Formation of a Crystalline EDA Complex between Copper Phthalocyanine and Potassium

By JOHN R. FRYER* and HIROKO MURATA

(*Chemistry Department, University of Glasgow, Glasgow*, G12 8QQ)

Summary Electron microscopy and electron diffraction of a thin film of complex formed between copper phthalocyanine and potassium revealed a unique crystalline structure.

ICHIKAWA and his colleagues[1] have studied the catalytic properties of EDA complexes of various phthalocyanines with alkali metals, and the spectral properties were also investigated. The catalytic activity of these compounds decreased on exposure to air.

No structural information on these compounds has been reported, but the sodium complex with non-graphitic carbon,[2] a planar molecule analogous to phthalocyanine, has shown random adsorption of sodium. Crystalline copper phthalocyanine is extremely anisotropic so that any structural characteristics of its complexes would be of importance in understanding their properties.

The complexes were prepared by co-evaporation of purified copper phthalocyanine and potassium metal under high vacuum, to give a thin film on an amorphous substrate of carbon or silica at room temperature. The specimens were immediately examined by electron microscopy, selected area diffraction also being employed. Pure copper phthalocyanine films were prepared under similar conditions for comparison.

The complex exhibited single-crystal and textured patterns the lattice spacings of which are in the Table. Polymorphic forms of copper phthalocyanine: α-,[3] β-,[4] and metastable,[5] are also shown. It is clear that the complex is different from the known forms, and qualitative observations of the relative intensities are also different. The electron micrographs showed that an island film structure existed, with single crystals of the complex being up to 1 μm in diameter, whereas pure copper phthalocyanine films were of a continuous, polycrystalline nature.

TABLE. Lattice plane spacings (in Å) of potassium–copper phthalocyanine complex compared to polymorphic forms of pure copper phthalocyanine, determined by electron diffraction.

α-Form[3]	β-Form[4]	Metastable[5]	Complex
			13·97
12·79	12·55	12·96	
12·19		11·96	
			10·71
	9·56		9·80
8·63	8·82	8·82	8·81
	8·32		
			7·53
7·20	7·04		7·03
6·42	6·27	6·48	6·21
	5·71	5·71	
		5·68	5·66
5·49		5·44	5·43

The thin films of complex were stable *in vacuo* but on exposure to air they degraded as the catalytic activity decreased.[1] The degradation was almost complete after 24 h exposure and only traces of the ordered structure were then observable by electron diffraction.

The visible and u.v. spectra of these complexes showed a shift, compared to the pure copper phthalocyanine prepared under the same conditions.

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