

## Complexed Bilayer Membranes with Novel Structural Features formed by Amphiphiles of Monoalkyl Derivatives of Ethylenediamine

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The  $\text{CuN}_4$  headgroups and the aliphatic tails in  $\text{Cu}^{2+}$ -complexed bilayer membranes exhibit two-dimensional ordered orientations which can be classified into two types with different structural features.

Complexed bilayer membranes formed by amphiphiles coordinating metal ions have shown very fascinating functions,<sup>1</sup> and given rise to interesting magnetic properties.<sup>2</sup> However, the structural characterization of such species has fallen behind the studies of their physical properties. We report herein complexed bilayer structures with a series of amphiphiles  $\text{C}_n\text{H}_{2n+1}\text{NHC}_2\text{H}_4\text{NH}_2$  ( $n = 8-18$ ) dispersed in dilute aqueous  $\text{Cu}(\text{NO}_3)_2$ . These structures are quite different from bilayers formed by the amphiphiles in pure water or in dilute acidic solution.<sup>3</sup>

The series of amphiphiles were synthesized as reported previously.<sup>3</sup> The samples were prepared by dissolving them in aqueous solutions of  $\text{Cu}(\text{NO}_3)_2$  ( $5 \text{ mmol dm}^{-3}$ ) and sonicating the solutions to give  $10 \text{ mmol dm}^{-3}$  dispersions [ $2 \text{ C}_n\text{H}_{2n+1}\text{NHC}_2\text{H}_4\text{NH}_2 \cdot \text{Cu}(\text{NO}_3)_2$ ]. The samples were investigated by transmission electron microscopy (JEOL Model JEM-200CX) and differential scanning calorimetry (SETARAM Model Micro-DSC), and their cast films studied by small-angle X-ray diffraction (Rigaku Model D/max-RA). The electronic reflectance spectra (Shimadzu Model UV-240) of solid powders of the samples obtained by vacuum drying at  $60^\circ\text{C}$  were recorded using  $\text{BaSO}_4$  as reference. All measurements were carried out at  $15-20^\circ\text{C}$ . The results are summarized in Table 1.

From Table 1 and Fig. 1 it can be seen that complexed bilayer membranes are formed by this series of amphiphiles in dilute aqueous  $\text{Cu}(\text{NO}_3)_2$ , all showing vesicular morphologies. However there are drastic differences between samples with  $n = 8$  and  $n = 12-18$  in the appearance of the dispersion, the phase transition temperature ( $T_c$ ) and bilayer thickness ( $D_n$ ). In the former case the aggregate is blue, with  $T_c = 41^\circ\text{C}$  and  $D_8 = 1.63L_8$ . The latter are purple with  $T_c$  values all  $>84^\circ\text{C}$  and with  $D_n$  smaller than  $L_n$  ( $n = 12-18$ ). However,  $D_n$  (in  $\text{\AA}$ ) exhibit good linearity with  $n$  according to eqn. (1).

$$D_n = 1.06n + 6.24 \quad (n = 12-18) \quad (1)$$

Obviously the amphiphilic aggregates can be categorized into two structurally differing types.

The differences between the two kinds of bilayers in solution colour and in their solid-state electronic spectra reveal configurational diversities in the coordination structures of the  $\text{Cu}^{2+}$ -complexed headgroups. As asymmetric derivatives of ethylenediamine,  $\text{ML}_2$ -type complexes of the  $\text{Cu}^{2+}$ -coordinated amphiphiles usually have planar  $\text{CuN}_4$  structures<sup>4</sup> with *cis* and *trans* isomers and with two water

molecules acting as axial ligands.<sup>5</sup> It has been established that complexes with *cis*-configuration show higher charge-transfer energies than those with *trans*-arrangements,<sup>6,7</sup> furthermore, square-coplanar  $\text{CuN}_4$  complexes show d-d transition energies in the range  $18-20 \times 10^3 \text{ cm}^{-1}$  while the range for tetrahedral  $\text{CuN}_4$  is  $12-16 \times 10^3 \text{ cm}^{-1}$ .<sup>8</sup> From the d-d and  $\text{N} \rightarrow \text{Cu}$  charge-transfer energies in Table 1 it can be deduced that when  $n = 8$  the complex adopts a *trans*-configuration with the headgroups coordinated so as to give a compressed tetrahedral  $\text{CuN}_4$  environment, while for  $n = 12-18$  a *cis*-configuration is adopted with the copper square-coplanar. For the  $n = 8$  amphiphilic aggregate, because the two  $\text{N}(\text{C}_8\text{H}_{17})$  moieties occupy opposite sites, the steric hindrance between them and the axial ligands in the bilayer formation process makes the  $\text{NC}_8\text{H}_{17}$  moieties deviate slightly from the  $\text{CuN}_4$  plane so leading to a compressed tetrahedral configuration. On the other hand, the  $\text{CuN}_4$  *cis*-configuration of the  $n = 12-18$  amphiphilic aggregates leads to rectangular-coplanar structures as the  $\text{Cu}-\text{NC}_n\text{H}_{2n+1}$  bond is significantly longer than the  $\text{Cu}-\text{NH}_2$  bond.<sup>9,10</sup>

Furthermore, for the  $n = 8$  structure the phase transition temperature of the complexed bilayer is relatively low, indicating loose packing of the hydrocarbon chains; while for  $n = 12-18$  the phase transition temperatures are fairly high indicating close chain packing; also  $D_8 = 1.63L_8$  while  $D_n <$

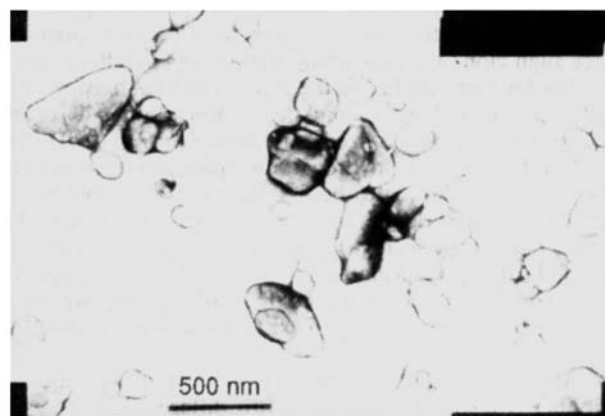


Fig. 1 Transmission electron micrograph of amphiphilic aggregates of  $\text{C}_{18}\text{H}_{37}\text{NHC}_2\text{H}_4\text{NH}_2$  in aqueous  $\text{Cu}(\text{NO}_3)_2$  (stained with 2 mass% uranyl acetate)

Table 1 TEM and DSC results on the morphology and phase transition temperatures of amphiphilic aggregates of  $\text{C}_n\text{H}_{2n+1}\text{NHC}_2\text{H}_4\text{NH}_2$  in aqueous  $\text{Cu}(\text{NO}_3)_2$ , along with small-angle XRD results of their cast films and electronic transitions of the solid powders

Amphiphile ( $n$ )	Solution appearance	Morphology (TEM)	$T_c/^\circ\text{C}$ (DSC)	$D_n/\text{\AA}$ (XRD)	Evaluated molecular length $L_n/\text{\AA}$	d-d Transition ( $10^{-3} \text{ \AA}^{-1}$ )	$\sigma-\sigma^*$ ( $10^{-3} \text{ \AA}^{-1}$ ) ( $\text{N} \rightarrow \text{Cu}$ )	
							I	II
8	Clear, blue	Vesicle	41	26.00	16	15.48	42.92	30.30
12	Emulsion, purple	Vesicle	84.5	18.97	21	—	—	—
14	Emulsion, purple	Vesicle	91	21.09	23.5	18.05	44.44	35.71
16	Emulsion, purple	Vesicle	94	23.23	26	—	—	—
18	Emulsion, purple	Vesicle	97	25.33	28.5	—	—	—

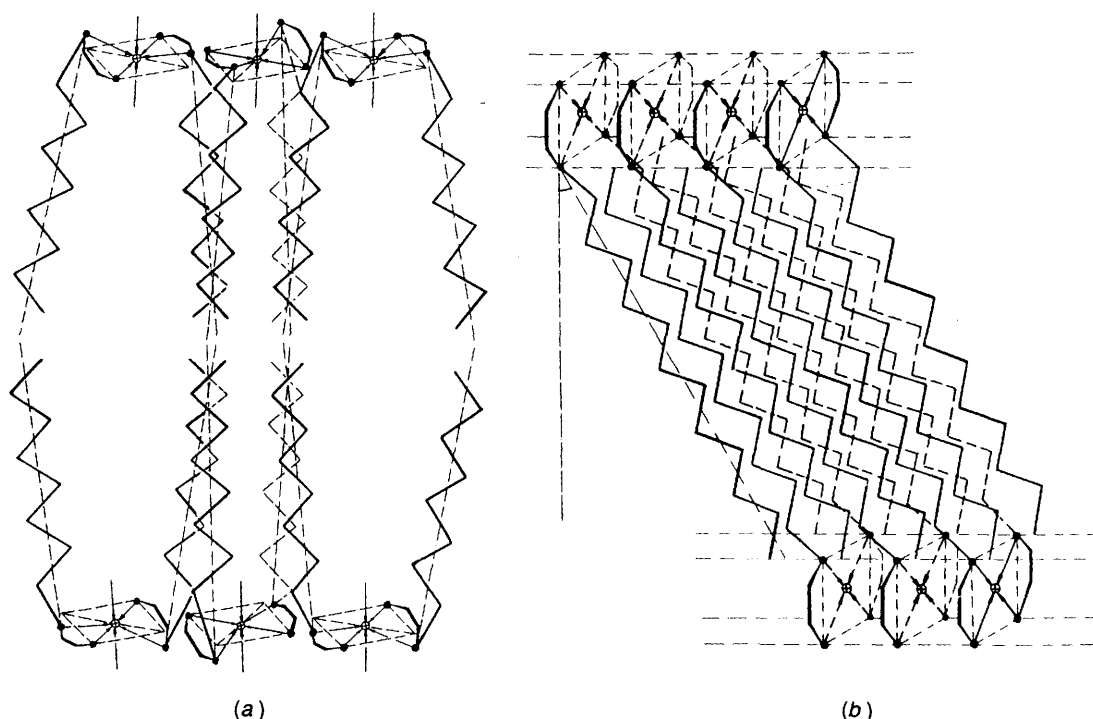


Fig. 2 Packing structure of the  $\text{Cu}^{2+}$ -complexed bilayers. (a) Tail-to-tail model; (b) interdigitation model. (O) and (●) designate copper(II) and nitrogen, respectively.

$L_n$  ( $n = 12-18$ ). It seems reasonable that when  $n = 8$ , the compressed tetrahedral  $\text{CuN}_4$  lies along the membrane surface with its central plane vertical to the membrane normal, and the aliphatic chains extend obliquely into the tail gap of the neighbouring amphiphiles in the same layer to form tail-to-tail bilayers [Fig. 2(a)]; in the case of  $n = 12-18$ , the chains strongly interdigitate in bilayers, and the  $\text{CuN}_4$  coordination planes align along the membrane normal and parallel to each other (under such conditions the steric repulsion between the axially coordinated water and the hydrocarbon tails of an adjacent layer are minimized), as shown in Fig. 2(b). The average tilt angle of the hydrocarbon chains can be evaluated by the slope of eqn. (1) to be  $\theta = \arccos(2 \times 1.06/2.54) = 33.4^\circ$ .<sup>11</sup> On the other hand, from the constant term of eqn. (1), the thickness of the headgroup region (headgroups and their hydration layer) is calculated to be 3.12 Å, which approximates to the longitudinal length of the  $\text{CuN}_4$  plane, indicating that no hydration layer seems to exist outside the coordination sphere.

A possible explanation for this series of amphiphiles exhibiting two kinds of bilayers with different structures is competition between the steric isomerization of the  $\text{CuN}_4$  headgroups and the spontaneous assembly of the aliphatic tails.

In conclusion, the  $\text{CuN}_4$  headgroups and the aliphatic tails exhibit two-dimensional ordered orientation structures in the complexed bilayers which differ distinctly depending on the length of the hydrocarbon tails. For amphiphiles with a short tail ( $n = 8$ ), the  $\text{CuN}_4$  headgroups adopt a *trans*-configuration and horizontal orientation, and the chains assemble in a

tail-to-tail way. For the long-tailed amphiphiles ( $n = 12-18$ ) the headgroups adopt a *cis*-configuration and vertical orientation, and the chain packing fashion is of an interdigitation mode. Apparently, the complexed bilayers formed by this series of amphiphiles possess novel structural features quite different from other synthetic bilayer membranes.

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