

## Synthesis and characterization of copper(II) complexes of adenine and aminoacids

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**Abstract.** Complexes  $[\text{Cu}(\text{CH}_3\text{COO})(\text{ade-H})(\text{H}_2\text{O})] \text{H}_2\text{O}$  (I),  $[\text{Cu}(\text{CH}_3\text{COO})(\text{ade-H})(0.5 \text{ ade})(0.5 \text{ H}_2\text{O})] 2\text{H}_2\text{O}$  (Ia),  $[\text{Cu}(\text{CH}_3\text{COO})(\text{ade-H})(\text{ade})] 2\text{H}_2\text{O}$  (Ib),  $[\text{Cu}(\text{ClCH}_2\text{COO})(\text{ade-H})(\text{H}_2\text{O})] \text{H}_2\text{O}$  (II),  $[(\text{Cu}(\text{CNCH}_2\text{COO})(\text{ade-H})(\text{H}_2\text{O})) \text{H}_2\text{O}]$  (III), where ade = adenine ( $\text{C}_5\text{H}_5\text{N}_5$ ), have been prepared. I, II and III on interaction with aminoacids such as glycine, alanine or glutamic acid give the complexes of the type  $[\text{Cu}(\text{XCH}_2\text{COO})(\text{aa})(\text{ade})(2\text{H}_2\text{O})]$ , where X=H, Cl or CN and Haa = aminoacid, which are characterized by elemental and thermal analyses, electronic, infrared and EPR spectroscopic studies and variable temperature magnetic susceptibility measurements. Simple adeninato complexes are found to be dimeric, involving the bridging of the anionic adenine through the imidazole (N9) and the pyrimidine (N3) nitrogens and the acetato group through the carboxylate oxygens, while mixed adenine–aminoacidato complexes are monomeric, involving the bonding of the N(7) of adenine, the oxygen of acetate and chelation of the aminoacid, in addition to the coordination of water molecules.

**Keywords.** Copper(II)–adeninato complexes; copper(II)–adenine–aminoacidato complexes.

### 1. Introduction

It is essential to understand the interactions between nucleic acids, proteins and their constituents with metal ions in order to follow many biological processes. The complexation of metal ions with adenine has been well studied and its binding site(s) has also been clearly elucidated (Cochran 1951; Kistenmacher 1973; Hodgson 1977). Both N(1) and N(3) are electronically favoured coordination sites for the metals (Pullman and Pullman 1963). However, due to tautomerization of the imidazole hydrogen atom between N(7) and N(9), the nitrogens N(3) and N(9) have also been involved in metal binding (Hodgson 1977). The complex  $[\text{Cu}(\text{ade-H})_2(\text{H}_2\text{O})] 6\text{H}_2\text{O}$  (Goodgame and Prince 1968; Sletten 1969) is dimeric, with the bridging of Cu(II) by the adeninate as observed in  $[\text{Cu}(\text{CH}_3\text{COO})_2\text{H}_2\text{O}]_2$  (Figgis and Martin 1956). Numerous adducts of copper(II) acetate with monodentate ligands (L), of composition  $[\text{Cu}(\text{CH}_3\text{COO})_2\text{L}]$ , have been isolated in which L occupies the axial positions of a  $\text{CuO}_4$  square plane, resulting in substantial antiferromagnetic interactions between the copper(II) atoms (Doedens 1976; Melnik 1982; Kato and Muto 1988).

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We report here the syntheses of copper(II) complexes containing both acetate and adenine bridges, and their reactivity towards aminoacids to form mixed ligand complexes.

## 2. Experimental

### 2.1 Materials and methods

Copper(II) acetate monohydrate, adenine and aminoacids used were commercially available samples. Copper(II) chloroacetate and cyanoacetate were prepared from the reaction of copper carbonate with the corresponding acids. The elemental analyses were performed using a Heraeus CHN-O-RAPID analyser and the infrared and electronic spectra were recorded on Shimadzu IR-470 and UV-3100 spectrophotometers respectively. Thermoanalytical studies were made on a Stanton simultaneous thermal analyser (model 781) in static air at a heating rate of 10°C/min. The EPR spectra of the powdered samples at room and liquid nitrogen temperatures were recorded at X-band on a Varian E-112 EPR spectrometer. Magnetic measurements were done using a George Associates (model 300) Lewis coil force magnetometer at a field of 0.1 tesla, in the temperature range, 10 K to 350 K. The error in the temperature was +0.2 K and in the susceptibility measurements was within 1%. The magnetic susceptibility was corrected for underlying diamagnetism using Pascal's constants.

### 2.2 Syntheses

2.2a  $[Cu(CH_3COO)(ade-H)(H_2O)]H_2O(I)$ : Adenine (1.0 mmol in 25 ml of  $H_2O$ ) solution was added to a copper(II) acetate monohydrate (1.0 mmol in 10 ml of  $H_2O$ ) solution and stirred continuously for 2 h. The resultant solution was concentrated on a water bath and kept overnight at room temperature. The green crystalline precipitate was collected by centrifugation, washed with hot water followed by acetone, and air dried. Yield(I): 85%.

2.2b  $[Cu(CH_3COO)(ade-H)(0.5 ade)(0.5 H_2O)]2H_2O(Ia)$  and  $[Cu(CH_3COO)(ade-H)(ade)]2H_2O(Ib)$ : Adenine (2.0 mmol in 50 ml of  $H_2O$  for Ia and 3.0 mmol in 75 ml of  $H_2O$  for Ib) solution was added to a copper(II) acetate monohydrate (1.0 mmol in 10 ml of  $H_2O$ ) solution and stirred continuously for 4 h. The resulting turbid solution was concentrated and the blue precipitate formed was collected by centrifugation, washed with hot water and acetone, and then air dried. Yield (Ia): 85% and (Ib): 90%.

2.2c  $[Cu(ClCH_2COO)(ade-H)(H_2O)]H_2O(II)$  and  $[(Cu(CNCH_2COO)(ade-H)(H_2O)]H_2O(III)$ : Copper(II) chloroacetate tetrahydrate (1.0 mmol in 15 ml of  $H_2O$ ) or cyanoacetate monohydrate (1.0 mmol in 15 ml of  $H_2O$ ) solution was added to adenine (1.0 mmol in 25 ml of  $H_2O$ ) solution and the resulting clear solution stirred for 3-4 h. The dark blue precipitate obtained was filtered, washed with hot water and acetone, and then air-dried. Yield (II): 75% and (III): 75%.

2.2d  $[Cu(XCH_2COO)(aa)(ade)(2H_2O)]$ : The complex I, II or III (1.0 mmol) was added slowly to an aqueous solution of aminoacid, Haa = glycine, alanine or glutamic acid (1.0 mmol in 10 ml of  $H_2O$ ) and stirred to get a homogeneous

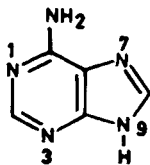


Figure 1. Structure of adenine

blue-coloured solution. The pH of the solution was maintained at about pH = 5 using 0.1N acetic acid. The addition of acetone to the concentrated solution yielded a blue precipitate. It was collected by centrifugation and air dried. Yield:  $\approx$  50%.

### 3. Results and discussion

The direct interaction of the purine base, adenine (ade) (figure 1) with copper(II) acetate results in the formation of the dimeric copper(II) adenine complex  $[\text{Cu}(\text{CH}_3\text{COO})(\text{ade}-\text{H})(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$ , by the substitution of an acetate by the adeninate moiety. The higher concentration of the ligand adenine in 1:2 or greater molar ratios results in the formation of copper(II)–adenine complexes in which the water molecule is slowly replaced by the adenine molecule. The copper(II)–adeninato complexes are insoluble in any of the common organic solvents and react with aminoacids in aqueous medium to form the monomeric copper(II)–adenine–aminoacidato complexes,  $[\text{Cu}(\text{XCH}_2\text{COO})(\text{aa})(\text{ade})(2\text{H}_2\text{O})]$ . Analytical data of the complexes are given in table 1.

#### 3.1 Thermal studies

Thermogravimetric and differential thermal analyses have been carried out in air in order to understand the thermal behaviour of the complexes. The simple adeninato complexes show two-step weight losses in air due to removal of the uncoordinated and coordinated water molecules. The first step takes place in the 70–85°C temperature range and the second in the 155–170°C, which are supported by the endothermic effect in the DTA curves. The oxidative decomposition of the ligands begins around 180°C and ends in the range 450–500°C with two exothermic peaks in the DTA curves. The mixed ligand complexes show two-stage weight losses, the first due to the removal of coordinated water molecules in the range 160–190°C and the second stage due to the oxidation of the ligands in the range 220–475°C. The final residue is CuO in all the complexes. The temperatures at the onset of decomposition suggest that the mixed ligand complexes are thermally more stable due to the chelation of the aminoacidato group.

#### 3.2 Electronic and IR spectral studies

The electronic spectra of the complexes exhibit intense peaks in the range 560–690 nm due to *d-d* transitions characteristic of a six-coordinated Cu(II) with a  $\text{CuN}_2\text{O}_4$  chromophore (Chow and McAuliffe 1972; Costes *et al* 1985). A weak intensity band at 360 nm is characteristic of dimeric Cu(II) as observed in Cu(II) adeninato complexes (Tsuchida and Yamada 1955; Christou *et al* 1990). Nitrogen-containing ligands are found to cause greater crystal field splitting, hence they exhibit bands in higher energy regions as compared to copper(II) acetate, with a  $\text{CuO}_6$  chromophore (Jorgensen 1962).

**Table 1.** Analytical (%)<sup>a</sup> and magnetic data.

Complexes	C	H	N	Cu	$\mu_{\text{eff}}$ (BM)
[Cu(CH <sub>3</sub> COO)	28.77	3.44	23.06	21.60	1.42
(ade-H)H <sub>2</sub> O]H <sub>2</sub> O	(28.72)	(3.78)	(23.72)	(21.71)	
[Cu(CH <sub>3</sub> COO)	33.23	3.68	32.33	14.57	1.60
(ade-H)(ade)]2H <sub>2</sub> O	(33.63)	(3.76)	(32.74)	(14.85)	
[Cu(CH <sub>3</sub> COO)(ade-H)	30.72	3.52	28.00	17.16	1.81
(0.5ade)(0.5H <sub>2</sub> O)]2H <sub>2</sub> O	(30.89)	(3.95)	(28.55)	(17.21)	
[Cu(ClCH <sub>2</sub> COO)	25.87	2.99	21.09	19.97	1.67
(ade-H)H <sub>2</sub> O]H <sub>2</sub> O	(25.61)	(3.07)	(21.35)	(19.37)	
[Cu(CNCH <sub>2</sub> COO)	32.13	2.94	28.69	21.58	1.74
(ade-H)H <sub>2</sub> O]H <sub>2</sub> O	(32.06)	(2.69)	(28.05)	(21.20)	
[Cu(CH <sub>3</sub> COO)	29.27	4.07	22.04	17.01	1.90
(Gly)(ade)2H <sub>2</sub> O]	(29.38)	(4.38)	(22.85)	(17.27)	
Cu(CH <sub>3</sub> COO)	32.63	4.28	19.72	14.09	1.94
(Glu)(ade)2H <sub>2</sub> O]	(32.77)	(4.58)	(19.11)	(14.44)	
[Cu(ClCH <sub>2</sub> COO)	26.76	3.59	19.97	14.19	1.96
(Gly)(ade)2H <sub>2</sub> O]	(26.87)	(3.75)	(20.89)	(15.80)	
[Cu(ClCH <sub>2</sub> COO)	28.69	4.15	20.62	15.29	1.92
(Ala)(ade)2H <sub>2</sub> O]	(28.85)	(4.12)	(20.19)	(15.27)	
[Cu(CNCH <sub>2</sub> COO)	30.89	3.94	23.58	16.10	2.00
(Gly)(ade)2H <sub>2</sub> O]	(30.58)	(3.85)	(24.97)	(16.18)	
[Cu(CNCH <sub>2</sub> COO)	31.38	4.18	19.61	11.22	1.97
(Glu)(ade)2H <sub>2</sub> O]	(31.11)	(4.68)	(19.54)	(12.69)	

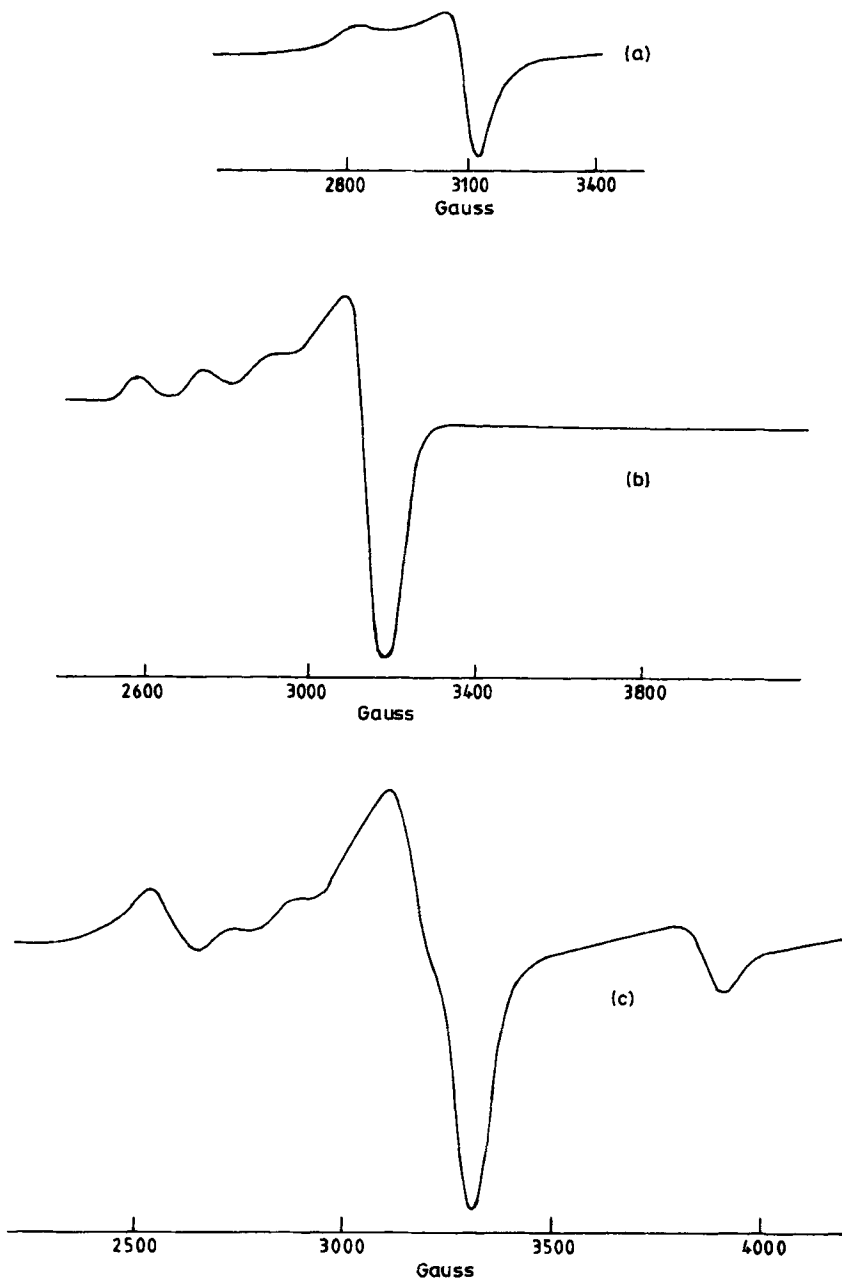
<sup>a</sup>Calculated values are given in parentheses

It is very difficult to assign IR bands unequivocally in the regions 1600 and 1400  $\text{cm}^{-1}$  due to overlapping of characteristic bands of H<sub>2</sub>O, -NH<sub>2</sub>, and the COO<sup>-</sup> of both acetate and aminoacidato groups. However, comparing the spectra of ligands and of adeninato and adenine-aminoacidato complexes, the following inferences are drawn (table 2). The copper(II)-adeninato complexes exhibit intense characteristic bands around 1600 and 1400  $\text{cm}^{-1}$  due to antisymmetric and symmetric stretching frequencies of the carboxylato group, suggesting the presence of a bridged acetate anion (Stephenson and Wilkinson 1967; Nakamoto 1986). The  $\delta_{\text{NH}_2}$  of adenine, observed around 1665  $\text{cm}^{-1}$ , has not shifted in its position in the complexes indicating its non-involvement in coordination or deprotonation (Prizant *et al* 1981). The imidazole ring frequencies (1415, 1330 and 1305  $\text{cm}^{-1}$ ) and pyrimidine ring frequencies (1600 and 1465  $\text{cm}^{-1}$ ) in the spectrum of free adenine are shifted to lower wavenumbers by about 30  $\text{cm}^{-1}$ , with reduction of intensity in the spectra of complexes indicating deprotonation and bridging of the adenine moiety through N(3) and N(9). The band observed around 1605  $\text{cm}^{-1}$ , as a shoulder in the mixed ligand complexes, is attributed to the  $\delta_{\text{NH}_2}$  of the aminoacid. The shoulder around 1370  $\text{cm}^{-1}$  is assigned to symmetric

Table 2. Infrared spectral data (values in  $\text{cm}^{-1}$ ).

Complexes	$\nu_{\text{N-H(ade)}}$ $\nu_{\text{O-H}}$	$\nu_{\text{C=N}}$	$\delta_{\text{NH}_2}$ (ade)	$\nu_{\text{asy(COO)}}$ , $\delta_{\text{H}_2\text{O}}, \delta_{\text{NH}_2}$ (aa)	$\nu_{\text{C=N}}, \nu_{\text{C=C}}$ $\nu_{\text{sym(COO)}}$	$\nu_{\text{C=N}}, \nu_{\text{C=C}}$ <sup>d</sup>	$\nu_{\text{Cu-N}}$	$\nu_{\text{Cu-O}}$
[Cu(CH <sub>3</sub> COO)(ade-H)H <sub>2</sub> O]H <sub>2</sub> O	3360 s 3216 s		1651 sh	1595 s,br 1627 m	1574 m 1450 m 1399 w	1334 w 1300 vw	450 m	380 w
[Cu(CH <sub>3</sub> COO)(ade-H)(ade)]2H <sub>2</sub> O	3360 s 3168 s		1658 sh	1582 s,br 1631 s	1571 sh 1449 m 1396 sh	1344 w 1299 w	476 m	345 w
[Cu(CH <sub>3</sub> COO)(ade-H)(0.5ade)(0.5H <sub>2</sub> O)]2H <sub>2</sub> O	3360 s 3220 s		1650 sh	1593 s,br 1620 s	1585 sh 1446 m 1403 w	1344 w 1300 vw	440 m	372 w
[Cu(CH <sub>3</sub> COO)(Gly)(ade)2H <sub>2</sub> O]	3290–3214 s <sup>a</sup> 3120–3100 s		1660 sh	1590 br 1611 sh 1622 s	1460–1450 w 1390 w 1365 sh	1350 w 1300 vw	452 m	352 w
[Cu(ClCCH <sub>2</sub> COO)(ade-33H)H <sub>2</sub> O]H <sub>2</sub> O	3376 s 3200 s		1651 sh	1597 s,br 1627 s	1580 sh 1442 m 1405 w	1344 w 1306 vw	474 m	370 w
[Cu(ClCH <sub>2</sub> COO)(Gly)(ade)2H <sub>2</sub> O]	3400–3371 s <sup>a</sup> 3212 s		1658 sh	1593 s,br 1608 sh 1632 m	1460–1450 w 1390 w 1371 sh	1351 m 1315 vw	457 m	371 w
[Cu(CNCH <sub>2</sub> COO)(ade-H)H <sub>2</sub> O]H <sub>2</sub> O	3408 s 3184 s	2240 m	1658 sh	1589 s,br 1635 s	1581 sh 1459 m 1402 w	1347 w 1306 vw	445 m	348 w
[Cu(CNCH <sub>2</sub> COO)(Gly)(ade)2H <sub>2</sub> O]	3392–3312 s <sup>a</sup> 3136 s	2244 m	1657 sh	1593 s,br 1602 sh 1629 s	1460 m 1412 w 1374 sh	1350 w 1306 vw	449 m	342 w

s—strong, m—medium, w—weak, br—broad, sh—shoulder, vw—very weak; <sup>a</sup>includes  $\nu_{\text{N-H}}$  aminoacid; <sup>b</sup>includes  $\nu_{\text{asy(COO)}}$  aminoacid; <sup>c</sup>pyrimidine ring stretch; <sup>d</sup>imidazole ring stretch.



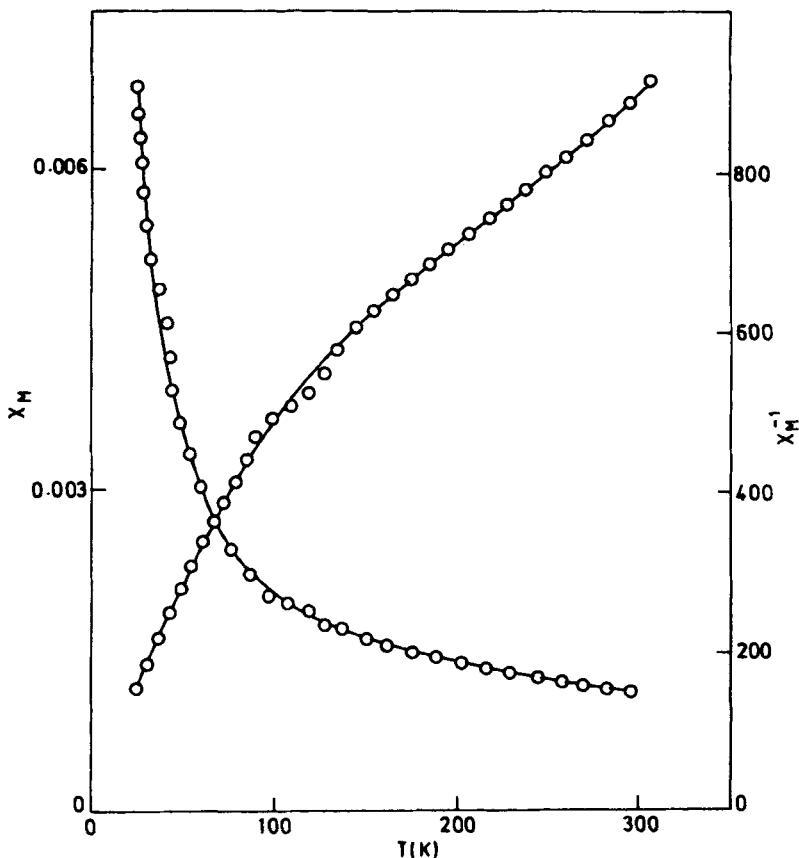
**Figure 2.** EPR spectrum of (a)  $[\text{Cu}(\text{CH}_3\text{COO})(\text{ade-H})(\text{ade})]2\text{H}_2\text{O}$ , (b)  $[\text{Cu}(\text{CH}_3\text{COO})(\text{ade-H})(\text{ade})]2\text{H}_2\text{O}$  at 1% Cu(II) doping concentration, and (c)  $[\text{Cu}(\text{CH}_3\text{COO})(\text{ade-H})(\text{ade})]2\text{H}_2\text{O}$  at 3% Cu(II) concentration, room temperature and X-band frequency.

stretching frequency of the monodentate acetate group (Nakamoto 1986) and there is only a slight shift in the imidazole ring vibrational frequencies of adenine, indicating the N(7) coordination to Cu(II) in the mixed ligand complexes. The absorptions at 440 and

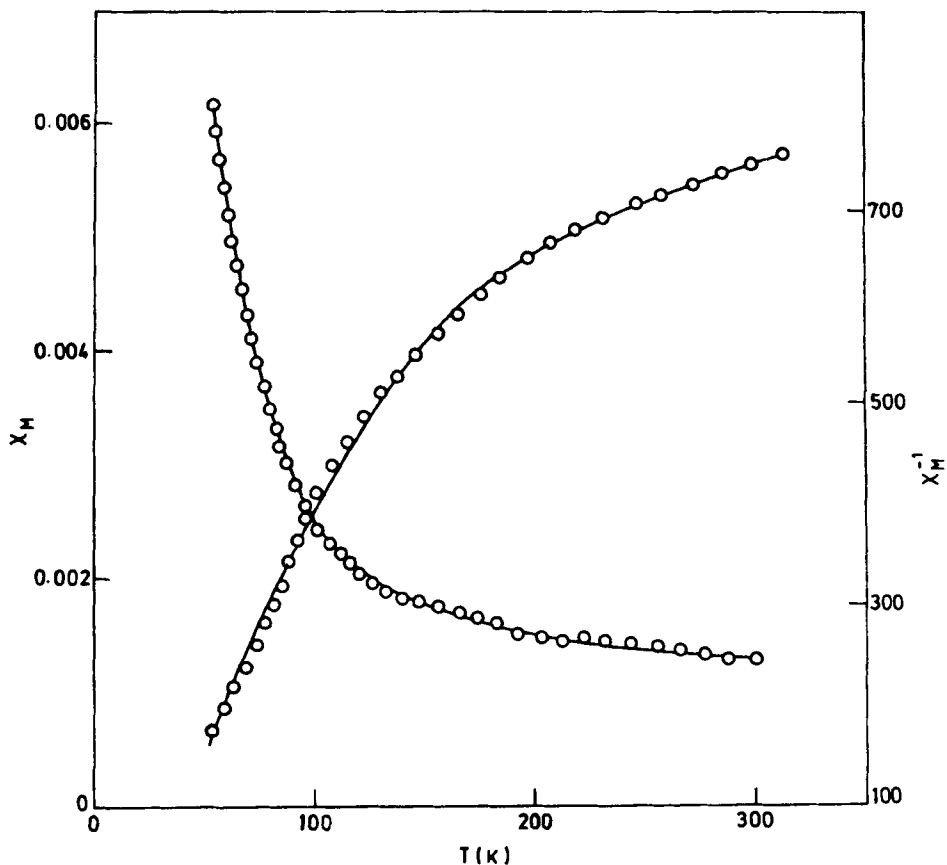
$342\text{ cm}^{-1}$  are assigned to the stretching frequencies of Cu-N and Cu-O respectively (Kincaid and Nakamoto 1976).

### 3.3 EPR studies

EPR studies of the adeninato complex, when measured in neat powder form, give an axially symmetric powder pattern (figure 2a) with  $g_{\parallel} = 2.26$  and  $g_{\perp} = 2.07$  characteristic of a  $d_{x^2-y^2}$  ground state and square planar or square pyramidal ligand field symmetry (Hathaway and Billing 1970). The Cu hyperfine splitting was not observed due to exchange broadening. In order to prepare diamagnetically diluted compounds, varied amounts ranging from 1–3% of  $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]_2$  were incorporated during the formation of the isomorphous zinc compounds. On doping with 1% Cu(II) only monomeric copper units were seen in the EPR spectra with well-resolved Cu hyperfine coupling (figure 2b) with  $g_{\parallel} = 2.31$ ,  $g_{\perp} = 2.08$  and  $A_{\parallel} = 150 \times 10^{-4}\text{ cm}^{-1}$ . When the Cu(II) concentration was increased to 3%, apart from the monomeric unit, dimeric Cu complexes characteristic of zero field splitting with  $2D = 1400\text{ G}$  could be seen



**Figure 3.** Temperature variation of susceptibility of  $[\text{Cu}(\text{ClCH}_2\text{COO})(\text{ade-H})\text{H}_2\text{O}]\text{H}_2\text{O}$  at a field of 0.1 T. Open circles represent experimental values. Solid lines represent calculated susceptibilities based on Bleaney–Bower's equation. Both  $\chi_M$  vs  $T$  and  $\chi_M^{-1}$  vs  $T$  are plotted.



**Figure 4.** Temperature variation of  $\chi_M$  and  $\chi_M^{-1}$  of  $[\text{Cu}(\text{CH}_3\text{COO})(\text{ade-H})(0.5 \text{ ade})(0.5 \text{ H}_2\text{O})]_2\text{H}_2\text{O}$ . Solid lines represent theoretically calculated susceptibilities, while circles indicate experimental points.

(figure 2c) characteristic of  $S = 1$  (Benelli *et al* 1985). All the EPR spectra can be interpreted in terms of square planar geometry with or without axial perturbation.

### 3.4 Magnetic studies

The temperature-dependent solid state magnetic susceptibility of  $[\text{Cu}(\text{ClCH}_2\text{COO})(\text{ade-H})(\text{H}_2\text{O})]_2\text{H}_2\text{O}$  (II) and  $[\text{Cu}(\text{CH}_3\text{COO})(\text{ade-H})(0.5 \text{ ade})(0.5 \text{ H}_2\text{O})]_2\text{H}_2\text{O}$  (Ia) are given in figures 3 and 4 respectively. The susceptibility decreases with increase in the temperature indicating ferromagnetic coupling. The general Hamiltonian which could be used to analyse the magnetic interaction is,

$$H = \sum_{i=1}^{N/2} J_1 S_{2i} S_{2i-1} + J_2 S_{2i} S_{2i+1}$$

where  $J_1$  and  $J_2$  are the exchange coupling constants of spin at  $2i$ , to its neighbouring spins at  $(2i - 1)$  and  $(2i + 1)$  respectively. The susceptibility data using the Van Vleck expression fit the dimer model very well (Bleaney and Bower 1952) and the exchange



interaction is satisfactorily given by the Hamiltonian including temperature-independent paramagnetism (TIP) as,

$$\chi_M = N g^2 \beta^2 / 3KT (1 + 1/3 e^{-2J/KT})^{-1} + N_x + \rho N g^2 \beta^2 / 4KT,$$

where  $2J$  is the singlet-triplet separation,  $N_x$  is the temperature-independent paramagnetism and  $\rho$  refers to paramagnetic impurity. The other terms ( $\chi_M$  = molar susceptibility,  $N$  = Avogadro's number,  $g$  = Lande splitting factor,  $\beta$  = Bohr magneton and  $K$  = Boltzmann constant) have their usual meaning. The parameters calculated for Ia and II are  $2J = 143$  and  $84 \text{ cm}^{-1}$ ,  $\rho = 1.6$  and  $2\%$  and  $N_x = 0.12 \times 10^{-5}$  and  $9.85 \times 10^{-5}$  respectively.

The magnetic susceptibility measurements of the copper(II) adenine aminoacidato complexes made at room temperature gave the calculated magnetic moment values in the range 1.9–2.0 BM (table 1) at the field of 10 kilo gauss which are as expected for magnetically non-interacting Cu(II) systems. However, Cu(II)-adeninato complexes have effective magnetic moment values in the range 1.4–1.8 BM, suggesting exchange interaction between the copper(II) ions in the dimeric structure, wherein ferromagnetic coupling exists, as indicated by the  $2J$  values.

#### 4. Conclusion

The interaction of adenine with  $[\text{Cu}(\text{XCH}_2\text{COO})_2(\text{H}_2\text{O})]$  to yield mixed ligand complexes of the type  $[\text{Cu}(\text{XCH}_2\text{COO})(\text{ade-H})\text{L}]\text{H}_2\text{O}$ , where  $\text{L} = \text{H}_2\text{O}$  or  $\text{ade}$ , and the ferromagnetic coupling in these complexes, is investigated by bulk magnetic susceptibility measurements and EPR studies. The copper(II)-adenine-aminoacidato complexes were obtained by the reaction of dimeric adeninato systems.

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