyes (and in their laccaic acid components, laccaic acids A and B). The bathochromic shifts observed are consistent with the lone pair electrons in the donor atoms (N and O in the lac dyes/laccaic acids) participating in metal ion coordination and stabilizing the excited state relative to the ground state. Support for this participation was obtained from

a modelling study on the proposed nickel (II)–laccaic acid A complex.

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