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Two-Dimensional Arrangement of Polynuclear Metal Complexes in the Interlayer of Multibilayer Cast Films[1)]

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Anionic vanadium complex, $[V_{10}O_{28}]^{6-}$, and cationic cadmium complex, $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$, were incorporated into oppositely-charged multibilayer cast films, respectively, by the ion-exchange method. The composite films possessed regular multilayer structures with alternating organic and inorganic layers.

Template synthesis of inorganic materials in well-defined microspaces (zeolites, inorganic layers, LB films) is an attractive method for the preparation and the controlled arrangement of nanoscale objects.[2-4)] Multibilayer films are readily prepared by casting of aqueous bilayer dispersions.[5)] They act as two-dimensional templates for the preparation of ultra-thin films of polysiloxanes,[6)] metal oxides[7)] and organic polymers.[8)] Recently, we successfully prepared anionic metal halide clusters by incorporating the starting molecular species ($PbBr_4^{2-}$, etc) into the interlayer space of cast films of ammonium bilayers by the ion-exchange method.[9)] The ion-exchange technique provides advantages over the cosonication procedure that were used by us[6-8)] and others,[10)] since the original regularity of cast films is usually maintained. Its disadvantage, on the other hand, is that the incorporation of charged species is limited by charge neutralization. In order to remedy some of these disadvantages, we conducted incorporation of representative polynuclear metal complexes of Fig. 1 by

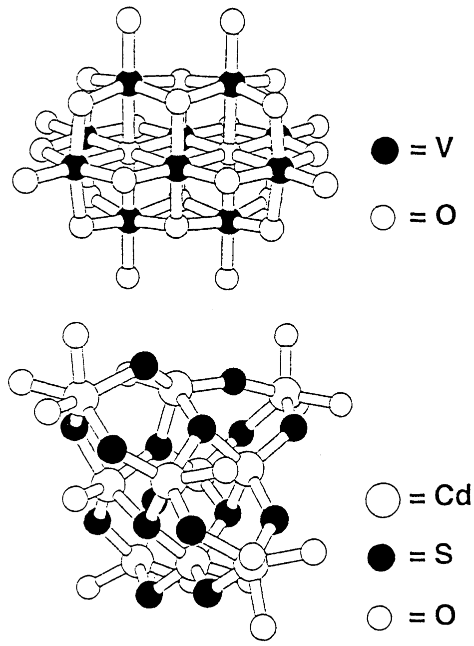
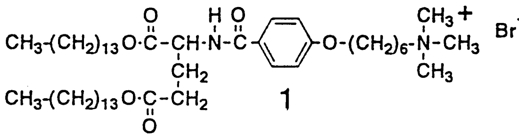
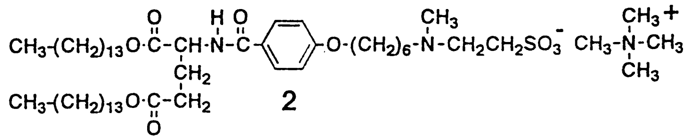


Fig. 1. Structures of $[V_{10}O_{28}]^{6-}$ and $[Cd_{10}(SCH_2CH_2\text{-}OH)_{16}]^{4+}$.[15,17)] Carbon and hydrogen atoms are omitted.

the ion-exchange method. Incorporation of nanoparticles and polynuclear complexes by the cosonication method has been reported.[7,10)]

Amphiphiles 1[11)] and 2[12)] are known to produce highly ordered multilayer films. They were cast on fluorocarbon membrane filters, and the resulting films of 1 and 2 were immersed for 5 days in aqueous solutions (10 mM each) of $6Na^+[V_{10}O_{28}]^{6-}$ [13)] and $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}4ClO_4^-$,[14)] respectively.

IR spectra of sodium decavanadate ($6Na[V_{10}O_{28}]\cdot18H_2O$), cast film 1 and their composite film are compared in Fig. 2. The composite film gave a spectrum that was virtually a superposition of the separate spectra, and possessed characteristic peaks of $[V_{10}O_{28}]^{6-}$ at 843 and 957 cm^{-1}. Therefore, the complex structure of decavanadate that consists of ten VO_6 octahedra sharing edges[15)] (see Fig. 1) was maintained in the composite film.

The UV absorption maximum of the $2\text{-}[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ composite film was found at 260 nm and shifted to 256 nm when it was dissolved in chloroform. The latter spectrum agrees very closely with that of aqueous $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ (absorption maximum: 256 nm).[16)] Furthermore, ^{113}Cd CP-MAS NMR spectroscopy revealed that the coordination environment of the cadmium complex in the composite film was very similar to that of $[Cd_{10}(SCH_2CH_2OH)_{16}]\cdot4ClO_4$ crystal (Fig. 3).[17)]

Figure 4 shows X-ray diffraction patterns of single-component cast films and their composite films.

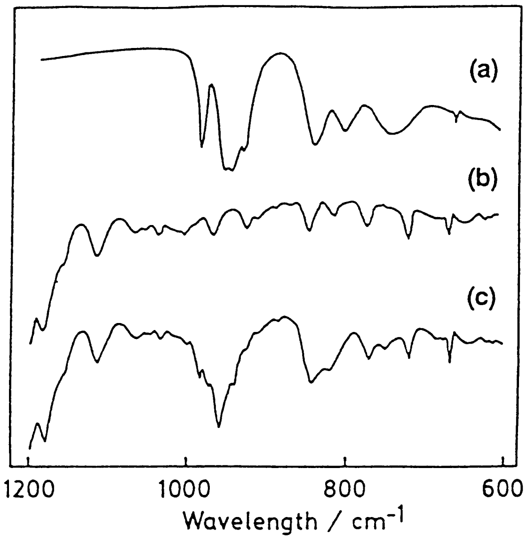


Fig. 2. IR spectra.
(a) $6Na[V_{10}O_{28}]\cdot18H_2O$, (b) cast film 1, and (c) $1\text{-}[V_{10}O_{28}]^{6-}$ composite film.

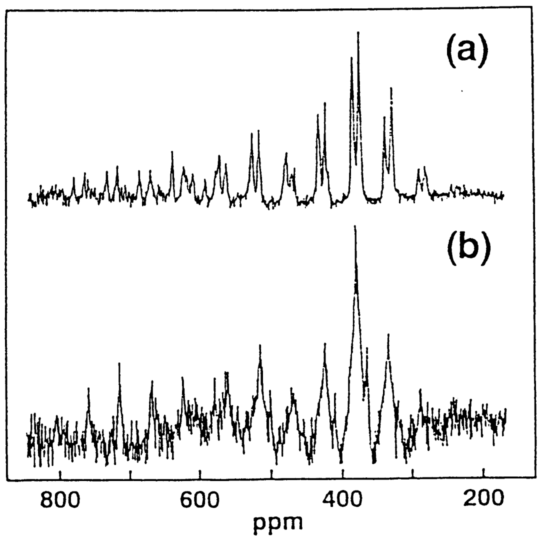


Fig. 3. ^{113}Cd CP-MAS NMR spectra. Spinning speed, 2500 Hz; reference, $Cd(ClO_4)_2\cdot6H_2O$
(a) $[Cd_{10}(SCH_2CH_2OH)_{16}]4ClO_4\cdot nH_2O$ and (b) $2\text{-}[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ composite film.

The higher-order reflection peaks observed substantiate the existence of regular multilayer structures. The long spacings of 1-$[V_{10}O_{28}]^{6-}$ and 2-$[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ composite films are 45.5 Å and 53.3 Å, respectively. These values are smaller than those of their original films (cast film 1: 66.2 Å, cast film 2: 62.6 Å), and suggest that bilayer components become even more tilted. The regular side-chain alignment is preserved in these films as confirmed by DSC measurement.[18] Obviously, alternating organic and inorganic layers are formed in the composite films.

The amount of vanadium in 1-$[V_{10}O_{28}]^{6-}$ composite film was 9.42 wt% as determined by ICP measurement. This value is close to six amphiphiles to one decavanadic acid (calculated content, 9.19 wt%). Thus, all the positive charges at the bilayer surface are neutralized by the decavanadate anion. The molecular area occupied by amphiphile 1 is estimated to be 75 ± 5 Å^2 from the cross section of two methylene units (40 Å^2) and the tilt angle derived from the long spacing (45.5 Å) and the extended molecular length (42 Å from the CPK model). The size of the $[V_{10}O_{28}]^{6-}$ complex estimated by molecular mechanics calculation (MM2, SONY Tektronix CAChe System) is $12.8 \times 10.2 \times 7.8$ Å^3 with the cross-sectional area of 105 ± 25 Å^2.

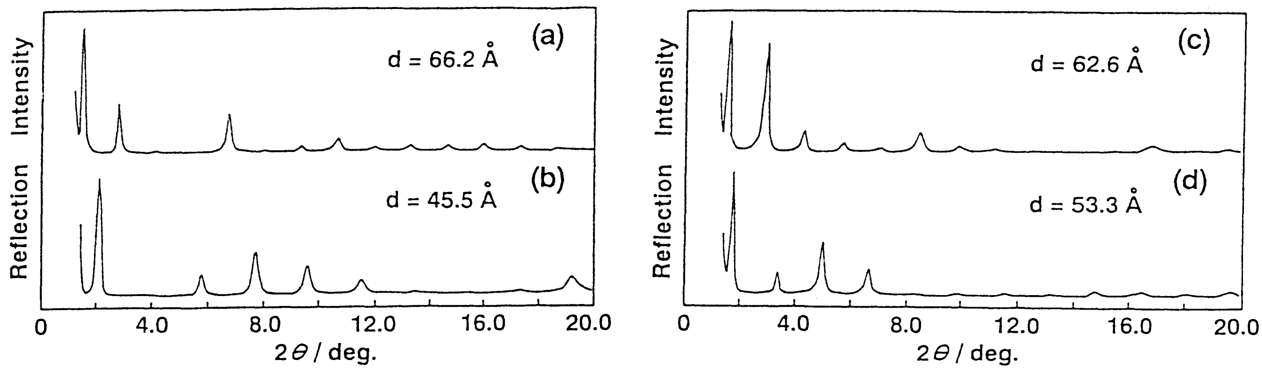


Fig. 4. Reflection X-ray diffraction of cast multibilayer films. (a) cast film 1, (b) 1-$[V_{10}O_{28}]^{6-}$ composite film, (c) cast film 2, (d) 2-$[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ composite film.

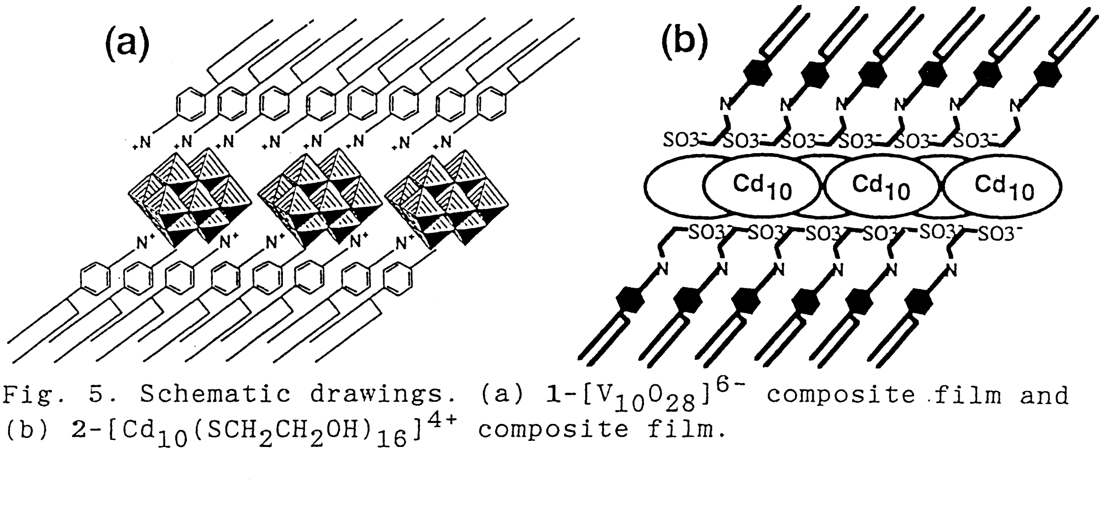


Fig. 5. Schematic drawings. (a) 1-$[V_{10}O_{28}]^{6-}$ composite film and (b) 2-$[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ composite film.

This area is smaller than the sum of the molecular area of paired amphiphiles (three molecules each from above and below). Therefore, the decavanadate ions do not completely fill in the space in contact with each other (see Fig. 5a). On the other hand, the cadmium content was found to be 15.2 wt%, and indicated the molar ratio of 2 and $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ of 5.7 : 1. The Cd complex is spherical in shape and its diameter is ca. 15 Å. Comparison of the molecular dimensions of the complex (180 $Å^2$) and the paired bilayer surface (130 ± 10 $Å^2$, two molecules on each side) suggest close packing of the complexes as shown schematically in Fig. 5b.

In conclusion, we demonstrated two-dimensional arrangements of polynuclear metal complexes in multibilayer cast films of cationic and anionic amphiphiles. It is noteworthy that regular multilayer structures are maintained in composite films, irrespective of sizes and charges of the complexes. Apparently, the bilayer structure is adjustable to the incoming guest particles because of its self-assembling property. This is an important advantage that is not realized by other rigid two-dimensional hosts such as graphite, layered metaloxides, zirconium phosphate, and LB films.

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18) cast film **1**: T_c = 68.2 °C, ΔH = 55.7 kJ/mol; cast film **2**: T_c = 64.2 °C, ΔH = 60.3 kJ/mol; **1**-$[V_{10}O_{28}]^{6-}$ composite film: T_c = 52 - 73 °C, ΔH = 55.8 kJ/mol; **2**-$[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ composite film: T_c = 63.4, 67.8 °C, ΔH = 56.4 kJ/mol.

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