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Epitaxic Growth of [2,3,9,10,16,17,23,24-Octacyano-29*H*,31*H*-phthalocyaninato(2 −)]metal Complex Crystals

By Hisao Yanagi, Sigehiko Hayashi, Nozomu Fujita and Michio Ashida

Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe 657, Japan

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Abstract. Thin films of (2,3,9,10,16,17,23,24-octacyanophthalocyaninato)metal complexes [$K_2(C_{40}H_{16}N_{16})$]–K [$K_2Pc(CN)_8$–K] and [$Cu(C_{40}H_{16}N_{16})$]–Cu [$CuPc(CN)_8$–Cu] crystals were prepared by vapor–solid reaction of 1,2,4,5-benzenetetracarbonitrile with substrates. The $K_2Pc(CN)_8$–K film on a KCl (001) surface was composed of thin crystals in which planar $K_2Pc(CN)_8$ molecules came into parallel contact with the substrate surface and were piled up along the *c* axis perpendicular to the substrate surface. Many crystallites with double-directional orientation intersected each other at an angle of about 23°. The double-directional orientation was ascribed to interaction between cyano groups of $K_2Pc(CN)_8$ molecules and a KCl crystal and to the crystal structure of the $K_2Pc(CN)_8$–K complex. The crystals took three types of mutual orientations on a (001) surface of KCl and the relative orientation of the deposited crystal to the KCl substrate was interpreted in terms of multiple positioning of the $K_2Pc(CN)_8$ molecules on an ionic lattice of the KCl surface. Electron micrographs from a thin film of the $CuPc(CN)_8$–Cu complex crystal produced on a Cu film showed various lattice fringes which suggested that the crystals took random orientation on the metal substrate. The $CuPc(CN)_8$ molecules came into contact with the substrate surface at various angles so that the column axes of the crystals inclined to the substrate surface.

Introduction. Oriented organic thin films have been generally prepared by the Langmuir–Blodgett (LB) method (Blodgett, 1935) and/or a vacuum-evaporation method. The former method can be applied to linear molecules having hydrophilic peripheral groups in a wet process and properties of LB films have been reported by many workers. On the other hand, the latter method has been investigated for epitaxic growth of both planar molecules such as phthalocyanines (Pc) (Uyeda, Ashida & Suito, 1965; Ashida, 1966*a*) and linear molecules such as paraffins (Ueda & Ashida, 1980) and polyethylene (Hattori, Ashida & Watanabe, 1975). CuPc films vacuum deposited on muscovite indicated two different orientations in which the *b* axis of the crystal was either perpendicular or parallel to the substrate, depending upon the conditions of the surface treatment (Ashida, 1966*b*). A paraffin film vacuum deposited on a KCl (001) surface at room temperature was composed of rod-like crystallites, in which their fiber axes oriented parallel to the [110] direction of the KCl crystal. In the case of derivatives of paraffins, the crystal morphology and orientation depended on their polar end groups such as hydroxyl and ester groups (Ueda, 1987). The orientation of a vacuum-deposited paraffin film was also affected by a substrate structure. A hexatriacontane film deposited on KCl covered with a gold film was composed of lamellar crystals which had their fiber axes perpendicular to the substrate surface (Ashida, Ueda & Yanagi, 1986). Various types of epitaxic growth were explained by different interactions between organic molecules and a substrate surface.

In a previous study (Yanagi, Ueda & Ashida, 1988), thin films of metal octacyanophthalocyanates [MPc(CN)$_8$] were prepared directly on substrates by a vapor–solid reaction of 1,2,4,5-benzenetetracarbonitrile (BTCN) with a KCl crystal and metal films. The [MPc(CN)$_8$] molecules were piled up in a column structure to form MPc(CN)$_8$–M complex crystals (Ashida, Ueda, Yanagi, Fujiyoshi, Uyeda & Fryer, 1988). The molecules rotated alternately around the *c* axis and their peripheral cyano groups coordinate to intercalated metal atoms as shown in Fig. 1. The crystal had a tetragonal lattice (space group *P*4/*mcc*) in which the cell parameter *c* was 0·68 nm, twice the interplanar distance of Pc molecules. The crystal morphology varied with the reaction temperature, pressure and kind of substrate material (Yanagi, Maeda, Hayashi & Ashida, 1988). It seemed that the crystal growth depended on diffusion of metal atoms from the substrate and the crystal orientation was affected by the surface structure of the substrate.

The present paper is concerned with epitaxic growth of the MPc(CN)$_8$–M complex crystals on substrates. Thin films were synthesized from BTCN on substrates, a cleavage surface of a KCl single crystal and a vacuum-evaporated Cu film. The

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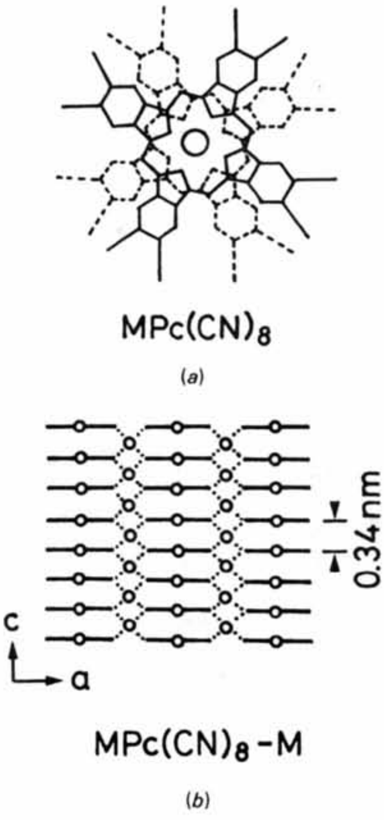
mechanism of epitaxic growth and mutual orientation between deposit and substrate crystals were examined by means of electron microscopy.

Experimental. A sample of BTCN was synthesized from pyromellitic dianhydride (Bailey, Henn & Langton, 1963). Substrate materials used were a (001) surface of a KCl single crystal cleaved in air and a vacuum-evaporated Cu film. As a Cu film composed of a single crystal, Cu was evaporated on a KCl (001) surface kept at 623 K in a vacuum of 0·1 mPa. The thickness of the Cu film was controlled at about 100 nm. A given amount of purified BTCN and the substrate material were sealed in an evacuated Pyrex-glass tube at a pressure of 10 Pa after flushing with argon gas. The tube was heated at a temperature between 573 and 623 K for 10 h in a hot-air oven. After films produced on the substrates had been reinforced with evaporated carbon films, specimen films were separated from the KCl substrates in water for electron microscopy. The residual Cu film was dissolved away in a dilute acid solution. The specimen film was mounted on a microgrid coated with an evaporated gold film. Electron microscopy was carried out on a JEM-200CX at 200 kV accelerating voltage. The relative orientation of the deposited crystals to the KCl substrate was determined from a step which had been made on the KCl (001) surface. The KCl substrate was thermally etched beforehand at 723 K at a pressure of 10 Pa for 5 h. Steps on the KCl (001) surface revealed regular edges parallel to the [100] direction of the KCl crystal.

Discussion. A green thin film of $K_2Pc(CN)_8$–K complex crystals was formed on a KCl (001) cleavage surface by reaction of BTCN with KCl. The film was composed of thin crystals with discrete disc-like crystallites as shown in Fig. 2. It shows square lattice networks with a spacing of 1·57 nm which coincides with lattice constants, *a* and *b*, of the tetragonal cell. It demonstrates that the crystals have their *c* axes perpendicular to the KCl (001) surface and $[K_2Pc(CN)_8]$ molecules are piled up parallel to the substrate. Many crystallites with double-directional orientation were observed in the film as shown in Fig. 3. Each dark dot aligned in the square lattice corresponds to the molecular column projected along the *c* axis. The molecular image in the wedge-shaped area cannot be clearly observed because molecular stacking may be disordered at the grain boundary. The *a* axes of the two crystallites make an angle of about 23° to each other. The double-directional orientation in the crystals was confirmed by a selected-area electron diffraction pattern of the film as shown in Fig. 4(*a*). This pattern is composed of the superposition of two single net patterns with C_{4v} symmetry, corresponding to a lattice spacing of 1·57 nm. The reflection spots are schematically represented in Fig. 4(*b*) which shows that the two *hk*0 diagrams rotate by 23° with respect to each other. It seems that the double-directional orientation is



(*a*)

(*b*)

Fig. 1. Crystal structure of the MPc(CN)$_8$–M complex. (*a*) Superposition of molecules projected along the *c* axis and (*b*) column structure projected along the *b* axis.

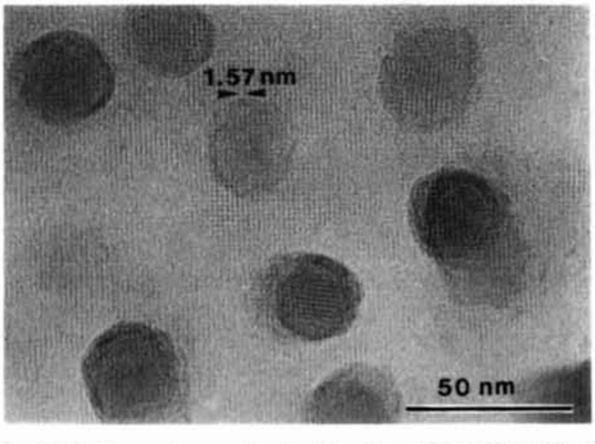


Fig. 2. Electron micrograph of a thin film of the $K_2Pc(CN)_8$–K complex crystal produced on a KCl (001) surface.

caused by interaction between the cyano groups of $K_2Pc(CN)_8$ molecules and the KCl crystal, and the intersecting angle of 23° is related to the crystal structure of the $K_2Pc(CN)_8$–K complex. Fig. 5 shows a schematic diagram of the molecular arrangement in the $K_2Pc(CN)_8$–K complex crystal projected along the c axis. $K_2Pc(CN)_8$ molecules are located at the corners of the square lattice and are rotated alternately around the c axis. Each molecule M_1 in the first layer, indicated by a solid line, is rotated clockwise by an angle ω and each molecule M_2 of the second layer, indicated by a dashed line, is rotated counter-clockwise by the same angle. The rotation angle was determined to be 27·4° directly from high-resolution molecular images by image simulation (Yanagi, Maeda, Ueda & Ashida, 1988*a*). A K atom is intercalated at the center of the square lattice and surrounded by a distorted cube of peripheral cyano groups from eight [$K_2Pc(CN)_8$] molecules in the successive layers. The superposed cyano groups coordinated to the K atom are arranged to make an intersecting angle φ as shown with lines L_1 and L_2. This angle was calculated to be 22·9° when the rotation angle ω was 27·4°, where the peripheral cyano groups bonded to the benzene ring were assumed to make an angle of 120° with the C—C bond corresponding to the molecular structure of the benzenetetracarbonitrile crystal (Prout & Tickle, 1973). This value of φ coincides well with the angle between the double-directional crystals, 23°. The peripheral cyano groups are more electronegative than parts of the π-electron macrocycle in a [$K_2Pc(CN)_8$] molecule and attract a certain amount of electron charge from a central K atom. A nearly straight row of ionic charges, $C{\equiv}N^{\delta-}{-}K^{+}{-}N^{\delta-}{\equiv}C$, is formed between two molecules located at diagonal positions of the square lattice in the $K_2Pc(CN)_8$–K complex. An interaction probably exists between this ionic charge and the KCl substrate. At an initial stage of nucleation, this ionic row is considered to have a very stable fitting

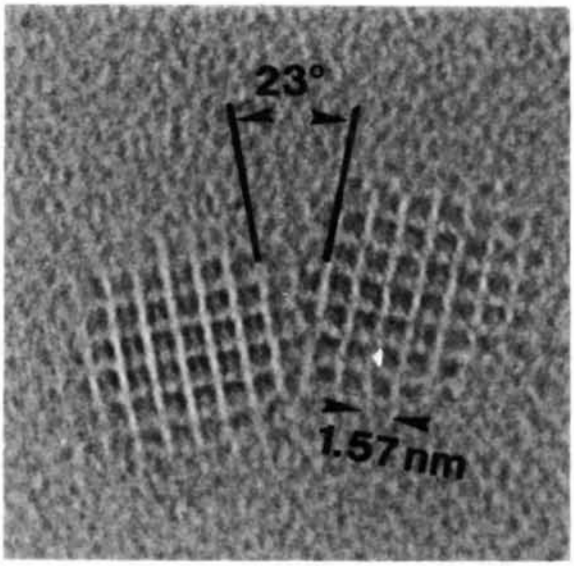
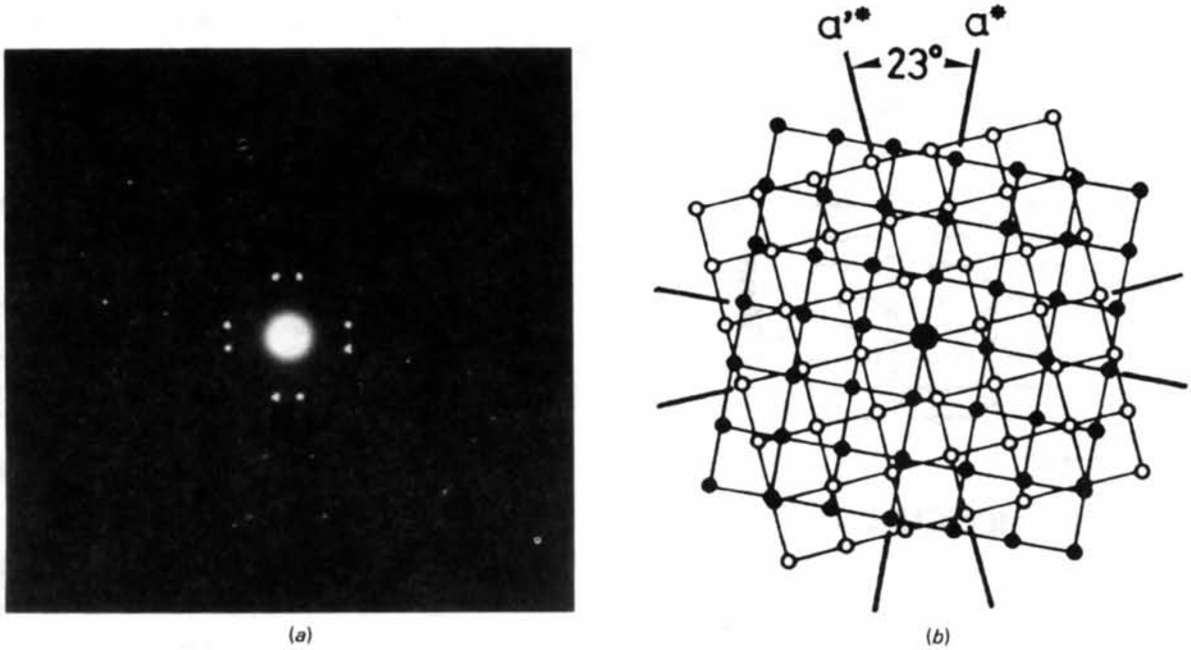


Fig. 3. Electron micrograph of the $K_2Pc(CN)_8$–K crystallites with double-directional orientation produced on a KCl (001) surface.



(*a*) (*b*)

Fig. 4. (*a*) A selected-area electron diffraction pattern of the $K_2Pc(CN)_8$–K crystal and (*b*) its schematic representation.

with the ionic arrangement of the KCl (001) surface. It is assumed that two different orientations of the crystals relative to the KCl lattice arise from two possible contacts of the ionic rows, L_1 and L_2, with the KCl surface. Consequently, the crystals take double-directional orientations so that their *a* axes make an angle of 23° with respect to each other.

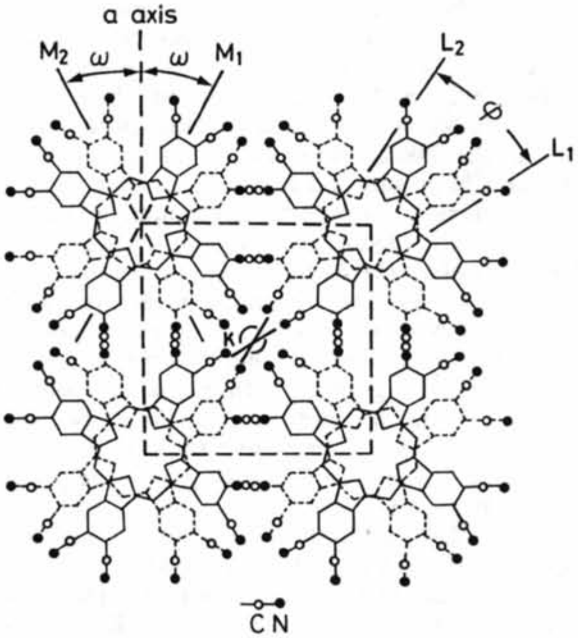


Fig. 5. Schematic diagram of the molecular arrangement in the $K_2Pc(CN)_8$–K crystal projected along the *c* axis.

In order to elucidate a mutual relation between the $K_2Pc(CN)_8$–K complex and the KCl substrate, films were produced on a KCl (001) surface etched thermally. Fig. 6 shows a representative electron micrograph of the film. As is well known, when alkali halides are etched thermally in vacuum, their (001) surfaces exhibit evaporation pits and other corrosion figures (Grinberg, 1963). A rectangular contour in the figure corresponds to a plateau which is made by thermal etching, and it reveals the [100] and [010] directions of the KCl crystal. The $K_2Pc(CN)_8$–K complex crystals are observed both inside and outside the contour of the step. These crystals have their *c*-axes perpendicular to the (001) surface of KCl, the same as those of the film in Fig. 2, and they show square lattice fringes with a spacing of 1·57 nm. Three different orientations of the square lattices can be observed in sites shown with arrowheads *A*, *B* and *C*. The representative areas outlined by *a*, *b* and *c* are enlarged in Figs. 7(*a*), (*b*) and (*c*), respectively. The crystallites in Fig. 7(*a*) show the double-directional orientation as mentioned above. The bisector of the two lattices makes an angle of 45° to the $[100]_{KCl}$ direction, that is, its direction coincides with

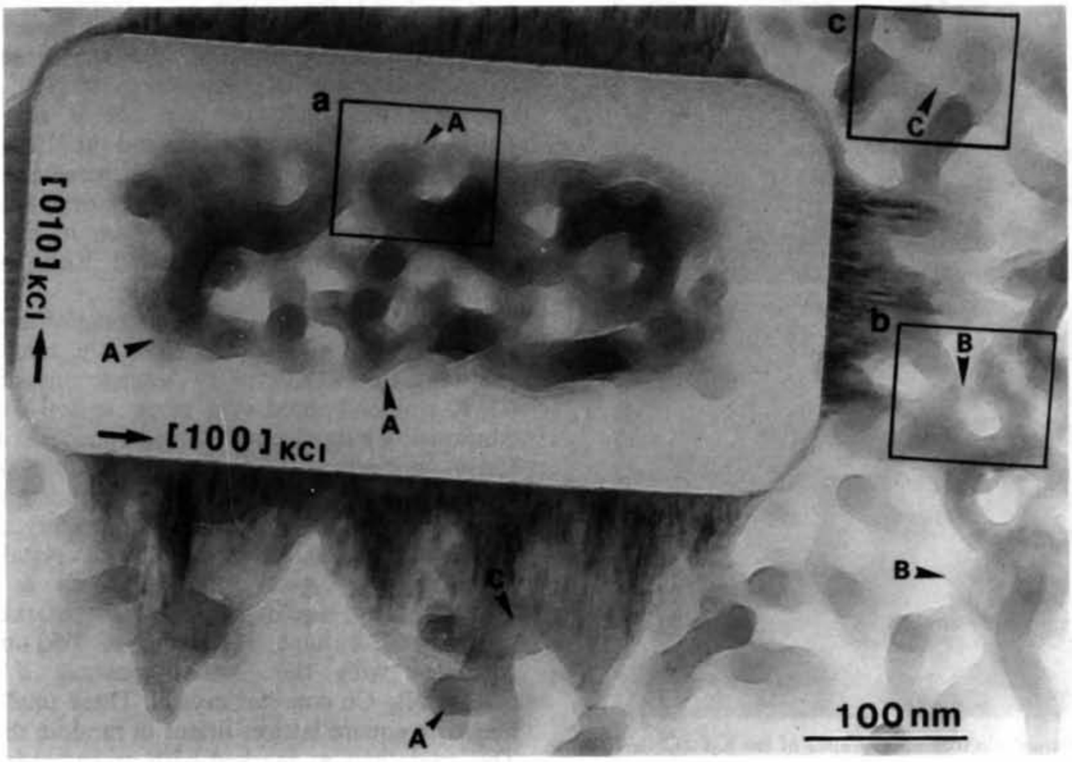


Fig. 6. Electron micrograph of a thin film of the $K_2Pc(CN)_8$–K complex crystal produced on a thermally etched KCl (001) surface.

the $[110]_{\mathrm{KCl}}$ direction. The *a* axis of one square lattice makes an angle of 33·5° to the $[100]_{\mathrm{KCl}}$ direction and the *a* axes of the crystallites in Figs. 7(*b*) and (*c*) make angles of 11·5 and 18° to the $[100]_{\mathrm{KCl}}$ direction, respectively.

From these mutual relations between the deposited and substrate crystal lattices, three types of nucleations of the $\mathrm{K_2Pc(CN)_8}$–K complex crystal on the KCl (001) surface were assumed as shown schematically in Figs. 8(*a*), (*b*) and (*c*), corresponding to the orientations in Figs. 7(*a*), (*b*) and (*c*), respectively. In the case of Fig. 8(*a*), four CN groups (n_1, n_2, n_3, n_4) of four $[\mathrm{K_2Pc(CN)_8}]$ molecules in the first layer come into close contact with four $\mathrm{K^+}$ ions surrounding a $\mathrm{Cl^-}$ ion. When the lines L_1 of CN groups are parallel to the $[100]_{\mathrm{KCl}}$ and $[010]_{\mathrm{KCl}}$ directions, the *a* axis of the $\mathrm{K_2Pc(CN)_8}$–K complex crystal makes an angle of 33·5° to the $[100]_{\mathrm{KCl}}$ direction. A similar interaction between CN groups and $\mathrm{K^+}$ ions has been reported in the epitaxic growth of tetracyanoquinodimethane (TCNQ) evaporated on a KCl (001) surface (Uyeda, Murata, Kobayashi & Suito, 1974). Another positioning of CN groups is assumed in the case of Fig. 8(*b*). Four CN groups (n_1, n_2, n_3, n_4) coordinate to a central $\mathrm{K^+}$ ion to form a complex crystal. The CN groups settle in grooves with minimum potential between $\mathrm{Cl^-}$ ions because electronegative CN groups tend to minimize the repulsive force by $\mathrm{Cl^-}$ ions. Consequently, the lines L_2 of CN groups are parallel to the $[110]_{\mathrm{KCl}}$ and $[1\bar{1}0]_{\mathrm{KCl}}$ directions, so that the *a* axis of the $\mathrm{K_2Pc(CN)_8}$–K complex crystal makes an angle of 11·5° to the $[100]_{\mathrm{KCl}}$ direction. The orientation in the case in Fig. 8(*c*) cannot be explained by interaction between CN groups and a KCl crystal. As is well known, electrons in a phthalocyanine ring are distributed on the *meso*-bridging N atoms ($\mathrm{N_1}$, $\mathrm{N_2}$, $\mathrm{N_3}$, $\mathrm{N_4}$) with the highest density (Kobayashi, 1961). These N atoms tend to be located close to $\mathrm{K^+}$ ions as reported for [CuPc] molecules deposited on a KCl (001) surface (Ashida, 1966*a*). Consequently, the molecular axis M_1 is parallel to the $[110]_{\mathrm{KCl}}$ direction and the angle between the *a* axis of the $\mathrm{K_2Pc(CN)_8}$–K complex crystal and the $[100]_{\mathrm{KCl}}$ direction is 17·6°, which coincides approximately with the observed value of 18°. As this orientation was observed in only a few crystallites in the film, it seems to be unstable compared with the other orientations.

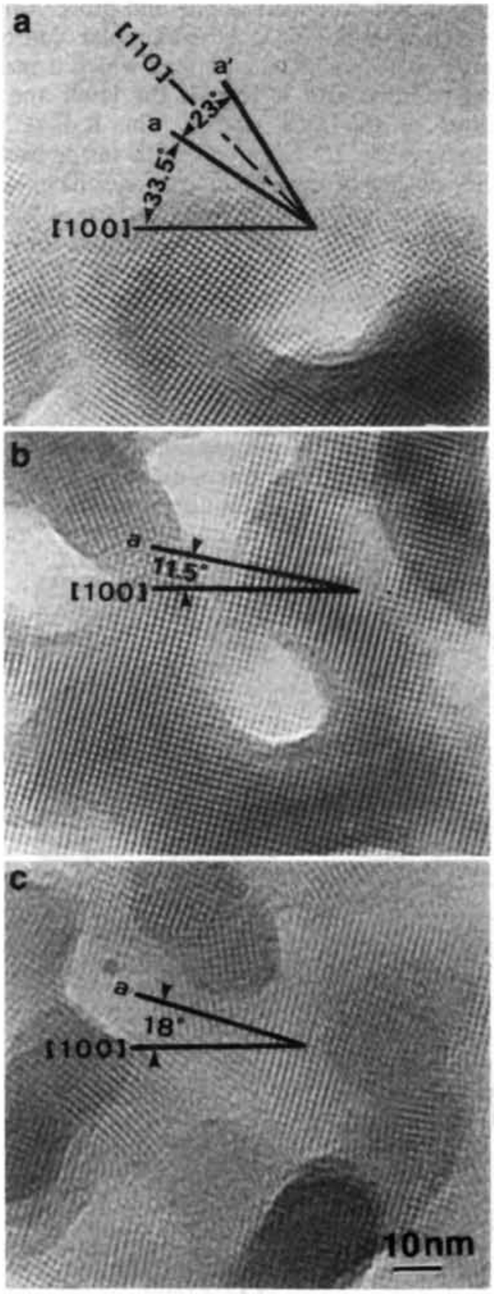


Fig. 7. Enlarged electron micrographs of the $\mathrm{K_2Pc(CN)_8}$–K complex crystals. (*a*), (*b*) and (*c*) correspond to the areas outlined by *a*, *b* and *c* in Fig. 6, respectively.

A film of the $\mathrm{CuPc(CN)_8}$–Cu complex crystal was synthesized on a Cu film. The Cu film vacuum evaporated on a KCl (001) cleavage surface kept at 623 K was composed of a single crystal which was confirmed by its electron diffraction pattern. Fig. 9 shows an electron micrograph of the film produced on the Cu film. The film showed various lattice fringes of the $\mathrm{CuPc(CN)_8}$–Cu complex crystal which was identified as an isomorphous crystal of the $\mathrm{K_2Pc(CN)_8}$–K crystal (Yanagi, Ueda & Ashida, 1988). Many square lattices as marked with arrowheads *A* have a spacing of 1·63 nm which coincides with the lattice constant *a* of the $\mathrm{CuPc(CN)_8}$–Cu complex crystal. These small crystallites with square lattices orient in random directions. The crystallites as marked with arrowheads *B* show raft-like images with a spacing of 1·63 nm. Fig. 10

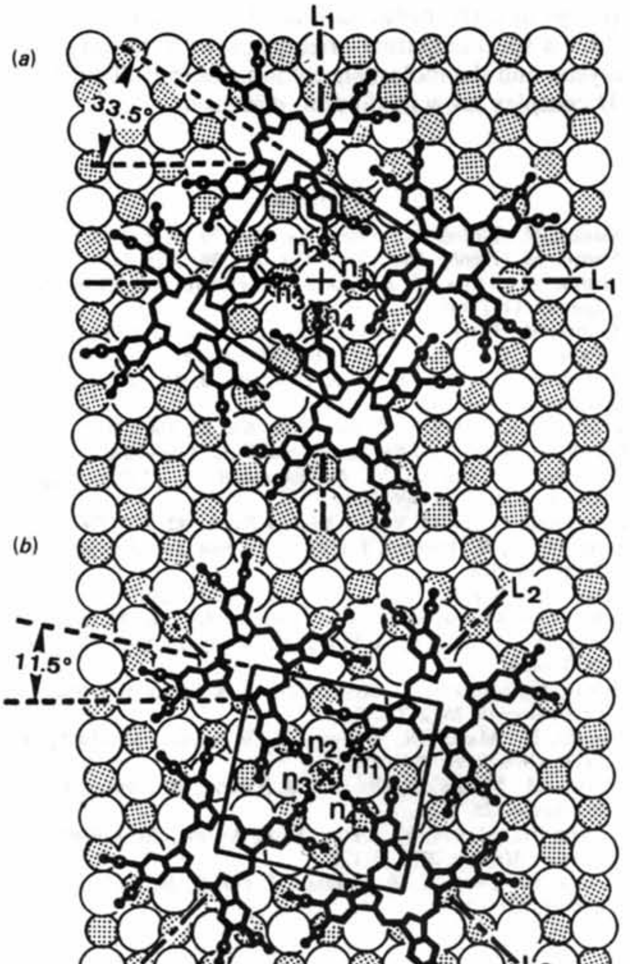


Fig. 8. Schematic description of mutual relations between the $K_2Pc(CN)_8$–K crystals and an ionic lattice of the KCl (001) surface. (*a*), (*b*) and (*c*) correspond to the orientations shown in Figs. 7(*a*), (*b*) and (*c*), respectively.

shows a high-resolution electron micrograph of the raft-like crystal. The crystallite grows in a long parallel column and indicates various lattice fringes along the column axis. Similar images have been observed in films produced on other metal films and were interpreted as projection images along different [*h*0*l*] zone axes of the MPc$(CN)_8$–M complex crystals (Yanagi, Maeda, Ueda & Ashida, 1988*b*). It demonstrates that the crystal columns of the CuPc$(CN)_8$–Cu complex in the raft-like images incline to the substrate surface at various angles. Consequently, it seems that the crystallites of the CuPc$(CN)_8$–Cu

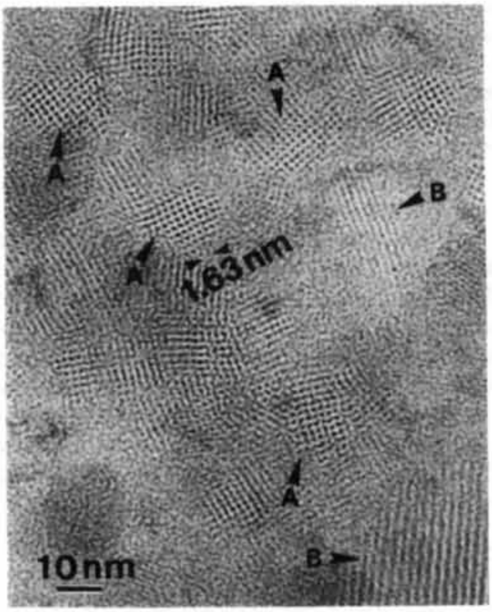


Fig. 9. Electron micrograph of a thin film of the CuPc$(CN)_8$–Cu complex crystal produced on a Cu film.

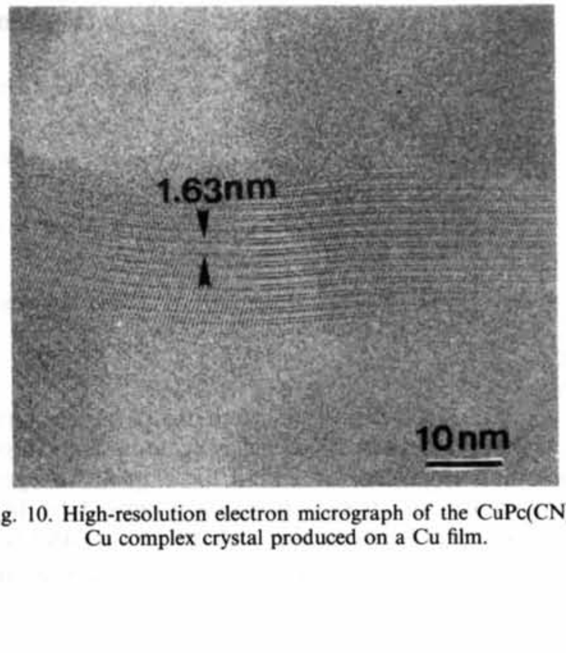


Fig. 10. High-resolution electron micrograph of the CuPc$(CN)_8$–Cu complex crystal produced on a Cu film.

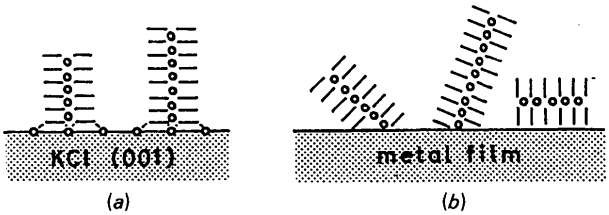


Fig. 11. Schematic description of epitaxic growth of (a) the $K_2Pc(CN)_8$–K crystal on a KCl (001) surface and (b) the $MPc(CN)_8$–M crystal on a metal film.

complex take a random orientation on the Cu film constructed with a single crystal and there is no specific relation between the deposit and substrate crystals.

Fig. 11 shows a schematic description of the epitaxic growth of the $K_2Pc(CN)_8$–K and $MPc(CN)_8$–M complex crystals on the substrates. In the case of the $K_2Pc(CN)_8$–K crystal on a KCl (001) surface, [$K_2Pc(CN)_8$] molecules make flat contact with the substrate surface owing to interaction between their cyano groups and K^+ ions on a KCl surface as shown in Fig. 11(a). Square lattices of the crystals take three different orientations depending on multiple positioning of [$K_2Pc(CN)_8$] molecules on the ionic lattice of the KCl crystal. Molecular columns of these crystals stand perpendicular to the substrate. In the case of the $MPc(CN)_8$–M complex crystal on a metal film, [$MPc(CN)_8$] molecules come into contact with the substrate surface at different angles because there is no anisotropic interaction between the cyano groups and the metal surface. These crystals do not show a specific mutual orientation with the substrate crystal and the molecular columns of the $MPc(CN)_8$–M complex grow in random directions.

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Structure of 1-Methyl-5-(D-*galacto*-1,2,3,4,5-pentaacetoxypentyl)-3-phenylpyrazole

BY C. F. CONDE AND A. CONDE

*Departamento de Física de la Materia Condensada, Instituto de Ciencias de Materiales,
Universidad de Sevilla–CSIC, Sevilla, Spain*

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Abstract. $C_{25}H_{30}N_2O_{10}$, $M_r = 518{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}303\,(2)$, $b = 25{\cdot}071\,(4)$, $c = 8{\cdot}823\,(5)$ Å, $V = 2721{\cdot}4\,(16)$ Å^3, $Z = 4$, $D_x = 1{\cdot}265$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}09$ mm^{-1}, $F(000) = 1076$, room temperature, final $wR = 0{\cdot}040$ for 1424 observed reflexions. Bond distances and angles are all within the expected ranges. The pyrazole and phenyl planes are twisted by 18°. Torsion angles between the acetoxy groups and the pentyl chain range from 45 to 80°. The crystal cohesion is mainly due to van der Waals interactions but there are two possible hydrogen bonds along [100] and [001]. Molecular-packing analysis in the atom–atom approach yields an equilibrium configuration close to the experimental structure.

Introduction. The structure determination of 1-methyl-5-(D-*galacto*-1,2,3,4,5-pentaacetoxypentyl)-3-

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