

Spectral and electrochemical properties of copper(II) complexes of alicyclic- α -amino acids

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Abstract. Spectral, cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies on some bis(alicyclic- α -amino acidato)copper(II) complexes, CuL_2 , where L is alicyclic α -amino acid, at various pH values have been carried out in aqueous media. Electronic absorption and ESR spectral studies at lower pH levels indicate formation of protonated species. At neutral pH these complexes undergo a reversible one-electron $\text{Cu(II)} \rightleftharpoons \text{Cu(I)}$ redox process at about -0.24 V vs saturated calomel electrode (SCE), at the hanging mercury drop electrode. The electrochemical behaviour of the complexes at lower pH values is discussed in terms of the different species present.

Keywords. Bis(alicyclic- α -amino acidato)copper(II) complexes; cyclic voltammetry; differential pulse voltammetry; redox behaviour; ESR spectroscopy.

1. Introduction

Involvement of copper enzymes in the biological activities of several α -amino acids has led to studies on copper(II) alicyclic α -amino acid complexes (Zand *et al* 1974; Graddon and Munday 1961, 1963; Yokoi *et al* 1972). Biosynthesis of plant growth hormone, ethylene, from methionine is found to proceed through 1-amino cyclopropane-1-carboxylic acid intermediate where copper is found to play an important role (Mapson and Wardle 1966; Adams and Yard 1978). Some of the other alicyclic- α -amino acids are also known to be biologically active (Connors *et al* 1958). While preparation and electronic spectra at neutral pH for some copper(II) alicyclic α -amino acid complexes are reported (Graddon and Munday 1961, 1963) their redox properties have not been investigated so far. Therefore, these properties have been examined by CV and DPV techniques at various pH levels. Structural changes at low pH values have been studied by electronic and ESR spectral methods.

2. Experimental

The complexes, bis(1-amino cyclopropane-1-carboxylato)copper(II) monohydrate (**1**), bis(1-amino cyclobutane-1-carboxylato)copper(II) (**2**), bis(1-amino cyclopentane-1-

* For correspondence

carboxylato)copper(II) (3), bis(1-amino cyclohexane-1-carboxylato)copper(II) monohydrate (4) and bis(1-amino cycloheptane-1-carboxylato)copper(II) (5) were prepared by known procedures (Mapson and Wardle 1966).

Electronic absorption spectra in aqueous medium were recorded at 300 K using a Shimadzu UV-200S Double Beam Spectrophotometer and ESR spectra on a JEOL JES FE-3X Spectrometer. Cyclic and differential pulse voltammograms were recorded at 300 K using PAR 370 Electro chemical system which includes 174 A Polarographic Analyzer, 175 Universal Programmer, RE0074 X-Y Recorder and a 377 A Cell system. Hanging mercury drop electrode was used as the working electrode along with a Pt wire auxiliary electrode. Approximately 1×10^{-3} M solutions of the complexes were used for the experiments. NaClO_4 (10^{-1} M) was the supporting electrolyte. The potentials reported are with reference to saturated calomel electrode at 300 K and are uncorrected for liquid junction potential. The pH adjustment was done by adding drops of pure HClO_4 acid or NaOH solutions.

3. Results and discussion

3.1 Spectral data

The purity of the complexes was checked by elemental analysis and IR spectra. They have the general composition CuL_2 where L represents various alicyclic amino acids. Electronic spectra of the complexes in aqueous media at neutral pH show an absorption maximum in the region 620–605 nm. The λ_{max} values are presented in table 1 and are in the order $1 > 2 > 3, 4 > 5$. Although variation of λ_{max} values is small, it reflects the increasing tetragonal distortion due to increasing ring size in complexes (Graddon and Munday 1961). At lower pH value λ_{max} shifts to higher wavelengths. It is known that in the case of bis(α -amino acidato)copper(II) complexes, the CuL_2 concentration decreases on lowering of pH with simultaneous formation of $[\text{CuL}]^+$ species with its maximum concentration at pH 4 (Beattie *et al* 1976). At pH < 3, Cu(II)(aq) is the major species. Concentration of species such as $[\text{CuL}_2]^+$, $[\text{CuHL}]^{2+}$ etc., are insignificant at pH < 3. The absorption spectrum of $[\text{CuL}]^+$ species exhibits a band at about 720 nm. The gradual shift of the $d-d$ transition from 620 nm at neutral pH to 720 nm on lowering the pH is due to the formation of $[\text{CuL}]^+$ species together with small amounts of other species. Based on the spectral data and known stability constants (Irving and Pettit 1963) generalized species distribution curves for the complexes are shown in figure 1. From these distribution curves it is clear that $[\text{CuL}]^+$ begins to form at pH 6.5. At pH 5.5, concentration of CuL_2 and $[\text{CuL}]^+$ species are very close to each other.

ESR spectra of the complexes at room temperature (300 K) at various pH values also support the species formation. At neutral pH the general four-line pattern ($g_{\text{iso}} = 2.11$ and $A_{\text{iso}} = 7.0$ mT) is obtained. In the pH range 6 to 4.5, the spectra show a high field component arising from the presence of $[\text{CuL}]^+$ species together with CuL_2 . At pH 4, the four-line pattern ($g_{\text{iso}} = 2.15$ and $A_{\text{iso}} = 5.5$ mT) reemerges. The g_{iso} and A_{iso} values in the pH range 6 to 4.5 are characteristic of $[\text{CuL}]^+$ species (Goodman *et al* 1981). Thus the ESR spectral changes clearly indicate the depletion of CuL_2 and formation of $[\text{CuL}]^+$ species at low pHs. Concentration of CuL_2 at pH < 5 is negligible compared to the concentration of $[\text{CuL}]^+$ species. ESR data are presented in table 1.

Table 1. Electronic and ESR spectral data of the copper complexes in aqueous media at 300 K.

Complex	pH	$\lambda_{\max}(\epsilon_{\max})$ (nm) ($M^{-1} \text{ cm}^{-1}$)	g_{iso}	A_{iso} (mT)
1	7.2	620(50)	2.144	7.03
	6.6	620	2.116	7.10
	5.6	630	2.144	5.67
	5.0	650	2.144	5.67
	4.0	680	2.144	5.67
2	7.2	615(70)	2.115	6.67
	6.5	630	2.115	6.60
	6.0	680	2.144	5.50
	5.1	720	2.143	5.80
	4.5	^a	2.144	5.80
3	7.2	610(65)	2.112	7.00
	6.2	625	2.139	5.23
	5.4	670	2.137	5.67
	4.7	710	2.139	5.67
	4.0	^a	^b	^b
4	7.2	610(75)	2.110	7.00
	6.5	615	2.141	5.67
	5.6	640	2.138	5.83
	4.7	690	2.139	6.00
	3.8	^a	^b	^b
5	7.2	605(80)	2.110	7.10
	6.5	630	2.142	5.30
	5.7	670	2.135	5.70
	5.0	690	2.135	5.67
	3.9	^a	^b	^b

^a Broad peak, could not be measured precisely; ^b ESR lines absent.

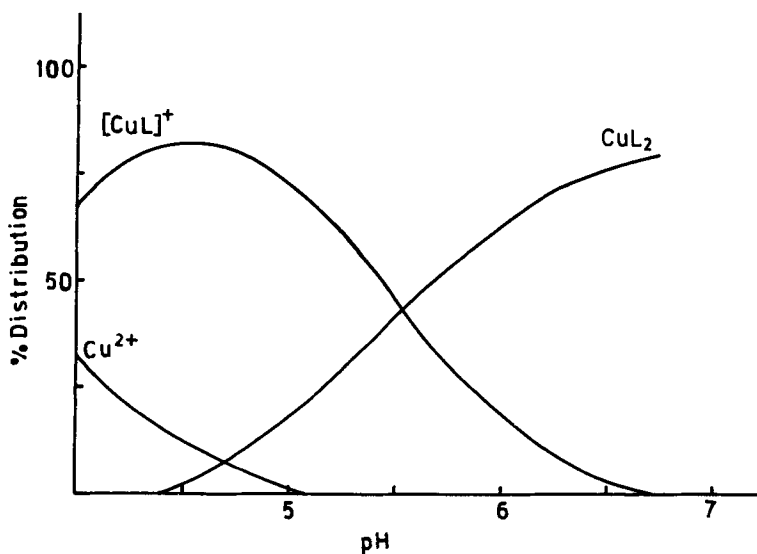


Figure 1. Possible species distribution for 1:2 copper(II)-alicyclic- α -amino acids as a function of pH.

3.2 Electrochemical data

Cyclic and differential pulse voltammetric data were collected at 300 K for the complexes in aqueous media. CV profiles of a representative complex are shown in figure 2. The major experimental observations are summarised below: (i) only one cathodic peak (C) is observed in the potential range -0.25 to -0.28 V in the first forward scan; (ii) during the reverse scan one anodic peak (D) in the potential range

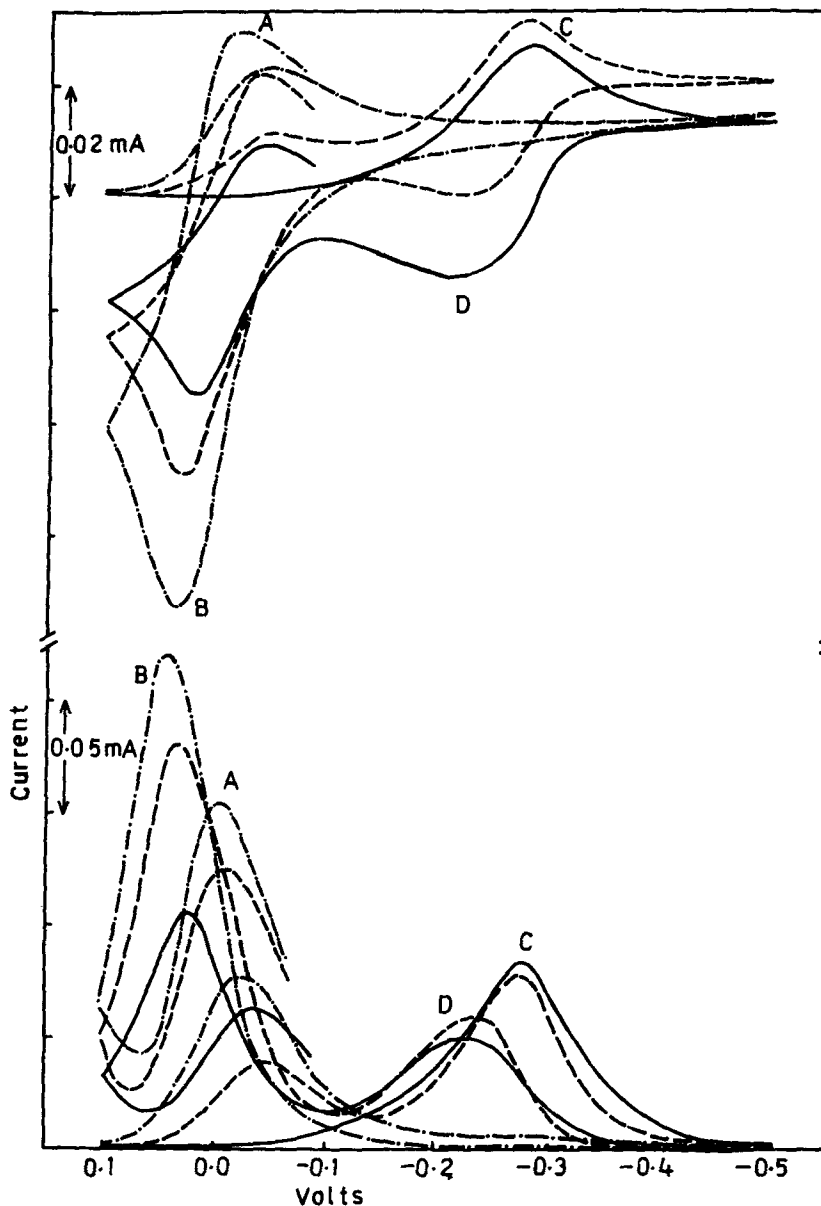


Figure 2. CV and DPV profiles of complex 2 at pH 7.2 (—) pH 6.0 (---); and pH 4.5 (—).

–0.19 to –0.22 V and another anodic peak (B) at 0.03 V are observed; (iii) a new cathodic peak (A) at –0.03 V appears from the second scan onwards; (iv) a substantial decrease in the current function value of A and B is observed with increasing scan rate; (v) peaks A and B do not appear if the scan is reversed at a potential \approx –0.15 V, i.e., before the appearance of peak C; (vi) holding the potential well past the peak C for a few minutes and scanning back, peak heights of A and B increase considerably while the effect on C–D peaks is marginal; (vii) the magnitude of separation between potentials of the peaks C and D (E_p (C, D)) is \approx 60 mV and the ratio of peak currents, $-i_c/i_a$ (C, D) is \approx 1. CV data of all these complexes at various scan rates are given in table 2.

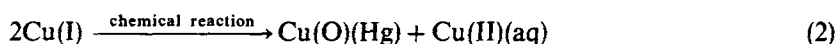
Careful consideration of the above observations leads to the following conclusions: peak C can originate from a one-electron $\text{Cu(II)} \xrightarrow{1e} \text{Cu(I)}$ reduction or a two-electron $\text{Cu(II)} \xrightarrow{2e} \text{Cu(O)}$ reduction of the CuL_2 complex. If peak C is due to one-electron reduction, the electrochemically generated Cu(I) species can undergo reoxidation to the starting complex resulting in peak D. In such case E_p (C–D) should be 60 mV. The E_p values for the complexes are in the range 60–80 mV at various scan rates and the $-i_c/i_a$ value relating to C–D peaks is found to be \approx 1 showing that the electron transfer is reversible. Observations (iii), (iv) and (v) clearly indicate that the electron transfer is

Table 2. Cyclic voltammetric data of the copper complexes at 300 K at the dissolution pH in aqueous solutions at different scan rates.

Complex	Sweep rate (V/s)	E_p (V)				$-i_c/i_a$
		A ^a	B	C	D	
1	0.01	–0.08	–0.03	–0.27	–0.21	0.87
	0.02	–0.08	–0.03	–0.27	–0.21	0.78
	0.05	^b	^b	–0.27	–0.20	0.91
	0.08	^b	^b	–0.27	–0.20	0.95
	0.10	^b	^b	–0.27	–0.20	0.94
2	0.01	–0.05	0.01	–0.28	–0.22	1.00
	0.02	–0.05	0.01	–0.28	–0.22	1.00
	0.05	–0.05	0.01	–0.28	–0.22	1.00
	0.08	–0.05	0.01	–0.28	–0.22	1.06
	0.10	–0.05	0.01	–0.28	–0.21	1.12
3	0.01	–0.03	0.02	–0.28	–0.22	1.00
	0.02	–0.05	0.02	–0.28	–0.22	1.00
	0.05	–0.06	0.02	–0.28	–0.21	0.96
	0.08	–0.06	0.03	–0.29	–0.21	0.93
	0.10	–0.06	0.03	–0.29	–0.21	1.03
4	0.01	–0.03	0.03	–0.28	–0.22	1.00
	0.02	–0.02	0.03	–0.28	–0.22	1.00
	0.05	–0.03	0.03	–0.28	–0.22	1.05
	0.08	–0.03	0.03	–0.29	–0.22	1.05
	0.01	–0.03	0.03	–0.29	–0.22	1.05
5	0.01	–0.03	0.03	–0.25	–0.19	1.00
	0.02	–0.03	0.03	–0.26	–0.20	1.00
	0.05	–0.03	0.01	–0.27	–0.20	1.00
	0.08	–0.03	0.01	–0.27	–0.20	1.05
	0.10	–0.03	0.01	–0.27	–0.20	1.05

^aPeak observed from the second scan; ^bpeak absent.

prerequisite for the observation of the peaks B and A. Peaks B and A are shown to result from $\text{Cu(O)} \xrightleftharpoons{2e} \text{Cu(II)}$ redox process by an independent experiment on pure copper(II) salts. Formation of Cu(O) can be due to partial decomposition/disproportionation of the electrochemically generated Cu(I) species. The overall electrode processes can be represented by



Similar electrochemical behaviour is reported for simple copper(II)- α -amino acid complexes and some of their derivatives (Thomas and Zacharias 1984, 1985; Arulsamy *et al* 1990). The second alternative of two electron process ($\text{Cu(II)} \xrightleftharpoons{2e} \text{Cu(O)}$) cannot explain the experimental observations and therefore is not considered further.

CV profiles of the complexes at lower pH values show the following changes: (i) heights of peaks C and D gradually decrease and these peaks disappear finally at

Table 3. Cyclic voltammetric data of the complexes in aqueous media at 300 K at different pHs at scan rate 0.01 V/s.

Complex	pH	E_p (V)				$-i_c/i_a$ (C, D)
		A ^a	B	C	D	
1	7.2	-0.08	-0.03	-0.27	-0.21	0.87
	6.6	-0.08	-0.02	-0.27	-0.21	0.93
	5.6	-0.08	-0.02	-0.27	-0.21	0.92
	5.0	-0.07	-0.01	-0.27	-0.21	0.92
	4.0	-0.06	-0.00	-0.26	-0.20	0.83
2	7.2	-0.05	0.01	-0.28	-0.22	1.00
	6.5	-0.05	0.03	-0.27	-0.21	1.00
	6.0	-0.03	0.03	-0.27	-0.21	1.00
	5.1	-0.02	0.03	-0.27	-0.21	0.86
	4.5	-0.02	0.04	^b	^b	—
3	7.2	-0.03	0.02	-0.28	-0.22	1.00
	6.5	-0.04	0.03	-0.28	-0.22	1.00
	5.4	-0.04	0.03	-0.27	-0.21	0.93
	4.7	-0.03	0.03	-0.27	-0.21	0.86
	4.0	-0.01	0.04	^b	^b	—
4	7.2	-0.03	0.03	-0.28	-0.22	1.00
	6.5	-0.03	0.03	-0.28	-0.22	1.09
	5.6	-0.03	0.04	-0.28	-0.22	1.09
	4.7	-0.04	0.04	-0.27	-0.21	0.83
	3.7	-0.01	0.04	^b	^b	—
5	7.2	-0.03	0.03	-0.25	-0.19	1.00
	6.5	-0.03	0.03	-0.25	-0.19	1.00
	5.7	-0.02	0.03	-0.25	-0.19	1.00
	5.0	-0.01	0.04	-0.25	-0.19	1.00
	3.9	-0.01	0.04	^b	^b	—

^a Peak observed from the second scan; ^b peak absent.

pH \approx 4; (ii) peak A begins to appear in the first scan itself as a broad peak below pH 6; (iii) peaks A and B increase in height as the heights of C and D decrease on further lowering of pH (figure 2). The CV data at low pH levels are collected in table 3. As it can be seen from figure 1 at neutral pH, CuL_2 is the major species. The CuL_2 species undergoes reversible one-electron redox process [(1)–(3)]. At pH \approx 4, $[\text{CuL}]^+$ is predominant and CuL_2 is absent. Presence of only the A–B peaks at this pH shows that the $[\text{CuL}]^+$ species undergoes two-electron redox process similar to free Cu(II)(aq) ions. Observations (ii) and (iii) can be explained since $[\text{CuL}]^+$ is present along with CuL_2 in the pH range 6–4.5.

Differential pulse voltammograms were recorded for all the complexes at various pHs with the same experimental conditions as those of CV experiments. DPV profiles of a representative complex are shown in figure 2 and data collected in table 4. DPV profiles at neutral pH show the four peaks C, D and A, B. The pH dependence of these peaks is clearly seen in figure 2. DPV results compare well with the CV data. The n value (n = number of electrons) calculated from $W_{1/2}$ values (Bard and Faulkner 1980) for the C–D peaks approximates to one indicating a one-electron redox process, a conclusion drawn from the CV data.

Table 4. Differential pulse voltammetric data of the complexes in aqueous media at different pHs at scan rate 0.010 V/s at 300 K.

Complex	pH	E_p (V)				$W_{1/2}$ (mV) ^c	
		A*	B	C	D	C	D
1	7.2	-0.06	-0.01	-0.26	-0.20	100	100
	6.6	-0.07	-0.01	-0.26	-0.21	100	100
	5.6	-0.07	0.01	-0.26	-0.21	90	100
	5.0	-0.06	0.00	-0.26	-0.20	90	90
	4.0	-0.05	0.00	-0.25	-0.20	90	90
2	7.2	-0.02	0.02	-0.27	-0.23	90	100
	6.5	-0.02	0.04	-0.27	-0.23	90	90
	6.0	-0.01	0.04	-0.27	-0.23	90	90
	5.1	-0.01	0.04	-0.27	-0.23	90	90
	4.5	-0.01	0.05	^b	^b	—	—
3	7.2	-0.02	0.02	-0.27	-0.22	100	100
	6.2	-0.02	0.05	-0.27	-0.21	90	90
	5.4	-0.02	0.06	-0.27	-0.21	90	90
	4.7	-0.01	0.04	-0.27	-0.21	90	90
	4.0	-0.01	0.05	^b	^b	—	—
4	7.2	-0.02	0.03	-0.28	-0.23	100	100
	6.5	-0.01	0.03	-0.28	-0.23	100	100
	5.6	-0.02	0.04	-0.28	-0.22	110	110
	4.7	-0.02	0.04	-0.28	-0.22	100	100
	3.8	-0.01	0.04	^b	^b	—	—
5	7.2	-0.01	0.05	-0.25	-0.20	100	100
	6.5	-0.01	0.04	-0.25	-0.20	90	100
	5.7	-0.01	0.04	-0.25	-0.20	90	100
	5.0	0.00	0.05	-0.24	-0.19	90	90
	3.9	0.00	0.05	^b	^b	—	—

*Peak observed from the second scan; ^bpeak absent; ^cthe number of electrons involved in C–D redox process can be calculated from $n = 90.4/W_{1/2}$ relation.

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