Electronic Spectral Studies of Nickel(II) Alanine Complexes

AWNI A. KHATIB* and MICHAEL H. ENGEL

School of Geology and Geophysics, The Energy Center, 100 E. Boyd St., University of Oklahoma, Norman, OK 73019 (U.S.A.)

(Received March 2, 1989; revised June 29, 1989)

Abstract

The electronic absorption spectrum of hydrated nickel(II) exhibits three bands, a broad band λ_{max} at 658 nm and two sharp bands with λ_{max} at 394 and 302 nm. The electronic absorption spectrum of Ni(II) and D- and L-alanine in aqueous solution shows the same three characteristic bands, but with λ_{max} at 618, 370 and 302 nm, with the absorption intensities increased for the first two bands. The three bands are assigned to the three spin-allowed d–d transitions $^3A_2g \rightarrow {}^3T_2g$, $^3A_2g \rightarrow {}^3T_1g(F)$ and $^3A_2g \rightarrow {}^3T_1g(P)$ of octahedral nickel(II). Information about the Ni(II) complex formation mechanism and nature of the products was obtained from isosbestic points and pH profile studies of electronic spectra and amino acid racemization rates.

Introduction

Previous studies have reported absorption spectra for solutions of nickel(II) and D,L-histidine in the visible [1], infrared and ultraviolet regions [2], the structures of bis(D,L-histidinato) nickel(II) in addition to the structure for single crystal Ni(D,L-his)$_2$·H_2O and Ni(L-his)$_2$·H_2O [3]. For both compounds, the histidine ion acts as a tridentate ligand, coordinating to the metal ion through three of the four possible functional groups. Hydrated nickel(II) ions [4–6] and other nickel(II) complexes with nitrogen and oxygen bidentate ligands have also been studied [6–12].

It has previously been shown that nickel(II), when complexed to L-alanine, retards the rate of racemization of L-alanine, in contrast to Cu(II), Cr(III), Co(III), Pd(II) and Pt(II), all of which enhanced the racemization rate of L-alanine [13]. Additional evidence for the novel behavior of nickel(II) was obtained by the reaction of benzylchloride with the glycine complex of Cu(II), Co(II) and Ni(II). Upon ultrasound irradiation, the formation of *N*-benzylglycine was enhanced by complexation with Cu(II) and Co(III) whereas no reaction was reported for the Ni(II) complex [14].

In this paper further documentation is presented for the apparently unique behavior of nickel(II) with respect to its complexation with amino acid enantiomers. We report electronic spectra for the complexation of Ni(II) with D- and L-alanine at varying pH. An attempt is also made to further assess the effects of Ni(II) on the racemization rate of L-alanine in the pH range of 2–10.

Experimental

Reagents

D-Alanine and L-alanine were obtained from Sigma Chemical Co. (St. Louis, MO). Nickel(II) nitrate and potassium hydroxide were obtained from Fisher Scientific (Houston, TX). All reagents were used without further purification.

Complex Formation and pH Treatment

Aqueous solutions of nickel(II) nitrate (0.1 M, pH 3.9), D-alanine (0.2 M, pH 5.5) and L-alanine (0.2 M, pH 5.5) were prepared. After recording the electronic spectra of the individual mother solutions, the D- and L-alanine solutions were added to the nickel(II) nitrate solution to give a final volume of 80 ml, with $[Ni^{2+}]$ = 0.05 M, [L-ala] = 0.05 M and [D-ala] = 0.05 M. The pH of this solution was 4.0. An electronic spectra of this solution was recorded prior to varying pH as discussed below.

The pH of the 80 ml solution containing nickel(II) nitrate, D-alanine and L-alanine was adjusted by the addition of aliquots of a 1.0 M solution of KOH. Four milliliter aliquots of the solution were withdrawn at pH values of 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 8.0, 8.5 and 9.5. Electronic spectral data were recorded for each of these aliquots. A portion of the solution that was removed at pH = 8.0 was allowed to crystallize. After three days, the resulting deep blue crystals were washed with ether and dried under vacuum. Elemental analysis of the crystals revealed that the complex nickel bis(alaninato)·2H_2O had formed. The elemental analysis was performed at

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

© Elsevier Sequoia/Printed in Switzerland

TABLE 1. Absorption spectra intensities at λ_{max} for nickel(II) solution with alanine at various pH

pH	$\lambda_{max\,1}$ (nm)	Intensity at $\lambda_{max\,1}$	$\lambda_{max\,2}$ (nm)[a]	Intensity at $\lambda_{max\,2}$	$\lambda_{max\,3}$ (nm)[a]	Intensity at $\lambda_{max\,3}$
3.9[b]	302	1.4887	394	0.5129	658	0.1847
4.0[c]	302	0.8139	394	0.2857	658	0.1057
4.5	302	0.6892	393	0.2440	657	0.0967
5.0	302	0.6907	390.5	0.2575	655	0.1157
5.5	302	0.6960	387	0.2793	649.5	0.1376
6.0	302	0.6701	382	0.2897	644	0.1530
6.5	302	0.6679	379.5	0.3183	635.5	0.1780
7.0	302	0.6687	376	0.3456	627	0.1978
8.0	302	0.6622	370.5	0.3828	619.5	0.2277
8.5	302	0.6851	370.5	0.4116	618.5	0.2432

[a]Note the gradual shift to lower wavelength and increased intensities for $\lambda_{max\,2}$ and $\lambda_{max\,3}$ with increasing pH. [b]0.1 M nickel(II) nitrate solution. It should be noted that the values reported for this solution are not in agreement with previously reported values [4, 5]. In the present study, absorptions for the nickel(II) nitrate solution (cm^{-1}) are 15 000, 25 000 and 33 000. Previous literature values [4, 5] were 8500, 13 800 and 25 300. Whereas sample concentration and instrumentation for this study differs from the previous work [4, 5], the explanation for this difference is as yet uncertain. [c]Whereas values at pH 3.9 are only for the nickel(II) nitrate solution, all values for pH 4.0–8.5 are for the nickel(II) alanine solution. Note that the concentration of nickel(II) in these solutions is 0.05 M.

Galbraith Laboratories, Knoxville, TN. Calc. for $[Ni(C_3H_6NO_2)_2(H_2O)_2]$: C, 26.59; H, 5.95; N, 10.33. Found: C, 26.72; H, 6.09; N, 10.31%.

Racemization Study

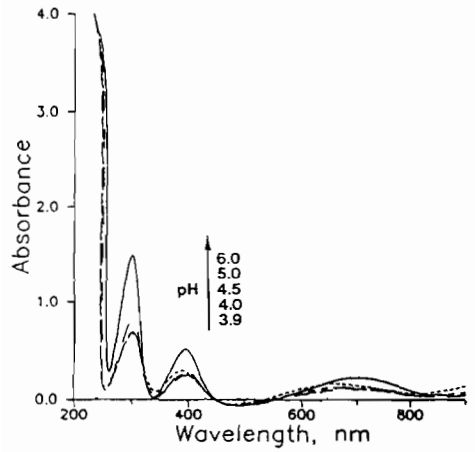
An aqueous solution consisting of 0.05 M nickel(II) and 0.1 M L-alanine was prepared as described above. Aliquots of this solution were adjusted to pH 2, 3, 7 and 10. Portions of the individual solutions were placed in Pyrex tubes which were subsequently sealed. An aqueous solution consisting of only L-alanine was also prepared. Aliquots of this solution were adjusted to pH 2, 3, 7 and 10, placed in individual Pyrex tubes and sealed. The sealed tubes were heated at 121 °C for varying lengths of time. After heating, the tubes containing the initial solution of nickel(II) and L-alanine were opened and the solutions were treated with sodium sulfide to release the amino acid from the complex. Aliquots of these solutions as well as the solutions of varying pH that contained only L-alanine as the starting material were evaporated to dryness. The individual amino acid residues were esterified and acylated for gas chromatographic analysis with a chiral stationary phase as previously reported [15]. Racemization rates for alanine in the individual solutions were calculated by plotting $0.5 \ln[(1 + D/L)/(1 - D/L)]$ versus time, where D and L are the concentrations of D- and L-alanine, respectively.

Instrumentation and Data Analysis

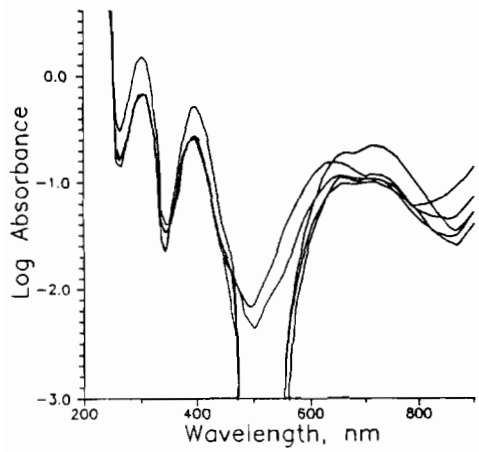
The pH measurements were recorded using a Fisher Model 140A pH meter and Fisher electrodes. The electronic spectra were recorded on Response™ using a UV–Vis spectrophotometer (Gilford A, Corning Lab. Sci. Co.) and Fisher brand UV rectangular curvets. The resulting spectral data were analyzed using a computerized statistical package.

Results and Discussion

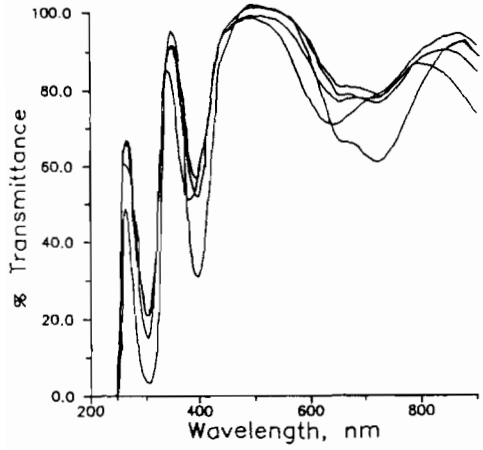
The electronic spectra of nickel(II) hexaqua ion and nickel(II) D- and L-alanine recorded in unbuffered aqueous solution at 900–200 nm (11 000–50 000 cm^{-1}) show three absorptions. At pH 3.9, the solution is pale green and has λ_{max} values of 302, 394 and 658 nm with molar absorbtivity (ϵ) of 15, 5 and 2 M^{-1} cm^{-1}, respectively (Table 1). These absorptions are typical of six-coordinated nickel(II) complexes [16]. As the pH of the system is raised from 3.9 to 8.5 the color gradually changes from green to deep blue with a gradual shift to shorter wavelengths and higher intensities. At pH 8.5 three λ_{max} are observed at 302, 370.5 and 618.5 nm with ϵ values of 14, 8 and 5 M^{-1} cm^{-1}, respectively (Figs. 1 and 2). In the pH range 3.9–8.5 the intensities and maximum absorption wavelengths (λ_{max}) of the band at 302 nm (33 000 cm^{-1}) remained constant. This absorption is assigned to the transition $^3A_2g \rightarrow {}^3T_1g(P)$ $(xz, yz \rightarrow z^2)$. The bands at 394 (25 000 cm^{-1}) and 658 (15 000 cm^{-1}) nm increased in intensity and shifted to lower wavelengths with increasing pH. This indicates that (1) the splitting field of the alanine ligand is stronger than that of water for the transitions $^3A_2g \rightarrow {}^3T_1g$ $(xz, yz \rightarrow x^2-y^2)$ and $^3A_2g \rightarrow {}^3T_2g(F)$ $(xy \rightarrow x^2-y^2)$ and (2) the axial position of the nickel(II) complex continued to be occupied by two water molecules from pH 3.9 through 8.5 (Fig. 3).



(a)

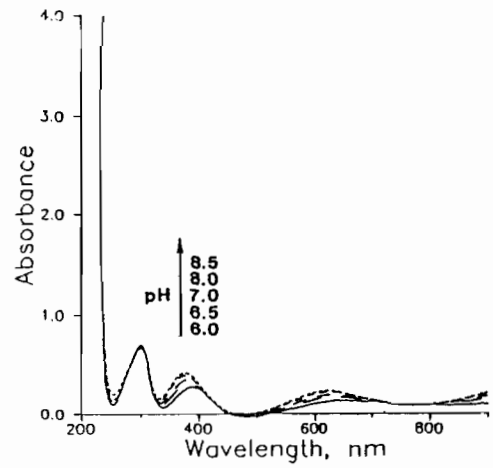


(b)

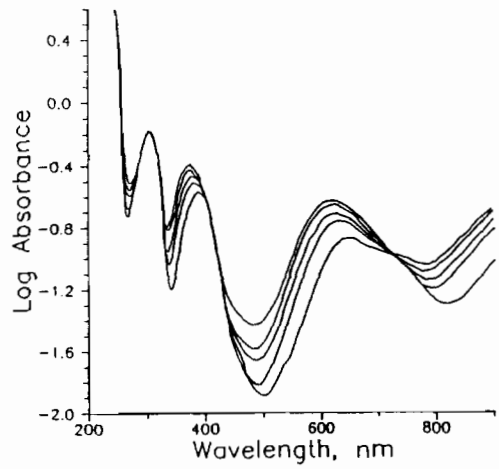


(c)

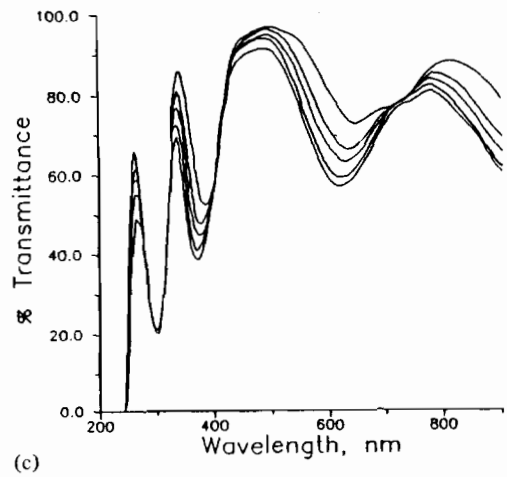
Fig. 1. The absorption spectra of an aqueous solution of the nickel(II) alanine complex at the pH values 3.9, 4.0, 4.5, 5.0 and 6.0. The spectra at pH 3.9 and 6.0 are taken to represent the diprotonated and monoprotonated nickel ion complexes, respectively. The spectra at intermediate pH represent mixtures of the two species.



(a)



(b)



(c)

Fig. 2. The absorption spectra of an aqueous solution of nickel(II) alanine at the pH values 6.0, 6.5, 7.0, 8.0 and 8.5. The spectra at pH 6.0 and 8.5 are taken to represent the monoprotonated and uncharged nickel complex, respectively. The spectra at intermediate pH represent mixtures of the two species. Both species have the same molar absorptivity at about 323, 420 and 730 nm. Consequently, the spectra all cross at these wavelengths forming isosbestic points.

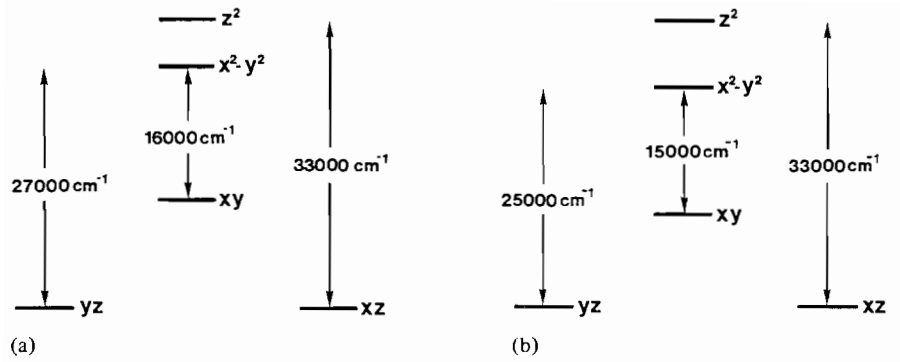
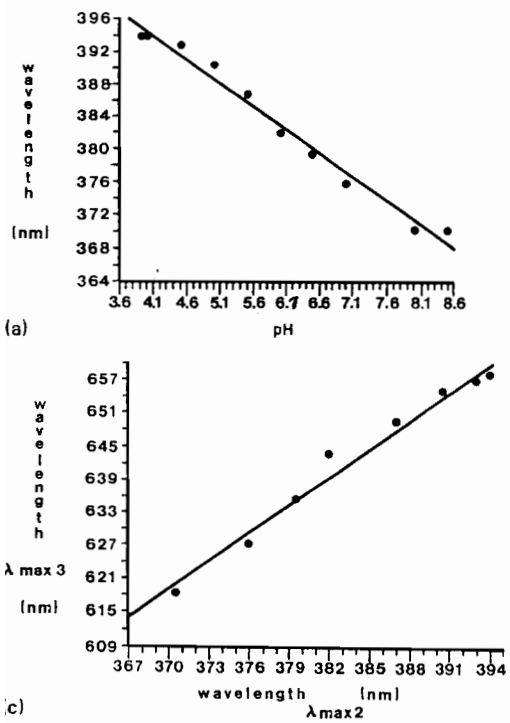


Fig. 3. The degenerate d orbitals are split by the hexaqua field (a) and the bis-alaninato diaqua field (b). The $xz, yz \rightarrow z^2$ energy difference remained constant for both fields, which indicates that the axial positions continued to be occupied by two water molecules.

The results of this pH study indicate that the maximum absorption wavelength of the nickel(II) alanine complex is linearly proportional to pH (Fig. 4). This linear relationship along with the isosbestic points at 323, 420 and 730 nm (sharp) suggest the stepwise binding of the amino acid with nickel(II). It is proposed that the formation of the uncharged complex (at pH = 8.5) proceeds through the formation of a singly charged nickel(II) (alaninato) (alanine) diaqua intermediate at pH = 6 by binding with two monodentate amino acid ligands (Fig. 5). The formation of the neutral nickel(II) bis-alaninato diaqua complex results from binding with the other end of the alanine bidentate ligand as ($NH_2(CH_3)$-CH–CO_2^-). The spectra at intermediate pH represent mixtures of the two species. Both species have the same molar absorptivity at the isosbestic points.

The increase in the racemization rates for alanine under acidic conditions (Table 2) may be due to the formation of the protonated alanine which will enhance the formation of the carbanion (racemization intermediate) in addition to the fact that the solution contains 0.05 M nickel(II) which increases the ionic strength. The retardation of the racemization rate at higher pH can be correlated to the stepwise formation of the nickel(II) bis-alaninato diaqua



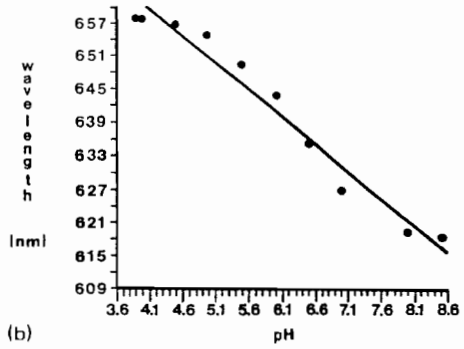


Fig. 4. The maximum absorption wavelength (λ_{max}) as a function of pH shows an almost linear relationship with a correlation coefficient ≥ 0.99. (a) $\lambda_{max\,2}$ vs. pH; (b) $\lambda_{max\,3}$ vs. pH; (c) $\lambda_{max\,3}$ vs. $\lambda_{max\,2}$.

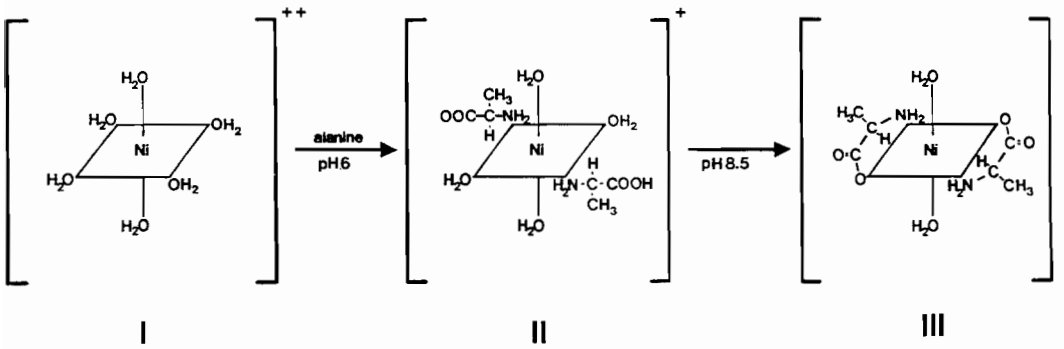


Fig. 5. The stepwise binding of the bidentate ligand as pH increases. The formation of the zwitterion resulted in II whereas the formation of the deprotonated alanine resulted in III.

TABLE 2. Reaction rate constants ($k \times 10^7$ s^{-1}) for the racemization of free and nickel(II) L-alanine complex at 121 °C

pH	Free alanine	Complex
2	0.288	0.445
3	0.882	1.130
7	1.740	1.060
10	3.720	1.860

complex under neutral and basic conditions. The formation of the planar carbanion might have been hindered due to the rigid structure of alanine in the stable complex. Moreover, the possible development of a partial negative charge on the amide (–NH–) or carboxyl coordination site would retard the formation of the carbanion.

As previously reported [13] and as indicated above, nickel(II) complexes with amino acids are apparently unique in that in the neutral to slightly basic pH range these complexes retard amino acid racemization whereas other metals apparently enhance it [13]. Additional experiments are planned to further evaluate the anomalous behavior of the nickel(II) complexes, in particular with respect to their possible role in enhancing the concentration of L-amino acid enantiomers in the primordial seas prior to the origin of life.

Acknowledgements

Awni A. Khatib wishes to thank Hebron University, West Bank for sabbatical leave and CIES for a Fulbright Scholarship for support of this research. M. H. Engel acknowledges the National Science Foundation, Division of Earth Sciences (Grant No. EAR-8352055) for partial support of this research.

References

1 C. K. Jorgensen, *Acta Chem. Scand., 10* (1956) 887.
2 P. L. Meredith and R. A. Palmer, *Inorg. Chem., 10* (1971) 1049.
3 K. A. Fraser and M. M. Harding, *J. Chem. Soc. A,* (1967) 415.
4 C. K. Jorgensen, *Adv. Chem. Phys., 5* (1963) 33.
5 A. Bose and R. Chatterjee, *Proc. Phys. Soc., 83* (1963) 23.
6 A. B. P. Lever, I. M. Walker and P. J. McCarthy, *Inorg. Chim. Acta, 44* (1980) L143.
7 C. K. Jorgensen, *Acta Chem. Scand., 9* (1955) 1362.
8 G. N. Rao and N. C. Li, *Can. J. Chem., 44* (1966) 1637.
9 W. F. Stack and H. A. Skinner, *Trans. Faraday Soc., 63* (1967) 1136.
10 S. Boyd, J. R. Brannan, H. S. Dunsmore and G. H. Nancollas, *J. Chem. Eng. Data, 12* (1967) 601.
11 A. B. P. Lever, P. Paoletti and L. Fabbrizzi, *Inorg. Chem., 18* (1979) 1324.
12 O. N. Puplikova, L. N. Akimova and I. A. Savich, *Vestn. Mosk. Univ., Khim., 21* (1966) 56.
13 G. G. Smith, A. Khatib and G. S. Reddy, *J. Am. Chem. Soc., 105* (1983) 293.
14 G. G. Smith and G. S. Reddy, *Inorg. Chim. Acta, 133* (1987) 1.
15 G. S. Reddy and G. G. Smith, *Inorg. Chim. Acta, 96* (1985) 199.
16 A. B. P. Lever, *Inorganic Electronic Spectroscopy,* Elsevier, Amsterdam, 1984, p. 507.